



Koordinationspolymere mit linearen, aromatischen N-Donor- Liganden für optische Eigenschaften und magneto- optische Komposite

Coordination polymers with linear, aromatic N-donor-ligands for optical properties and
magneto-optical composites

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"Es gibt noch viel zu tun, und ich bin sehr beschäftigt."

Wilhelm Conrad Röntgen

Für Emma und Levi

Kurzzusammenfassung

Im Rahmen dieser Arbeit wurden magneto-optische Kompositmaterialien auf Basis von Koordinationspolymeren (CPs) mit optischen Eigenschaften und magnetischen Eisen- bzw. Eisenoxidpartikeln entwickelt. In diesem Zusammenhang konnte der sogenannte *All White Magnet* generiert werden, welcher unter ultraviolettem Licht weiß luminesziert und zudem unter Tageslicht ein weißes Erscheinungsbild aufweist. Essenziell hierfür ist eine partikuläre TiO_2 -Beschichtung der magnetischen Partikel, welche eine diffuse Reflexion bzw. Refraktion einfallenden Lichtes zur Folge hat. Als weiß lumineszierender Partner diente IFP-1 (*imidazolate framework Potsdam 1*), welches mit Terbium- und Europiumionen imprägniert war (EuTb@IFP-1). Unter UV-Bestrahlung ist simultan rote, grüne und blaue Lumineszenz beobachtbar, wodurch das emittierte Licht weiß erscheint. Mit der bei Tageslicht „weißen“ Farbe und der Emission weißen Lichtes widerspricht der *All White Magnet* der lange Zeit bestehenden Annahme, magnetische Materialien hätten ein dunkles Erscheinungsbild.

In gegensätzlicher Weise zu oben beschriebenem Aufbau, bei welchem die lumineszierende Komponente des Komposits als Teil der äußeren Schicht um einen magnetischen Kern vorliegt, wurde weiterhin ein Komposit generiert, bei welchem diese Rollen vertauscht sind. Superparamagnetische Eisenoxid-Nanopartikel (SPIONs) bilden gemeinsam mit den Gerüstverbindungen $\frac{3}{2}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ und/oder $\frac{3}{2}[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (BDC = Benzol-1,4-dicarboxylat) Komposite, in welchen die Lanthanoid-Verbindungen als Kernmaterialien fungieren, welche mit SPIONs als Satellitenpartikel beschichtet sind. Über die Verhältnisse der Bestandteile ist sowohl die Magnetisierbarkeit als auch die Lumineszenzintensität exakt einstellbar. Zudem weisen die Kern-Satellit-Komposite eine außerordentliche Stabilität auf. Diese besonderen Eigenschaften machen einen Einsatz dieser magneto-optischen Komposite beispielsweise zur Fälschungssicherung oder als lumineszierendes Sensormaterial denkbar.

Auch die Synthese neuartiger Substanzen mit optischen Eigenschaften ist ein wesentlicher Teil der Erforschung magneto-optischer Komposite. So wurde als potenzieller alternativer Weißlichtemitter für *All White Magnets* in der vorliegenden Arbeit ein Zink-basiertes Koordinationspolymer entwickelt, welches sich in eine Vielfalt an ebenso neuen Verbindungen auf Basis von 2-(1,2,4-1*H*-Triazol-3-yl)pyridin (Hpt) einreicht. In Abhängigkeit der enthaltenen Übergangsmetallionen ergeben sich optische Eigenschaften, wie intensive Farbe, thermochrome Effekte oder Photolumineszenz. Letztere kann, in Analogie zu EuTb@IFP-1 , genutzt werden, um für den *All White Magnet* den potenziell alternativen Weißlichtemitter $\text{EuTb@}^1[\text{Zn}(\text{pt})_2]$ auf einfache Weise zu synthetisieren.

Abstract

Within the scope of this work, magneto-optical composite materials based on coordination polymers (CPs) with optical properties and magnetic iron or iron oxide particles were developed. In this context, the so-called *All White Magnet* was generated, which features white light emission under ultraviolet light as well as a white appearance under daylight. An essential criterion is a particulate TiO₂ coating of magnetic particles, which enables diffuse reflection or refraction of incident light. IFP-1 (imidazolate framework Potsdam 1), which was impregnated with terbium and europium ions (EuTb@IFP-1), functions as white light emitting partner. Under UV irradiation, red, green, and blue luminescence can be observed simultaneously, causing the emitted light to appear white. With its "white" colour in daylight and the emission of white light, the *All White Magnet* contradicts the long-held assumption that magnetic materials have a dark appearance.

In contrast to the composite described above, in which the luminescent component is a part of the outer layer around a magnetic core, a composite was generated in which these roles are interchanged. Superparamagnetic iron oxide nanoparticles (SPIONs) in combination with the coordination framework compounds $\frac{3}{2}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ and/or $\frac{3}{2}[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (BDC = benzene-1,4-dicarboxylate) form composites in which the lanthanoid-containing compounds act as core materials, which are coated with SPION satellite particles. The luminescence intensity can be tuned precisely by adjusting the ratios of the components. In addition, the core-satellite composites exhibit extraordinary stability. These special properties enable a potential application of these magneto-optical composites as e.g. counterfeit protections or as luminescent sensor materials.

The synthesis of novel substances with optical properties is also a key aspect of magneto-optical composite research. Thus, in this work, a zinc-based coordination polymer was developed as a potential alternative white light emitter for *All White Magnets*. This CP joins a variety of equally novel compounds based on 2-(1,2,4-1H-triazol-3-yl)pyridine (Hpt). Depending on the transition metal ions present, optical properties such as intense colour, thermochromic effects, or photoluminescence can be observed. In analogy to EuTb@IFP-1, the latter can be utilized to easily synthesize the potentially alternative white light emitter EuTb@¹[Zn(pt)₂] for the *All White Magnet*.

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1 Einleitung

Viele Wissenschaftler sind sich einig: Von den fünf Sinnen des Menschen (sehen, hören, fühlen, riechen, schmecken) stellt der Sehsinn diejenige Art der Wahrnehmung dar, welche den Großteil der sensorischen Interaktion mit der Umwelt ausmacht.^[1] Obgleich von einem genetischen Standpunkt die olfaktorische Wahrnehmung die komplexeste ist und der Tastsinn mit der Haut über das größte sensorische Organ verfügt, ist es das Sehen, was nicht nur die Aufmerksamkeit eines Menschen auf ein entferntes Objekt lenken kann, sondern zeitgleich auch dessen Lokalisierung und Bestimmung von Größe, Form und Farbe erlaubt.^[2] Vor allem das letztgenannte Charakteristikum fasziniert Menschen seit Langem. So wurden bereits Jahrtausende vor unserer Zeitrechnung Kleidungsstücke aufwändig eingefärbt,^{[3]–[5]} um unter anderem auch den sozialen Status des Trägers zu betonen.^[5] Ohne ein Wissen um deren Identität und Struktur wurden auch Koordinationsverbindungen als Beizmittel genutzt, um Pigmente dauerhaft an Stofffasern zu binden. Vieler solcher Beizen enthalten einfache Salze der Metalle Aluminium, Chrom, Eisen, Kupfer oder Zinn, welche aufgrund ihrer Fähigkeit, koordinative Bindungen mit funktionellen Gruppen zahlreicher Substanzen einzugehen, Pigmente dauerhaft an Stofffasern binden können.^[3]

Es ist nicht verwunderlich, dass – aufgrund geopolitischer, wirtschaftlicher und verarbeitungstechnischer Schwierigkeiten natürlich vorkommender Pigmente – mit der Zeit synthetische Farbstoffe entwickelt wurden.^[6] Ein bekanntes Beispiel für einen solchen Farbstoff stellt die Anfang des 18. Jahrhunderts entdeckte Verbindung Eisen(III)-hexacyanidoferrat(II/III) dar, welches sicherlich nicht nur unter Chemikern als *Berliner Blau* bestens bekannt ist und als das erste synthetische Farbpigment gilt.^{[6]–[8]} Dessen blaue Farbe, ebenso wie die Farbigkeit vieler Koordinationsverbindungen, kann durch die elektronische Struktur und den daraus resultierenden Übergängen erklärt werden. Fällt weißes Licht auf einen farbigen Körper, so werden die Wellenlängen des Lichtes absorbiert, welche energetisch einer resonanten elektronischen Anregung entsprechen. Die übrigen Wellenlängen werden reflektiert bzw. transmittiert.^[9] Die Farbigkeit von nichtleuchtenden Pigmenten kann so über Absorption, Transmission und Reflexion einfallenden Lichts je nach Art des Farbstoffes den gesamten Bereich des sichtbaren, elektromagnetischen Spektrums abdecken.^[6] Geht man über zu Koordinationsverbindungen der Selten-Erd-Metalle, im Detail den dreiwertigen Kationen dieser Elemente, kann (neben Absorption und Reflexion) auch Lumineszenz als weiteres optisches Phänomen auftreten. Die meisten Koordinationsverbindungen der Selten-Erd-Elemente sind farblos. Jedoch sind fast alle dreiwertigen Lanthanoide – mit Ausnahme von La^{3+} und Lu^{3+} – photolumineszierend und decken in Bezug auf die Chromatizität des emittierten Lichtes von UV (z.B.: Gd^{3+}), über Grün (z.B.: Tb^{3+}) und Rot (z.B.: Eu^{3+}), bis hin zu

NIR (z.B.: Nd^{3+} , Er^{3+} , Yb^{3+}) ebenfalls das gesamte sichtbare Spektrum und Bereiche darüber hinaus ab.^[10] Lanthanoid-basierte Verbindungen überzeugen auch durch intensive und schmalbandige spektrale Banden und somit einer großen Farbreinheit und -brillanz.

Die potenziellen Anwendungen von Koordinationsverbindungen der Übergangsmetalle und Lanthanoide beschränken sich selbstredend nicht nur auf rein ästhetische Applikationen als leuchtende und nichtleuchtende Pigmente. Auch ein medizinischer Einsatz,^{[11]–[15]} die Verwendung bei der Speicherung von Energie^{[16],[17]} oder der Energiegewinnung in Solarzellen,^[18] katalytische Anwendungen^{[19]–[23]} und der Einsatz als Verbindungen mit optischen Eigenschaften in Displays^[24] sowie die Verwendung als Sensormaterialien für verschiedenste Stimuli^{[25],[26]} sind nur einige, wenige Beispiele, welche die Vielseitigkeit von Koordinationsverbindungen anschaulich präsentieren. Heutzutage werden derartige Verbindungen mit optischen Eigenschaften auch zur Fälschungssicherung genutzt. In den vergangenen Jahrzehnten haben sich hierfür Sicherheitsmerkmale von einfachen Wasserzeichen über Hologramme, bis hin zur RFID^a-Technologie entwickelt.^[27] Diese Merkmale sind jedoch verhältnismäßig leicht zu kopieren,^{[27],[28]} weshalb intensiv an Methoden zur kolorimetrischen und fluorimetrischen Fälschungssicherung geforscht wird.^[27] Vor allem Lanthanoid-haltige Verbindungen haben sich in diesem Bereich aufgrund ihrer optischen Eigenschaften, wie hoher Emissionsintensität, Lumineszenzlebensdauern oder diverser Anregungsmechanismen (optisch, mechanisch, chemisch, etc.) etabliert.^[28]

Die Kombination von Koordinationsverbindungen, welche optische Eigenschaften aufweisen, mit diversen, weiteren Substanzen in Form von Kompositen stellt eine elegante Möglichkeit dar, die vielseitigen Eigenschaften beider Kompositpartner synergetisch zu vereinen. Vor allem die Kombination mit magnetischen Materialien zur Herstellung magneto-optischer Komposite ist ein attraktives Forschungsgebiet. Das Hinzufügen von Magnetismus zum Eigenschaftsportfolio ermöglicht sowohl eine magnetische Separation nach der Anwendung als auch eine gezielte Steuerung der Koordinationsverbindung zum gewünschten Einsatzort. Damit können magneto-optische Komposite einen wichtigen Beitrag zur Therapie von Krebserkrankungen mittels Tumorbildgebung^{[29],[30]} oder Hyperthermie leisten.^[25] Bei Verwendung von Koordinationsverbindungen, welche sensorische Eigenschaften aufweisen, ist eine Verwendung in der Spurenanalytik denkbar. Durch die magnetische Separation des Sensors nach der Analyse kann der entsprechende Analyt fast vollständig zurückgewonnen werden.^{[31],[32]}

Es zeigt sich, dass sowohl Koordinationsverbindungen als auch magneto-optische Komposite aufgrund ihrer inhärenten Eigenschaften und möglichen Eigenschaftskombinationen

^a Funkfrequenzidentifikation, von engl. *radio frequency identification*

vielversprechende Kandidaten für verschiedenste Applikationen sind. Aufgrund stetig neu entwickelter Koordinationsverbindungen eröffnet sich ein breites Forschungsgebiet, welches immerwährend faszinierende Entdeckungen zulässt. Die vorliegende Arbeit greift aus diesem Grund die Investigationen im Bereich von Koordinationsverbindungen mit optischen Eigenschaften und magneto-optischer Komposite auf. Im Rahmen dessen konnten neuartige Verbindungen synthetisiert werden, welche intensiv Farbe, Thermochromie oder Photolumineszenz zeigen. Weiterhin wurden magneto-optische Komposite auf Basis von Koordinationsverbindungen hergestellt, welche simultan Magnetismus und Lichtemission von roter, grüner oder gelber Farbe bis hin zu Weißlichtemission bei gleichzeitigem weißem Erscheinungsbild als Eigenschaften aufweisen.

2 Grundlagen und Stand der Forschung

2.1 Photolumineszenzprozesse und Lumineszenz der Lanthanoide

Photolumineszenz beschreibt das Phänomen der Lichtemission nach einer Anregung mittels einfallender Photonen. In diesem Kapitel werden wichtige Begrifflichkeiten in Bezug auf dieses Phänomen, wie Auswahlregeln, mögliche Anregungs-Depopulations-Prozesse, Quantenausbeute, Lebensdauer sowie die Lumineszenz der Lanthanoide und der Antenneneffekt definiert und erläutert.

2.1.1 Optische Auswahlregeln für Photolumineszenz

Die elektronischen Zustände und Mikrozustände von Atomen und Ionen werden häufig über Termsymbole zusammengefasst, welche allgemein als $^M L_J$ über die Spinmultiplizität M , den Gesamtbahndrehimpuls L , sowie den Gesamtdrehimpuls J definiert sind. Ausgehend von einer vernachlässigbaren Spin-Bahn-Wechselwirkung können die Gesamtspinquantenzahl S und die Gesamtbahndrehimpulsquantenzahl L als Summe der entsprechenden Quantenzahlen s_i , bzw. l_i aller Elektronen des betrachteten Atoms oder Ions gebildet werden. Zusammengefasst wird dies – ebenso wie die Berechnung der Spinmultiplizität M – durch die nachfolgenden Gleichungen:^[33]

$$S = \sum_i s_i \quad (2.1)$$

$$M = 2S + 1 \quad (2.2)$$

$$L = \sum_i l_i \quad (2.3)$$

Die Gesamtdrehimpulse ergeben sich nach dem *Russel-Saunders-Formalismus* (LS-Kopplung) zu

$$J = |L - S|, |L - S| + 1, \dots, L + S - 1, L + S, \quad (2.4)$$

woraus in Summe $2J+1$ Mikrozustände folgen.^[33] Der Grundzustand eines Atoms oder Ions ist gemäß der *Hundschen Regeln* derjenige, bei welchem M und L maximal sind. Weiterhin gilt, dass J minimal für Systeme mit weniger als halb gefüllten ($J = |L - S|$) bzw. maximal für Systeme mit mehr als halbgefüllten Unterschalen ist ($J = |L + S|$).^[34]

Eine Anregung eines Atoms kann über diverse Mechanismen erreicht werden. So erfolgen beispielsweise optisch induzierte, elektronische Übergänge eines Atoms oder Ions aufgrund der Wechselwirkung der elektrischen bzw. magnetischen Anteile elektromagnetischer

Strahlung. Demnach handelt es sich hierbei um elektrische oder magnetische Dipol- bzw. Quadrupolübergänge,^[33] wobei aufgrund der größeren Oszillatorstärke vor allem elektrische Dipolübergänge beobachtet werden können.^[35] Es existieren Auswahlregeln, welche diese in „erlaubt“ und „nicht erlaubt“ klassifizieren.^[10] Für elektrische Dipolübergänge gilt das Interkombinationsverbot, welches besagt, dass sich die Gesamtspinquantenzahl S bzw. im Rahmen des LS-Formalismus die Spinmultiplizität nicht ändern darf ($\Delta S = 0$, $\Delta M = 0$).^{[33],[36]} Des Weiteren muss sich gemäß der Impulserhaltung bei Absorption oder Emission eines Photons, welches einen Impuls von $1 \cdot \hbar$ besitzt, der Bahndrehimpuls um den Betrag 1 ($\Delta l = \pm 1$) ändern.^[37] Im Rahmen des LS-Formalismus ist auch eine Änderung der räumlichen Orientierung des Bahndrehimpulses möglich ($\Delta m_l = \pm 1$), wodurch sich für Mehrelektronensysteme im Gesamten L nicht ändert. In Kombination mit $\Delta S = 0$ ergibt sich so die Auswahlregel für den Gesamtdrehimpuls $\Delta J = 0, \pm 1$, wobei der Übergang zwischen zwei Zuständen mit $J = 0$ verboten ist.^[37] Für ein zentrosymmetrisches Ligandenfeld besagt zudem das *Laporte*-Verbot, dass nur Übergänge erlaubt sind, bei welchen sich die Parität beteiligter Orbitale bzw. Zustände ändert ($g \rightarrow u$ bzw. $u \rightarrow g$).^{[10],[33]}

2.1.2 Photoanregung und Photoemission

Eine elektronische Anregung eines Atoms, Ions oder Moleküls kann über mehrere Wege erreicht werden. Erfolgt die Anregung durch Absorption von Photonen, wird dies als Photoanregung bezeichnet. Diese erfolgt von einem elektronischen und vibronischen Grundzustand in jenen angeregten Zustand, welcher den größten Überlapp der Schwingungswellenfunktionen aufweist.^{[36],[38]} In Abhängigkeit der jeweiligen Überlappintegrale kann eine Anregung auch in mehrere Schwingungszustände erfolgen.^[36] Im Rahmen dieses Kapitels wird beispielhaft von $S_1 \leftarrow S_0$ Anregung aus dem Singulett-Grundzustand (S_0) in ein elektronisch angeregtes Singulett-Niveau (S_1) ausgegangen.

Einem $S_1 \leftarrow S_0$ Anregungsprozess folgt die Relaxation des angeregten Zustandes, wofür mehrere Pfade existieren. Von einem elektronisch und vibronisch angeregten S_1 -Niveau kann die angeregte Spezies über innere Umwandlung (IC^b) in einen vibronisch hochangeregten S_0 -Zustand übergehen, worauf eine strahlungslose Schwingungsrelaxation (VR^c) in den S_0 -Grundzustand folgt.^[36] Aufgrund des häufig großen energetischen Abstands zwischen S_0 und S_1 , verläuft IC jedoch nur langsam und der vibronische Grundzustand von S_1 wird erreicht, bevor IC stattfinden kann. Von jenem aus kann dann eine strahlende Relaxation durch Emission von Photonen in einen vibronisch angeregten S_0 -Zustand erfolgen, woraufhin

^b *internal conversion*, engl. innere Umwandlung

^c *vibronic relaxation*, engl. vibronische Relaxation

der S_0 -Schwingungsgrundzustand wiederum über VR erreicht wird.^[38] Somit erfolgt strahlende Relaxation meist aus dem Schwingungsgrundzustand eines elektronisch angeregten Niveaus, was als *Kasha-Regel* bezeichnet wird.^d Liegt der energetische Abstand der beteiligten Niveaus in einem Bereich zwischen ca. 1.6 – 3.4 eV, weisen emittierte Photonen eine Wellenlänge zwischen 360 nm und 760 nm auf^[10] und sind demzufolge sichtbar.^e Da in dem beschriebenen $S_1 \rightarrow S_0$ Prozess das angeregte Niveau und der Grundzustand die gleiche Spinmultiplizität aufweisen, wird die Lumineszenzerscheinung als Fluoreszenz (F) bezeichnet.^[36] Weiterhin ist ein Übergang von einem S_1 -Zustand zu einem Niveau anderer Spinmultiplizität über Interkombination (ISC^f) möglich. Analog zu IC findet der Übergang vom S_1 -Zustand in ein isoenergetisches Schwingungsniveau beispielsweise eines elektronisch angeregten Triplett-Zustandes (T_1) statt. Nach VR zum T_1 -Schwingungsgrundzustand kann eine strahlende $T_1 \rightarrow S_0$ -Relaxation zu einem vibronisch angeregten S_0 -Niveau erfolgen, welche aufgrund unterschiedlicher Spinmultiplizitäten von T_1 und S_0 als Phosphoreszenz (P) bezeichnet wird. Derartige Übergänge sind gemäß des Interkombinationsverbots formal nicht erlaubt (s. Kap. 2.1.1). Deshalb laufen sie nur mit geringer Wahrscheinlichkeit und damit langsam ab, wodurch die Lebensdauer des T_1 -Zustandes höher als die eines S_1 -Zustandes ist. Demzufolge weist auch die beobachtete Phosphoreszenz in der Regel eine längere Lebensdauer als Fluoreszenz auf.^{[33],[36],[39]} Zusammenfassend sind die hier beschriebenen Prozesse in einem sogenannten *Jablonski-Diagramm* in Abb. 1 grafisch dargestellt. Der zusätzlich abgebildete Anregungsprozess über einen *Sensitizer* (Antennen-Effekt) wird in Kap. 2.1.3 näher erläutert.

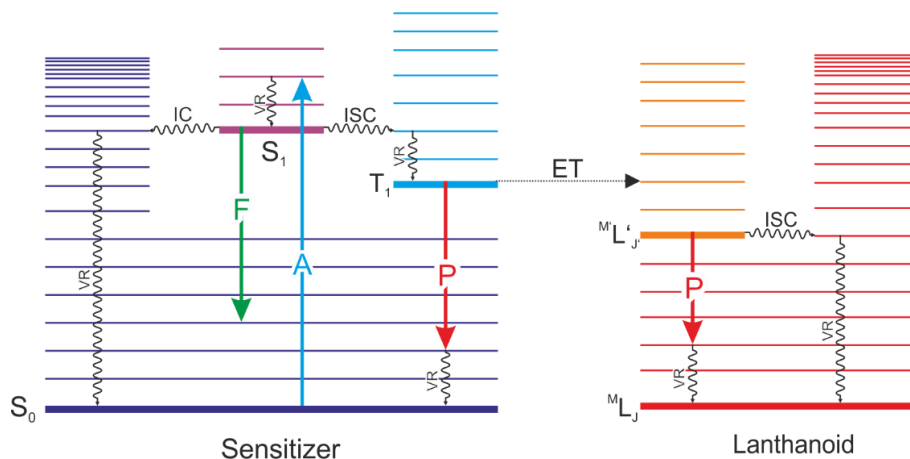


Abb. 1. Vereinfachte Darstellung eines *Jablonski-Diagramms*. Gewinkelte Pfeile stellen strahlungslose Prozesse dar. Gerade, durchgängige Pfeile entsprechen strahlenden Prozessen bzw. der Photoanregung. Dicke, horizontale Linien deuten die Schwingungsgrundzustände der jeweiligen elektronischen Zustände an. Dünne Linien stellen zugehörige, angeregte Schwingungsniveaus dar. S_0 = Singulett-Grundzustand, S_1 = angeregter Singulett-Zustand, T_1 = angeregter Triplett-Zustand, A = Absorption, F = Fluoreszenz, P = Phosphoreszenz, IC = innere Umwandlung (*internal conversion*), ISC = Interkombination (*intersystem crossing*), ET = Energietransfer, VR = Schwingungsrelaxation (*vibronic relaxation*), 4L_J = Grundzustand eines Lanthanoids, 5d = angeregter Zustand eines Lanthanoids.

^d Es sollte beachtet werden, dass es auch Ausnahmen von dieser Regel gibt.

^e Die hier angegebenen Grenzen des sichtbaren Spektralbereichs werden häufig verwendet. Sie sind jedoch nicht streng definiert.

^f *inter system crossing*, engl. Interkombination

Durch die Gegenüberstellung der Anzahl emittierter Photonen n_e und der Anzahl absorbierter Photonen n_a kann über

$$\phi = \frac{n_e}{n_a} \quad (2.5)$$

die intrinsische Quantenausbeute berechnet werden. Sie ist gemäß

$$\phi = \frac{\sum k_{\text{rad}}}{\sum k_{\text{rad}} + \sum k_{\text{nr}}} \quad (2.6)$$

eng verknüpft mit der Ratenkonstanten der strahlenden Depopulationen (k_{rad}), sowie den entsprechenden Konstanten nichtstrahlender Prozesse (k_{nr}), wie beispielsweise vibrations-induzierter Depopulation oder photoinduzierter Elektronentransfer-Prozesse.^{[39],[40]} Weiterhin erfolgt die Emission von Photonen über einen gewissen Zeitraum, wobei die mit der Zeit abnehmende Lumineszenzintensität mit der Exponentialfunktion

$$I(t) = I_0 \cdot e^{-\frac{t}{\tau}} \quad (2.7)$$

beschrieben werden kann. $I(t)$ bezeichnet hier die Intensität zum Zeitpunkt t , I_0 die initiale Intensität (Zeitpunkt $t = 0$) und τ die Lumineszenzlebensdauer. τ steht in Bezug zu allen, den betrachteten Zustand depopulierenden Prozessen.^[41] Sie ist äquivalent zum reziproken Wert der Summe der Ratenkonstanten des strahlenden (k_{rad}) und der nichtstrahlenden Desaktivierungen (k_{nr}):^{[33],[41]}

$$\frac{1}{\tau} = k_{\text{rad}} + \sum k_{\text{nr}} \quad (2.8)$$

Die Lumineszenzlebensdauer τ entspricht der auf einen Anregungspuls folgenden Zeitspanne, in welcher die Intensität des emittierten Lichtes auf $1/e$ -fache der Intensität zum Zeitpunkt $t = 0$ abgefallen ist.^{[41],[42]} Die Lebensdauer kann je nach Lanthanoidion, Art der Verbindung oder zugrundeliegendem Lumineszenzprozess variieren. Für Spin-erlaubte Fluoreszenzprozesse liegen Lebensdauern beispielsweise im Bereich von Pikosekunden bis Nanosekunden. Phosphoreszenzprozesse weisen typischerweise Lebensdauern im Mikrosekunden- bis Sekundenbereich auf.^[41]

2.1.3 Lumineszenz von Lanthanoiden und Antenneneffekt

Da bei Lumineszenzprozessen der dreiwertigen Lanthanoide zumeist Übergänge zwischen f -Orbitalen betrachtet werden und diese in einem zentrosymmetrischen Ligandenfeld eine ungerade Parität besitzen, sind entsprechende intra- $4f$ -Übergänge formal paritätsverboten (s. Kap. 2.1.1).^[36] Jedoch wird durch verschiedene Mechanismen dieses

Verbot gelockert. So existieren durch Einbringen von Ln^{3+} in ein nicht-zentrosymmetrisches Ligandenfeld keine geraden oder ungeraden Paritäten mehr, woraufhin einige d - und f -Orbitale mit formal gegensätzlichen Paritäten mischen können und sogenannte induzierte elektrische Dipolübergänge beobachtbar werden.^[43] Weiterhin kann eine Kopplung mit asymmetrischen Schwingungen stattfinden, welche eine temporäre Variation in der geometrischen Anordnung um die Ionen und damit eine Erniedrigung der Symmetrie zur Folge haben. Hierüber werden Übergänge zwischen Orbitalen formal gleicher Parität möglich.^{[36],[44]}

Zudem kommt für Lanthanoide, deren Hauptemissionszustand eine Spinmultiplizität besitzt, welche sich von M des Grundzustandes unterscheidet (bspw. Eu^{3+} : $^5\text{D}_0 \rightarrow ^7\text{F}_J$), das Interkombinationsverbot zum Tragen (s. Kap. 2.1.1). Da jedoch für schwere Elemente wie Lanthanoide die Spin-Bahn-Wechselwirkung nicht vernachlässigbar ist, können M und S (ebenso wie L) nicht als „gute Quantenzahlen“ angesehen werden. Dies hat zur Folge, dass Zustände mit identischem J in Abhängigkeit ihres energetischen Abstandes mischen können, wodurch auch das Interkombinationsverbot gelockert wird.^[43]

Insgesamt sind die Begriffe „verboten“ und „erlaubt“ in Bezug auf $4f$ -Übergänge der Lanthanoide nicht wörtlich zu interpretieren und geben eher Hinweis darauf, ob die Wahrscheinlichkeit der Beobachtung eines bestimmten Überganges mehr oder weniger von Null differiert.^[10] Demzufolge sind bei der Photoanregung von Ln^{3+} -Ionen direkte intra- $4f$ -Übergänge beobachtbar, weisen jedoch nur geringe molare Absorptionskoeffizienten auf. Die direkte f - f -Anregung ist somit ineffizient und zeigt nur geringe spektrale Intensitäten,^{[36],[45]} weshalb für diesen Prozess eine Lichtquelle hoher Intensität benötigt würde.

Um Lanthanoidionen effizient anregen zu können, wird häufig auf den sogenannte Antenneneffekt zurückgegriffen. Hierbei wird ein stark absorbierender *Sensitizer* – auch als Antenne bezeichnet – in räumlicher Nähe zu Lanthanoidionen durch einfallende Photonen elektronisch angeregt.^{[33],[45]} Der Prozess der Energieübertragung von *Sensitizer* auf Lanthanoid ist aufgrund beteiligter Mechanismen komplex. So können ein Dexter-Energietransfer (Elektronenübergang zwischen Donor und Akzeptor), Förster-Energietransfer (Energieübertrag durch Dipol-Dipol-Wechselwirkung), sowie Dipol-Multipol-Wechselwirkung oder Charge-Transfer-Übergänge zur Population angeregter Zustände des Lanthanoidions beitragen.^[10] In Einklang mit den in Kap. 2.1.2 beschriebenen Mechanismen wird häufig von einer $S_1 \leftarrow S_0$ Anregung, vibronischen Relaxation und Interkombination (ISC^9) für das Antennenmolekül ausgegangen, was in einem angeregten Triplett-Zustand (T_1) des *Sensitisers* resultieren würde. In Anwesenheit von Schwermetallionen, wie Lanthanoiden, ist ein derartiger ISC-Übergang von einem angeregten Singulett-Zustand erleichtert.^{[33],[45]} Für

⁹ engl. **I**nter**s**ystem **C**rossing

ISC spielt die energetische Lage des niedrigsten *Sensitizer*-Triplett-Zustandes relativ zur Lage des lumineszierenden Zustandes des Lanthanoidions eine entscheidende Rolle. Ist die energetische Differenz zu gering, kann ein Rücktransfer der Energie von Metallion auf Antenne erfolgen.^[33] Ebenfalls wirken sich Fluoreszenz, bzw. IC und VR im elektronischen System des Antennenmoleküls selbst auf die Effizienz des Antenneneffekts aus. Vom angeregten Triplett-Zustand des *Sensitisers* erfolgt ein Energietransfer (ET) zu einem Ln-T₁-Zustand. Analog zu oben beschriebener Phosphoreszenz erfolgt nach VR zum T₁-Schwingungsgrundzustand des Lanthanoids eine strahlende Relaxation in den S₁-Zustand.^[46] Der beschriebene Pfad der Anregung des *Sensitisers*, des Energieübertrags auf das Lanthanoid sowie dessen Lumineszenz ist ein typisches Musterbeispiel für den Antenneneffekt.^[10] Aufgrund der Abschirmung von 4*f*-Orbitalen durch die diffuseren 5*s*- und 5*p*-Orbitale werden 4*f*-Elektronen kaum von der chemischen Umgebung der Ionen beeinflusst.^[47] Hierdurch sind entsprechende Linien in Lumineszenzspektren schmalbandig^[48] und unabhängig von der chemischen Umgebung immer bei nahezu identischen Wellenlängen vorzufinden.^[40] Jedoch existieren bei Lanthanoid-basierten Koordinationsverbindungen auch einige intra-4*f*-Übergänge, welche in Abhängigkeit ihrer chemischen Umgebung Intensitätsänderungen aufweisen – sogenannte hypersensitive Übergänge. Es wird angenommen, dass die Hypersensitivität auf ein von den Lanthanoid-4*f*-Elektronen induziertes Dipolmoment in Liganden zurückzuführen ist.^{[33],[49]} Alle beschriebenen Depopulationsprozesse, ebenso wie Anregungsprozesse, können in einem sogenannten *Jablonski*-Diagramm zusammengefasst werden, welches beispielhaft in Abb. 1 gezeigt ist.

2.2 Arten von Magnetismus

Magnetismus ist eine Stoffeigenschaft, welche auf der elektronischen Struktur enthaltener Atome basiert. Es wird zwischen atomaren, magnetischen Eigenschaften sowie kooperativen magnetischen Phänomenen unterschieden, welche in diesem Kapitel näher beleuchtet werden. Ebenso wird der Superparamagnetismus magnetischer Nanopartikel erläutert.

2.2.1 Paramagnetismus und Diamagnetismus

Die magnetischen Eigenschaften einer chemischen Verbindung werden maßgeblich über die Elektronenkonfiguration enthaltener Atome und Ionen beeinflusst.^[50] Im Detail sind Bahndrehimpuls und Spin der Elektronen ursächlich für ein magnetisches Moment.^[51] Bei abgeschlossenen Elektronenschalen ($J = 0$), heben sich die magnetischen Momente der Elektronen vollständig auf. Aus dem Vorhandensein ungepaarter Elektronen hingegen

resultiert ein magnetisches Moment. Materialien, welche kein initiales magnetisches Moment aufweisen, werden als Diamagneten bezeichnet. Beim Anlegen eines äußeren Magnetfeldes (H -Feld) wird in derartigen Materialien ein dem H -Feld entgegengerichtetes magnetisches Moment induziert, wodurch die magnetische Flussdichte im Inneren des Diamagneten verringert wird.^[34] Beinhalten Materialien Atome mit ungepaarten Elektronen, kann im Gesamten ein magnetisches Moment resultieren und entsprechende Substanzen werden als Paramagneten bezeichnet. Ohne ein externes Magnetfeld sind die magnetischen Einzelmomente statistisch verteilt, weshalb zunächst keine Magnetisierung der Substanzen beobachtbar ist. Unter dem Einfluss eines externen Magnetfeldes, erfolgt eine Ausrichtung der einzelnen Momente parallel zum H -Feld. Dieses Phänomen wird als *Curie*-Paramagnetismus bezeichnet.^[51]

Ein Maß für die Magnetisierung stellt die magnetische Suszeptibilität χ dar, welche für geringe externe magnetische Feldstärken H als das Verhältnis der Magnetisierung M zu H ausgedrückt werden kann:^{[34],[50]}

$$\chi = \frac{M}{H} \quad (2.9)$$

Für diamagnetische Substanzen ist χ aufgrund der antiparallelen Ausrichtung der Magnetisierung relativ zum externen H -Feld negativ. Entsprechend ist χ für paramagnetische Verbindungen positiv.^{[50],[52]} Der Ausrichtung magnetischer Momente entlang des externen Magnetfeldes wirkt die thermisch bedingte Bewegung von Atomen und Ionen entgegen. Dies resultiert in einer umgekehrt proportionalen Temperaturabhängigkeit^h der magnetischen Suszeptibilität, welche über das *Curie*-Gesetz beschrieben wird:^{[34],[51]}

$$\chi_m = \frac{C}{T} = \frac{N_A \mu^2}{3k_B T} \quad (2.10)$$

Hierbei entspricht χ_m der molaren magnetischen Suszeptibilität, T der Temperatur, C der *Curie*-Konstante, μ dem magnetischen Moment, N_A der Avogadro-Konstante und k_B der Boltzmann-Konstante.^[34] Das *Curie*-Gesetz ist nur für freie Atome bzw. Ionen bei moderaten externen Magnetfeldern und Temperaturen gültig und berücksichtigt keine Interaktionen zwischen Atomen.

^h Es existieren auch nahezu temperaturunabhängige Formen des Paramagnetismus (z.B.: Pauli-, oder Van-Vleck-Paramagnetismus),^[50] die jedoch nicht Gegenstand dieser Arbeit sind.

2.2.2 Kooperative magnetische Phänomene

In realen Festkörpern können aufgrund interatomarer Wechselwirkungen Bereiche entstehen, in welchen sich magnetische Momente von Ionen oder Atomen parallel zueinander ausrichten – sogenannte *Weiss*-Bezirke. Hieraus resultiert ein kooperatives magnetisches Moment. Die Orientierungen der Summenmomente der Bereiche liegen statistisch verteilt vor, weshalb makroskopisch zunächst kein permanenter Magnetismus beobachtbar ist.^[53] Durch Anlegen eines äußeren Magnetfeldes können die Momente der *Weiss*-Bezirke ausgerichtet werden und ein makroskopisches, permanentes magnetisches Moment evoziert, was als Ferromagnetismus bezeichnet wird.^{[53],[54]} Für die Beschreibung der Ursache von Ferromagnetismus hat sich weiterhin die *Stoner*-Theorie etabliert. Diese besagt, dass Ferromagnetismus nur bei solchen Elementen auftreten kann, bei welchen die Zustandsdichte in der Nähe des Fermi-Niveaus hoch ist. Elektronen, welche Zustände nahe des Fermi-Niveaus besetzen können die Ausrichtung ihres Spins umkehren, wodurch ein ferromagnetischer Zustand mit einer bevorzugten Spin-Ausrichtung resultiert.^[55]

Ordnen sich in den *Weiss*-Bezirken die magnetischen Momente antiparallel aus und die Momente innerhalb der Bezirke heben sich demzufolge gegenseitig auf, resultiert Antiferromagnetismus. Eine antiparallele Ausrichtung magnetischer Momente unterschiedlicher Beträge, bei welcher sich die magnetischen Momente nicht vollständig gegenseitig auslöschen sondern lediglich abschwächen, hat Ferrimagnetismus zur Folge.^{[53],[54]} Abb. 2 zeigt eine schematische Darstellung dieser kooperativen Ausrichtungen magnetischer Momente bei entsprechenden Arten von Magnetismus.

Die Änderung der Orientierung magnetischer Momente beim Übergang von einem *Weiss*-Bezirk in eine angrenzende Domäne erfolgt nicht abrupt sondern graduell über mehrere hundert Atomdurchmesser.^[56] Dabei wird zwischen sogenannte *Néel*- und *Bloch*-Wänden unterschieden. In ersteren, welche bei dünnen ($< 800 \text{ \AA}$), ferromagnetischen Filmen auftreten, erfolgt die Änderung der Magnetisierungsrichtung in der Ebene des magnetischen Filmes. In *Bloch*-Wänden, wie sie im Bulk-Material beobachtet werden können, ändert sich die Magnetisierungsrichtung in der Ebene der Domänenwand.^[57] Zur Verdeutlichung soll Abb. 2 dienen. Den geordneten Ausrichtungen innerhalb der *Weiss*-Bezirke wirkt die thermisch bedingte Atombewegung entgegen. Oberhalb einer materialspezifischen kritischen Temperatur – für Ferromagneten als *Curie*-Temperatur, für Antiferromagneten als *Néel*-Temperatur bezeichnet – geht die magnetische Ordnung innerhalb der Bezirke verloren und die Materialien verhalten sich paramagnetisch.^[50]

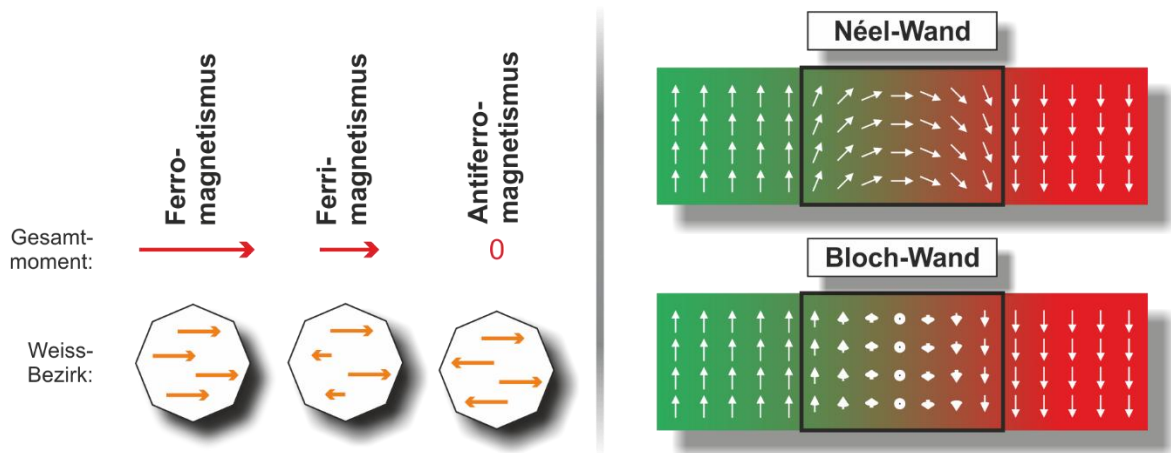


Abb. 2. Schematische Darstellungen der Orientierung magnetischer Momente innerhalb von *Weiss*-Bezirken sowie resultierendes magnetisches Gesamtmoment von ferromagnetischen, ferrimagnetischen und antiferromagnetischen Materialien (links) neben der graduellen  nderung der Magnetisierungsrichtung und der Ausbildung von *N el*- bzw. *Bloch*-Dom nenw nden (rechts). Im Falle von *N el*-W nden wird die Magnetisierungsrichtung in der Filmebene (entspricht hier der Papierebene) gedreht. Bei *Bloch*-W nden erfolgt eine Drehung der Magnetisierung parallel zur Dom nenwand-Ebene (senkrecht zur Papierebene).

Die magnetische Suszeptibilit t kann dann  ber das sogenannte *Curie-Weiss*-Gesetz beschrieben werden, das eine Erweiterung von Gleichung (2.10) mit Θ als *Weiss*-Konstante darstellt:^{[34],[54]}

$$\chi_m = \frac{C}{T - \Theta} = \frac{N_A \mu^2}{3k_B (T - \Theta)} \quad (2.11)$$

Ein Auftrag der Magnetisierung M eines ferromagnetischen Festk rpers gegen die Magnetfeldst rke H eines  u eren Magnetfeldes resultiert in einer Hysteresekurve. Daraus wird ersichtlich, dass mit steigender H -Feldst rke auch M bis zum Erreichen einer S ttigungsmagnetisierung M_s zunimmt. Bei Reduktion von H nimmt M ebenfalls ab.^{[53],[54]} Jedoch zeichnet sich ein anderer M - H -Verlauf als bei der Initialmagnetisierung ab, da im Material neue *Bloch*-W nde ausgebildet bzw. verschoben werden m ssen.^[56] Ohne externes Feld ist demnach eine Restmagnetisierung des Festk rpers, welche auch als Remanenz M_R bezeichnet wird, zu beobachten. Wird die Feldrichtung des H -Feldes nun umgekehrt, kann bei Erreichen der sogenannte Koerzitivfeldst rke ($-H_C$) die Remanenz aufgehoben werden ($M = 0$) und der Festk rper ist entmagnetisiert. Analog kann nun auch in entgegengesetzter Richtung unter Variation des H -Feldes eine S ttigungsmagnetisierung $-M_s$ und Remanenz $-M_R$ eingestellt werden.  ber die Koerzitivfeldst rke H_C kann erneut das Material entmagnetisiert werden und bei weiterer Erh hung der H -Feldst rke die Hystereseschleife geschlossen werden.^{[51],[53],[54]} Verdeutlicht wird dieser Mechanismus durch Abb. 3.  ber die Koerzitivfeldst rken und damit die breite der Hystereseschleife erfolgt eine Einteilung in hart- und weichmagnetisches Verhalten. Materialien niedrigen Koerzitivfeldst rken ($H_C < 10 \text{ A cm}^{-1}$) werden als weichmagnetisch bezeichnet. Zur Umkehr der Magnetisierung ist nur eine geringe externe Magnetfeldst rke n tig. Im Gegensatz hierzu weisen hartmagnetische Materialien eine breite Hysteresekurve und damit hohe Koerzitivfeldst rken auf.^[54]

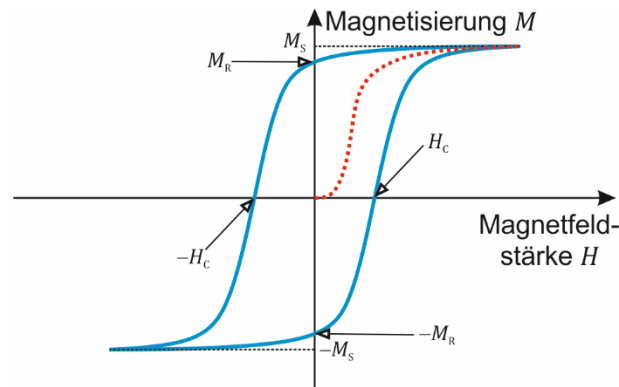


Abb. 3. Schematische Darstellung einer magnetischen Hysteresekurve. M_S = Sättigungsmagnetisierung, M_R = Remanenz, H_C = Koerzitivfeldstärke. Negative Vorzeichen indizieren eine Umkehrung der Polarität der Felder. Die gepunktete, rote Linie entspricht dem M - H -Verlauf bei initialer Magnetisierung.

2.2.3 Superparamagnetismus nanoskaliger Materialien

Als Nanopartikel werden Materialien bezeichnet, welche eine Partikelgröße zwischen 1 nm und 100 nm aufweisen.^[58] Bereits im Jahr 1930 wurde von *Frenkel* und *Dorfman* vorhergesagt, dass unterhalb einer materialspezifischen, kritischen Partikelgröße einer magnetischen Substanz, welche in der Größenordnung von Nanopartikeln liegt, dieses Partikel nur noch aus einem einzigen *Weiss*-Bezirk besteht.^[59] Hieraus ergeben sich besondere magnetische Eigenschaften in Bezug auf Remanenz, welche im Folgenden erläutert werden.

Ein magnetisiertes Material kann mit der Zeit seine Remanenz M_R verlieren, wenn die nötige Energiebarriere zur Umkehr der Magnetisierung überschritten wird. Diese energetische Barriere ist unter anderem von der Partikelgröße des magnetischen Materials abhängig. Unterhalb einer kritischen Partikelgröße, welche im Nanometer-Bereich liegt, kann die Energiebarriere so klein werden, dass bereits aufgrund der thermischen Energie $k_B T$ bei einer definierten Temperatur (häufig Raumtemperatur) die Magnetisierung mit der Zeit verloren geht. Ist diese Zeitspanne kleiner als die Dauer, in welcher eine magnetische Messung durchgeführt wird, kann keine Remanenz M_R und somit keine Hysterese mehr detektiert werden.^{[60],[61]} Über diese Beziehung kann auch eine kritische Temperatur – die sogenannte *blocking temperature* – definiert werden, für welche die thermische Energie $k_B T$ klein genug ist, so dass für Partikel definierter Größe bei bestimmter Messdauer keine thermisch induzierte Magnetisierungsumkehr erfolgen kann und die Magnetisierung „geblockt“ ist.^{[61],[62]} Da das Fehlen von M_R ebenso ein Charakteristikum eines Paramagneten ist, hat sich für das beschriebene magnetische Verhalten Superparamagnetismus etabliert.^{[56],[63]} Dieses Verhalten kann bei Nanopartikeln magnetischer Materialien, wie den in dieser Arbeit verwendeten SPIONsⁱ, beobachtet werden.

ⁱ SPIONs = superparamagnetic iron oxide nanoparticles, engl. superparamagnetische Eisenoxid-Nanopartikel

2.3 Koordinationsverbindungen, CPs und MOFs

Koordinationsverbindungen können gemäß der *IUPAC*-Definition für Koordination^[64] als Lewis-Säure-Base-Addukte beschrieben werden. Dabei fungieren bei Bindungsknüpfung die Liganden als Lewis-Basen und somit als Elektronenpaar-Donoren. Im Umkehrschluss können von den Liganden koordinierte Zentraltelchen (häufig Metallatome, -ionen oder Cluster) als Lewis-Säuren und damit als Elektronenpaar-Akzeptoren angesehen werden.^{[54],[65]} Ein Ligand, welcher zu einer derartigen Koordination imstande ist, wird als *L*-Typ klassifiziert. Da die Herkunft von Bindungselektronen nach der Bindungsknüpfung nicht feststellbar ist und auch eine radikalische Reaktion (*X*-Typ-Ligand) zwischen Zentralatom und Ligand oder eine Rückbindung von Zentralatom zum Liganden (*Z*-Typ-Ligand) möglich ist, stellt der Ursprung des Bindungselektronenpaares kein hinreichendes Kriterium zur Definition einer koordinativen Bindung dar.^[34] Allgemeiner lässt sich eine Koordinationsverbindung darüber definieren, dass ein oder mehrere Zentraltelchen, bei denen es sich üblicherweise um Metallatome oder -ionen handelt, Bindungen zu umgebenden Atomen bzw. Atomgruppen (Liganden) bildet. Dabei werden häufig mehr Liganden gebunden, als über deren Valenz zu erwarten ist.^{[34],[54]}

Eine besondere Klasse von Koordinationsverbindungen stellen die Koordinationspolymere (CPs^k) dar. Sie zeichnen sich durch einen polymeren Aufbau koordinativer Entitäten aus.^{[66],[67]} Zentrale Einheiten (sogenannte SBUs^l) werden über multidentate Liganden (Linker) miteinander verbrückt,^{[8],[67]} wodurch sich eindimensionale Stränge, zweidimensionale Schichten oder dreidimensionale Gerüste ergeben. In Relation zu klassischen, organischen Polymeren weisen CPs häufig eine höhere thermische und chemische Stabilität auf.^[68] Als Beispiel für Linker, welche zur Synthese von CPs verwendet werden, seien an dieser Stelle die prominenten Vertreter Terephthalsäure (H₂BDC^m), Imidazol (ImH), 1,2,4-1*H*-Triazol (TzH) und 4,4'-Bipyridin (Bipy) genannt, welche in Abb. 4 dargestellt sind. Sowohl diese Moleküle als auch ihre Derivate, sind aufgrund mehrerer, funktioneller Gruppen bzw. Heteroatome und resultierender Mehrzähnigkeit in der Lage, SBUs polymer zu verbrücken.^[69]

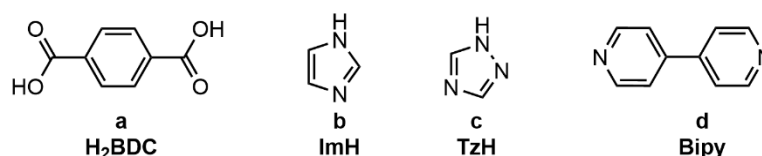


Abb. 4. Gerüstformeln von 1,4-Benzoldicarbonsäure (a), Imidazol (b), 1,2,4-1*H*-Triazol (c) und 4,4'-Bipyridin (d) als Beispiele für häufig genutzte Liganden zur Herstellung von CPs und MOFs.

^j *International Union of Pure and Applied Chemistry*, engl. Internationale Union für reine und angewandte Chemie

^k Von engl. *coordination polymers*

^l Von engl. *secondary building units*

^m Von engl. 1,4-*benzenedicarboxylic acid*

Eine Untergruppe der CPs stellen die sogenannten *metal-organic frameworks* (MOFs) dar. Koordinationspolymere, welche potenzielle Porosität aufweisen, werden *per definitionem* zu dieser Verbindungsklasse gezählt.^[67] Hierbei ist zu beachten, dass sich für die Bezeichnung „*metal-organic*“ die Übersetzung „metallorganisch“ etabliert hat, was dem englischen Begriff „*organometallic*“ entspricht. Dies suggeriert das Vorhandensein von Metall-Kohlenstoff-Bindungen, welche jedoch in Koordinationspolymeren wie auch MOFs in der Regel nicht vorliegen. Aus diesem Grund wird entsprechend der Übersetzung der IUPAC-Empfehlungen^[70] in dieser Arbeit die Bezeichnung „Metall-organisch“ verwendet. Bereits seit den 1960er Jahren werden MOFs intensiv erforscht.^{[69],[71]} Unter anderem die Forschungsgruppen um *Omar Yaghi*,^{[72],[73]} *Mohamed Eddaoudi*,^{[73],[74],[75]} *Wei Liu*,^[76] *Susumu Kitagawa*^{[69],[77]} oder *Richard Robson*^[78] haben zahlreiche Publikationen über deren Synthese, strukturelle Charakterisierung und Eigenschaften verfasst. Erst jüngst (08.10.2025) wurden *Omar Yaghi*, *Susumu Kitagawa*, und *Richard Robson* für Entwicklung Metall-organischer Gerüstverbindungen mit dem Nobelpreis für Chemie honoriert,^[79] was die Signifikanz und das Potenzial dieser Verbindungen verdeutlicht. Für viele MOFs haben sich bereits Trivialnamen bzw. Abkürzungen, wie beispielsweise ZIFⁿ, MIL^o, HKUST^p, MOF^q oder UiO^r, etabliert.

Durch die intrinsischen Eigenschaften von MOFs ergeben sich zahlreiche potenzielle Applikationen, weshalb nach der Anwendbarkeit für verschiedenste Problemstellungen geforscht wird. Anwendungen beispielsweise in der Katalyse chemischer Reaktionen,^{[19]–[23],[80]} Gasspeicherung, -reinigung und Separation von Gasen,^{[81],[82],[83]} die Verwendung für elektrochemische Zwecke,^{[16]–[18],[84]} medizinische Applikationen wie etwa als MRT^s-Kontrastmittel oder Trägermaterial für Krebsmedikamente^{[11]–[15],[85],[86]} sowie die Speicherung diverser Verbindungen^{[75],[87]} sind möglich. In den folgenden Kapiteln werden Vertreter dieser Verbindungsklassen anhand von Beispielen und potenziellen Anwendungen näher beleuchtet.

2.3.1 Koordinationsverbindungen auf Basis von Übergangsmetallen

Ein Beispiel für Übergangsmetall-basierte MOFs stellt die Verbindung IFP-1 dar, welche auch in der vorliegenden Arbeit zur Synthese opto-magnetischer Komposite genutzt wurde. Die Bezeichnung IFP (*imidazolate framework Potsdam*)^[83] suggeriert bereits, dass es sich bei IFP-1 um eine Gerüstverbindung handelt, welche ein Imidazolat-Derivat als Linker

ⁿ *zeolitic imidazolate framework*, engl. zeolithische Imidazolat-Gerüstverbindung

^o *Matériaux de l'Institut Lavoisier*, franz. Materialien des Lavoisier-Instituts

^p *Hong Kong University of Science and Technology*. engl. Hongkong-Universität für Wissenschaft und Technologie

^q Einige MOFs werden in Kombination mit einer Nummer abgekürzt, wie beispielsweise MOF-74.

^r *Universitetet i Oslo*, norw. Universität von Oslo

^s MRT = *Magnetresonanztomographie*

aufweist. Enthaltenes 4-Amido-5-imidato-2-methylimidazol (Abb. 5b, Verbindung 2) wird *in situ* aus 4,5-Dicyano-2-methylimidazol (Abb. 5b, Verbindung 1) gebildet und verknüpft über Amido- und Imido-Funktionalitäten sowie die Imidazol-Heteroatome je sechs Zinkionen pro Linker. Jedes Metallion wird durch einen Liganden über das N-Atom an Position 1 des Imidazol-Ringes und der benachbarten Imidogruppe koordiniert. Weiterhin findet eine Koordination eines zweiten Linkers über das Imidazol-N-Atom an Position 3 und das Sauerstoffatom der benachbarten Amido-Gruppe statt. Durch Koordination eines dritten Ligandmoleküls über das Sauerstoffatom der Imido-Gruppe, wird die Koordinationssphäre der Zinkionen komplettiert. Somit stellt dieses Netzwerk ein seltenes Beispiel einer Verbindung dar, in welcher Zink fünffach – hier zudem homoleptisch – koordiniert vorliegt.^[83] Ein Ausschnitt der Struktur ist in Abb. 5a dargestellt. Durch Variation des enthaltenen Metallions oder der Funktionalität an Position 2 des Imidazol-Liganden können weitere, zueinander isoretikuläre IFP-Netzwerke synthetisiert werden. So weisen beispielsweise IFP-1, -2, -3, -4, -5 und 8, deren Liganden in Abb. 5c skizziert sind, diese strukturelle Verwandtschaft auf.^{[81],[88]}

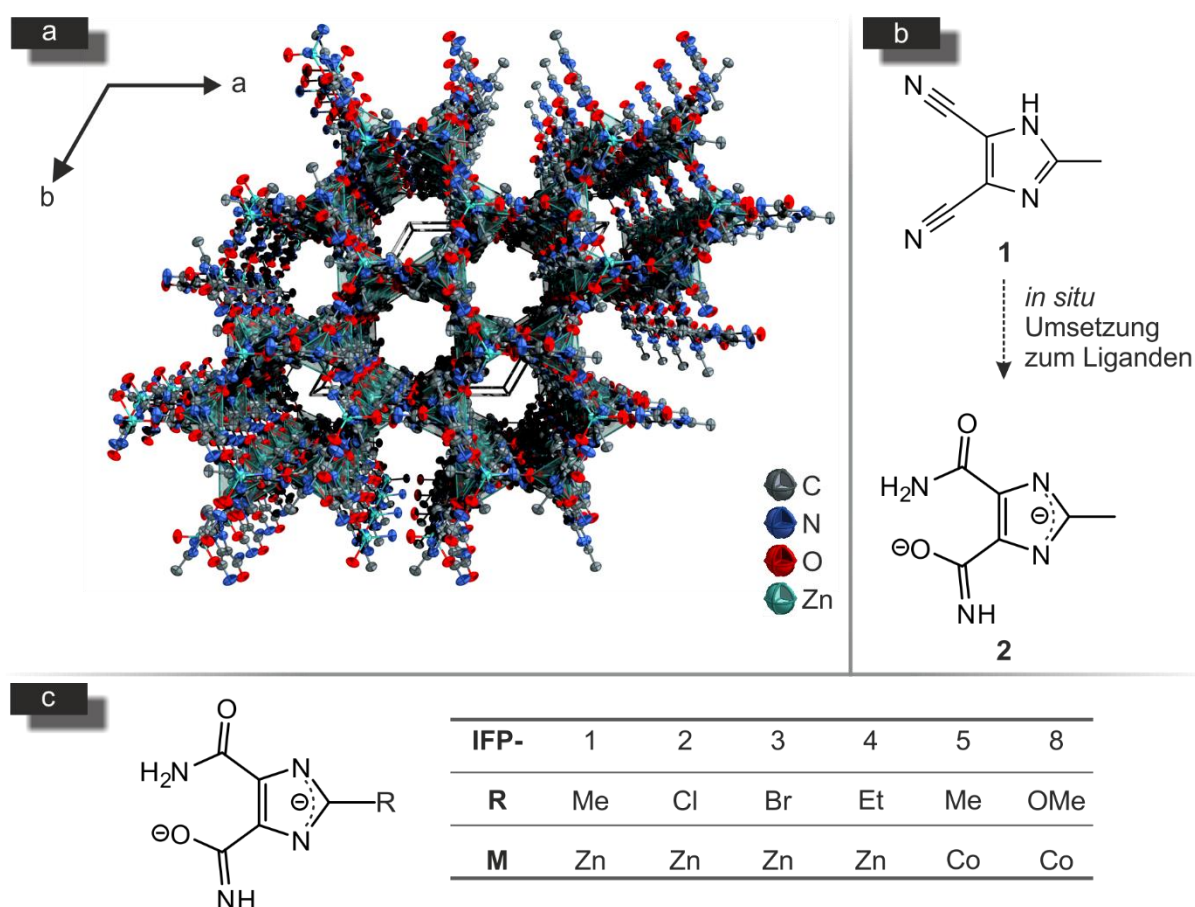


Abb. 5. **a:** Dreidimensionaler Ausschnitt aus der Kristallstruktur von IFP-1 entlang der kristallographischen c-Achse. Zur besseren Übersicht sind Wasserstoffatome nicht dargestellt. Erstellt unter Zuhilfenahme veröffentlichter Einkristallstrukturdaten;^[83] **b:** Gerüstformeln der zur Synthese des MOFs eingesetzten, organischen Verbindung 4,5-Dicyano-2-methylimidazol (1) und des *in situ* gebildeten Liganden 4-Amido-5-imidato-2-methylimidazol (2);^[83] **c:** Liganden und Metallionen verschiedener IFP-Netzwerke.^{[81],[88]}

Aufgrund ihrer großen inneren Oberflächen werden IFP-Netzwerke intensiv auf Anwendbarkeit in der Gasspeicherung und -separation erforscht.^{[75],[77],[83]} Daneben kann durch Zugabe von $\text{Eu}(\text{NO}_3)_3$ und $\text{Tb}(\text{NO}_3)_3$ bei der Synthese von IFP-1 das MOF *in situ* mit den Lanthanoidionen kodotiert werden. Eu^{3+} und Tb^{3+} können anschließend über den Linker (Antenneneffekt, s. Kap. 2.1.2) zur jeweils charakteristischen Lumineszenz angeregt werden. In Kombination mit der Ligand-basierten, blauen IFP-Lumineszenz bildet EuTb@IFP-1 einen RGB^t-Emitter. Die Chromatizität emittierten Lichtes ist abhängig von den Verhältnissen der einzelnen Komponenten und der Temperatur und kann bis hin zur Weißlichtemission eingestellt werden.^[89]

2.3.2 Koordinationsverbindungen auf Basis von Lanthanoiden

Unter dem Begriff „Lanthanoide“ werden Lanthan und die im Periodensystem darauffolgenden 14 Elemente (Cer, Praseodym, Neodym, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, Lutetium) bezeichnet. Gemeinsam mit Yttrium und Scandium bilden sie die Gruppe der Selten-Erd-Metalle. Obgleich „Lanthanoide“ gleichzusetzen ist mit „dem Lanthan Ähnliche“, wird üblicherweise das Element Lanthan ebenfalls zu dieser Gruppe gezählt.^[90]

Ebenso wie Übergangsmetalle sind auch Lanthanoide (Ln) in der Lage, Koordinationspolymere und Metall-organische Gerüstverbindungen zu bilden. Häufig sind bei Lanthanoidhaltigen Koordinationsverbindungen hohe Koordinationszahlen von acht und neun bis hin zu zwölf vorzufinden.^{[91],[92]} Durch geeignete Wahl der Bestandteile können entsprechende Verbindungen – neben struktureller Rigidität, Porosität und großer innerer Oberfläche – die lanthanoidspezifische Photolumineszenz oder Magnetismus als weitere Eigenschaften zugeführt werden. Vor allem die dreiwertigen Ionen von Europium und Terbium, welche rote bzw. grüne Photolumineszenz aufweisen, sowie von Neodym und Ytterbium (NIR^u-Emitter) sind prominente Vertreter, die zur Darstellung von CPs und MOFs genutzt werden.^[92] Aufgrund der charakteristischen Lumineszenz werden Ln-MOFs häufig als Sensormaterialien für unterschiedliche Stimuli genutzt. So ist beispielsweise Eu-haltiges MOF-76 ($[\text{Eu}(\text{BTC})(\text{H}_2\text{O})]$, BTC = Benzol-1,3,5-tricarboxylat) einsetzbar als *turn-off* Sauerstoffsensor.^[25] Das Netzwerk Eu-TDA-DHTP (TDA = 2,5-Thiophendicarboxylat, DHTP = 2,5-Dihydroxyterephthalat) könnte Anwendung als ratiometrischer Sensor für einen Anthrax-Biomarker finden.^[93] Die Verbindung $[\text{Ln}_2(\text{AATA})_3(\text{DMF})_4]$ (Ln = Tb, Eu, Gd, AATA = 2,5-Diacetylamidoterephthalat, DMF = *N,N*-Dimethylformamid) ist zur ratiometrischen Detektion von NO_2 und SO_2 verwendbar.^[94] Mit

^t RGB = **R**ot-**G**rün-**B**lau

^u *near-infrared*, engl. nahes Infrarot

$[\text{Ln}_2(\text{L})_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Tb}$; $\text{L} = 5\text{-(1,2,4-Triazol-1-yl)benzol-1,3-dicarboxylat}$) ist eine ratiometrische Detektion von 1-Hydroxypyren, einem Abbauprodukt von PAKs^v in menschlichem Urin möglich.^[95]

Ein Vertreter Lanthanoid-basierter MOFs, welcher auch in dieser Arbeit Anwendung in magneto-optischen Kompositen findet, ist ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$.^[96] In diesem MOF werden enthaltene Tb^{3+} -Ionen von sechs Terephthalat-Molekülen (BDC) über je ein Sauerstoffatom einer Carboxygruppe koordiniert. Zudem koordinieren zwei Wassermoleküle an das Lanthanoidion. Somit liegen enthaltene Tb^{3+} achtfach koordiniert vor. Jedes weitere Sauerstoffatom der BDC-Linker bindet an ein weiteres Tb^{3+} -Ion. Demzufolge verknüpft ein Linkermolekül vier Lanthanoidionen, wodurch sich insgesamt die dreidimensional polymere Struktur ergibt, für welche ein Ausschnitt Abb. 6 festgehalten ist. Die Tb^{3+} -Ionen dieses Netzwerks können aufgrund des Antenneneffekts über den Liganden angeregt werden, woraufhin deren charakteristische grüne Lumineszenz beobachtbar ist.^[96] Dieses MOF, bzw. die dazu isotype Verbindung ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ wurde erfolgreich auf Anwendbarkeit im Radiolumineszenz-Imaging,^[86] als Sensor für Cu^{2+} -Ionen,^[97] zum Nachweis latenter Fingerabdrücke^[98] oder in Kombination mit Spiropyran als Fälschungssicherungsmerkmal erforscht.^[99]

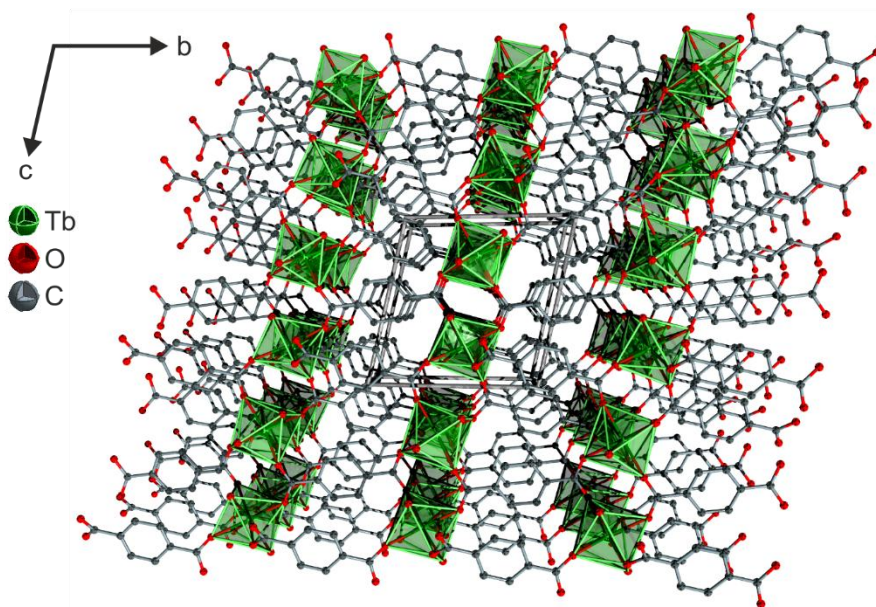


Abb. 6. Dreidimensionaler Ausschnitt aus der Kristallstruktur von ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ entlang der kristallographischen a -Achse. Zur besseren Übersicht sind Wasserstoffatome nicht dargestellt. Koordinationspolyeder um Tb-Atome sind in Grün dargestellt. Erstellt unter Zuhilfenahme veröffentlichter Einkristallstrukturdaten.^[96]

^v PAKs = polyzyklische aromatische Kohlenwasserstoffe

2.3.3 Koordinationsverbindungen mit 2-(1,2,4-1*H*-Triazol-3-yl)pyridin

Auch der Ligand 2-(1,2,4-1*H*-Triazol-3-yl)pyridin (Hpt, s. Abb. 7a), auf dessen Basis im Rahmen dieser Arbeit neuartige Koordinationsverbindungen entwickelt wurden, wird seit einiger Zeit zur Synthese von Koordinationsverbindungen mit vielfältigen Eigenschaften erforscht. So zeigt der Komplex $[\text{Fe}(\text{Hpt})_3](\text{BF}_4) \cdot \text{H}_2\text{O}$, in welchem Fe(II) oktaedrisch von drei Hpt-Ligandmolekülen koordiniert vorliegt, einen temperatur-abhängigen *spin-crossover*^[100] und damit thermochromes Verhalten. Die Kombination von $[\text{Re}(\text{CO})_5\text{Cl}]$ und Hpt resultiert in der Koordinationsverbindung $[\text{Re}(\text{Hpt})(\text{CO})_3\text{Cl}]$, in welcher Rhenium oktaedrisch von einem Chlorido-, drei Carbonyl- und einem Hpt-Liganden koordiniert ist. Sie kann genutzt werden, um sowohl elektrokatalytisch,^[101] als auch photokatalytisch (mit bereits niedrigen Intensitäten an sichtbarem Licht) CO_2 zu Kohlenmonoxid zu reduzieren.^[102]

In der deprotonierten Form ist das resultierende Molekül 3-(Pyridin-2-yl)-1,2,4-triazolat (Abb. 7b) auch in der Lage SBUs miteinander zu verknüpfen und Koordinationspolymere zu bilden, wie beispielsweise für $[\text{Cu}(\text{OAc})(\text{pt})]$ ^[103] oder $[\text{Cu}(\text{L})(\text{pt})]$ (mit L = Pyridin-4-carbonsäure)^[104] berichtet wurde. Hierbei koordinieren die benachbarten *N*-Atome des Triazol-Ringes an zwei verschiedene Kupferionen. Auch photolumineszierende Koordinationsverbindungen auf Lanthanoid-Basis wurden mit Hpt bzw. pt synthetisiert. Der Ligand bildet mit Y, Sm, Eu, Gd und Tb Komplexe mit der allgemeinen Summenformel $[\text{Ln}(\text{pt})_3(\text{H}_2\text{O})_3]$, in welchen die Selten-Erd-Elemente durch drei zweizählige pt-Moleküle und drei Wassermoleküle neunfach koordiniert vorliegen. In Abhängigkeit des enthaltenen Lanthanoids weisen diese Verbindungen die entsprechende charakteristische Lumineszenz auf. Die Anregung erfolgt aufgrund des Antenneneffekts über den pt-Liganden.^[105] Hierüber zeigt sich, dass Hpt bzw. pt ideale Kandidaten zur Synthese neuer, optisch aktiver Koordinationsverbindungen sind.

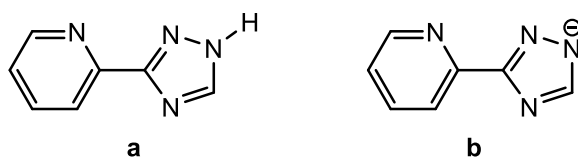


Abb. 7. a: Gerüstformel des Liganden 2-(1,2,4-1*H*-Triazol-3-yl)pyridin bzw. 3-(Pyridin-2-yl)-1,2,4-1*H*-triazol (Hpt); b: Gerüstformel der deprotonierten Form von Hpt, 3-(Pyridin-2-yl)-1,2,4-triazolat (pt).

2.3.4 Postsynthetische Modifizierung von MOFs

Die postsynthetische Modifizierung (PSM) von MOFs stellt eine Möglichkeit dar, Metall-organische Gerüstverbindungen nach erfolgter Darstellung mit Funktionalitäten zu versehen und so deren Eigenschaften zu variieren oder zu erweitern. Zudem wird über PSM die

Herstellung neuer MOFs ermöglicht, welche nicht über eine *de novo* Reaktion synthetisierbar wären oder deren nötige Edukte nicht stabil wären.^{[106],[107]} Der Begriff postsynthetische Modifizierung umfasst SBU-basierte, Ligand-basierte oder Gastmolekül-basierte Variationen bestehender MOFs.^[106] Dies beinhaltet beispielsweise den Austausch von Liganden,^[108] Reaktionen am Linker,^[109] Transmetallierungen^[110] oder den Austausch bzw. die Einbringung von Gastmolekülen in das Porensystem^w der MOFs.^{[111],[112]} Vor allem die postsynthetische Modifizierung der Poren durch Gastspezies ist eine attraktive Methode zum Einbringen diverser Spezies mit optischen Eigenschaften, um damit beispielsweise Lumineszenz zur Palette der Eigenschaften von üblicherweise nicht-lumineszierenden MOFs hinzuzufügen.^[113] So können beispielsweise in die Poren des MOFs DUT^x-5(Al) ($\frac{3}{2}$ [Al(OH)(BPDC)], BPDC = 1,1'-Biphenyl-4,4'-dicarboxylat) Eu³⁺-Ionen integriert werden, wodurch über Ausnutzen der Photolumineszenz und Oxophilie des Lanthanoids ein hochsensibler *turn-off* Sauerstoffsensor entsteht.^[114] Die Imprägnierung des MOFs {[Ni₂(odip)(H₂O)₄(DMF)]·DMF·2H₂O}_n (odip = 5,5'-Oxydiisophthalat) mit Eu³⁺ resultiert in einer Verbindung, welche als selektives Sensormaterial für Asparaginsäure anwendbar ist, in deren Anwesenheit Lumineszenzlöschung auftritt.^{[43],[115],[116]}

2.4 Superparamagnetische Eisenoxid-Nanopartikel (SPIONs)

Zur Herstellung superparamagnetischer Nanopartikel (s. Kap. 2.2.3) werden häufig die Metalle Eisen, Cobalt oder Nickel, bzw. deren Oxide herangezogen.^[117] Sie können über diverse Synthesemethoden gewonnen werden. Vor allem Kopräzipitation,^[118] Hydrothermalsynthese^[119] oder thermische Zersetzung^{[116],[120]} haben sich als Methoden etabliert. Aufgrund der großen Oberfläche bei zeitgleich niedrigem Volumen und damit einhergehender großer Anzahl an Oberflächendefekten, weisen nanopartikuläre Materialien eine hohe Oberflächenenergie auf. Um diese zu minimieren, neigen die Partikel zur Agglomeration und Aggregation, wodurch Eigenschaften verloren gehen können, welche mit der kleinen Partikelgröße korrelieren. Dies kann verhindert werden, indem die Oberfläche von Nanopartikeln so modifiziert wird, dass eine Agglomeration oder Aggregation nicht mehr möglich ist. Für superparamagnetische Eisenoxid-Nanopartikel (SPIONs), wie sie auch in der vorliegenden Arbeit zur Synthese opto-magnetischer Komposite Anwendung fanden, werden unter Anderem langkettige Fettsäuren wie Ölsäure,^[121] Polymere,^[122] Silica^[123] oder Citrat^[124] als Stabilisatoren verwendet, die elektrostatisch bzw. kovalent an die Nanopartikel binden.^[125]

^w Das Porensystem hochporöser MOFs ist nach der Synthese selten frei von Gastmolekülen. Vielmehr sind die Kavitäten von Solvensmolekülen oder Reaktanden besetzt,^[111] welche durch eine Aktivierung entfernt werden können.

^x DUT = Dresden University of Technology, engl. Technische Universität Dresden

Superparamagnetische Eisenoxid-Nanopartikel (SPIONs) sind die einzigen, für den klinischen Einsatz erprobten Metalloxid-Partikel,^[126] weshalb sie vor allem im medizinischen Sektor für vielseitige Anwendungen erprobt werden. So ist es möglich Fe₃O₄-Nanopartikel zur Krebstherapie mittels Hyperthermie,^[127] oder als Kontrastmittel für MRT-Untersuchungen einzusetzen.^[128]

2.5 Multifunktionale, magnetische Komposite

Durch die Oberflächenfunktionalisierung von SPIONs kann nicht nur eine Stabilisierung gegen Agglomeration und Aggregation erreicht, sondern auch eine Kombination mit weiteren funktionellen Substanzen ermöglicht werden, wodurch Kompositmaterialien entstehen. Diese sind gemäß IUPAC als Material aus mehreren (nicht gasförmigen) Komponenten definiert, von welcher mindestens eine Substanz eine kontinuierliche Phase ist.^[129]

Einige Komposite auf Basis von SPIONs sind ebenfalls vielversprechende Kandidaten für zahlreiche potenzielle Anwendungen. So könnte künftig ein Komposit aus einem Copolymer von Polylactid-co-Glycolid und Polyethylenglycol, dem Medikament Methotrexat und SPIONs für gezielten Transport und die anschließende Freisetzung des Arzneimittels in der Krebstherapie eingesetzt werden.^[126] Ebenso eignet sich ein Komposit aus Citrat-stabilisierten Eisenoxid-/Hydroxylapatit Nanopartikeln und dem Zytostatikum 5-Fluorouracil zum magnetischen Medikamententransport in Kombination mit Hyperthermietherapie von Tumoren.^[130] Das Kompositsystem bestehend aus SPIONs und einem Copolymer-Hydrogel von Acrylsäure und Vinylsulfonsäure wurde erfolgreich auf die Anwendung zur Separation gesundheitsschädlicher Methylenblau-Farbstoffen aus Abwässern getestet, wodurch ein wichtiger Beitrag zum Umwelt- und Gesundheitsschutz geleistet werden kann.^[131] Ebenso ist die Darstellung von Kompositen auf Basis superparamagnetischer Eisenoxid-Nanopartikel und Metall-organischer Gerüstverbindungen (MOFs) möglich, welche im Folgenden genauer erläutert werden.

2.5.1 MOF-basierte Komposite mit SPIONs

Die Kombination magnetischer Partikel mit Metall-organischen Gerüstverbindungen resultiert in Kompositen, welche auch als *magnetic framework composites* (MFCs) bezeichnet werden. In diesen werden synergistisch der Superparamagnetismus der SPIONs mit den vielseitigen Eigenschaften von MOFs kombiniert, wodurch ein magnetischer Transport bzw. eine magnetische Separation der MFCs nach deren Einsatz ermöglicht wird. Für die Synthese

von MFCs werden häufig Vertreter der bereits oben erwähnten MOF-Stoffgruppen (s. Kap. 2.3) gewählt.

Ein Beispiel für ein MFC ist das Komposit bestehend aus Fe_3O_4 -Nanopartikeln und ZIF-8 ($^3[\text{Zn}(\text{im})_2]$, im = Imidazolat, s. Abb. 8a), welches dazu verwendet werden kann, Pb(II) und das Antibiotikum Oxytetracyclin (OTC) aus wässrigen Medien zu separieren.^[132] In ähnlicher Art und Weise ist es möglich das Komposit $\text{Fe}_3\text{O}_4@\text{mSiO}_2/\text{NH}_2\text{-MIL-101(Fe)}$ – bestehend aus SPIONs und einem Amino-funktionalisierten, Eisen-haltigen Analogon von MIL-101 (s. Abb. 8b) in einer Chloropropyl-modifizierten SiO_2 -Matrix – zur Separation von Pb(II) und Cd(II) einzusetzen.^[133]

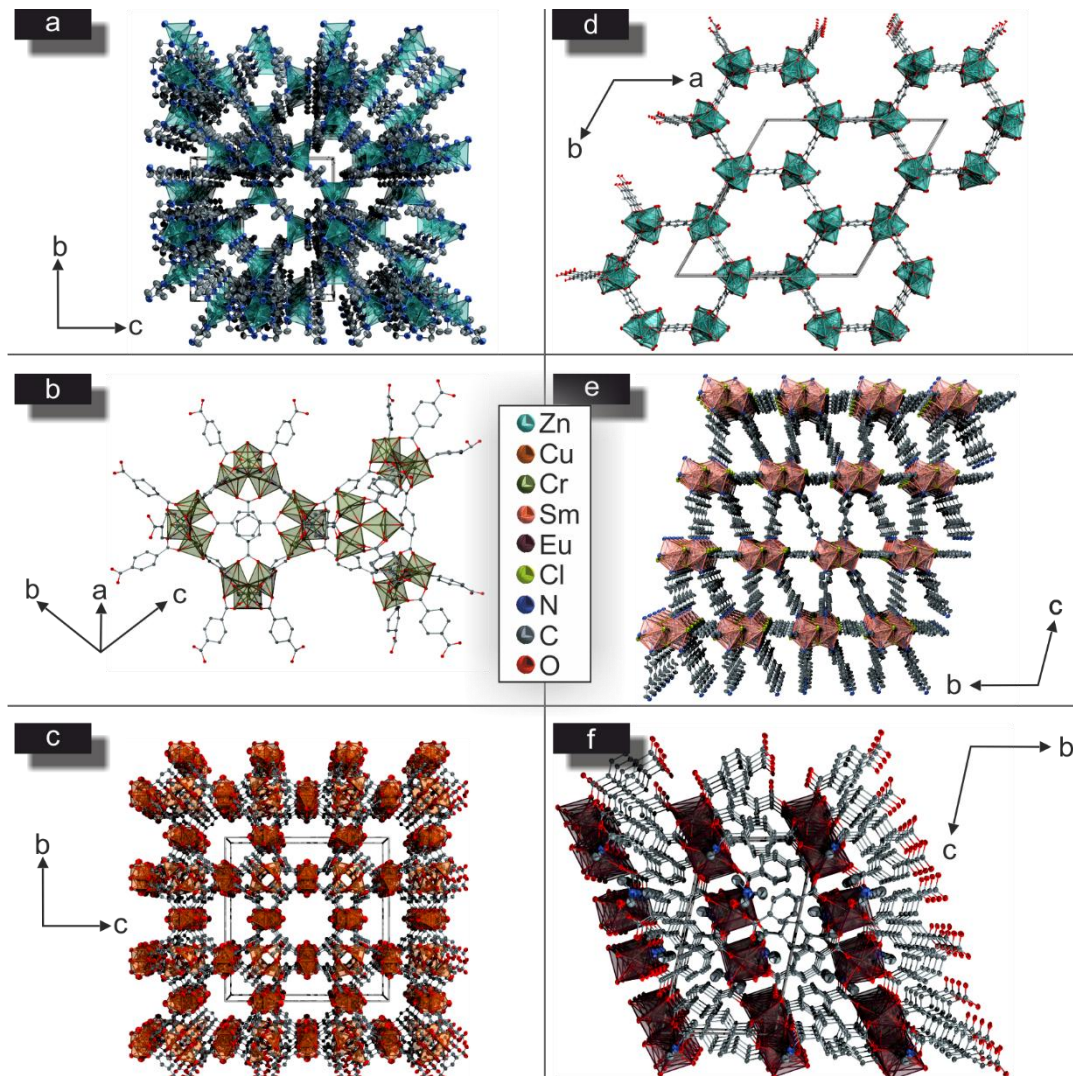


Abb. 8. Ausschnitte aus den Kristallstrukturen diverser MOFs, welche als Kompositpartner für MFCs dienen können. Polyeder um Metallionen sind in den jeweiligen Farben der Ionen dargestellt. Aus Gründen der Übersichtlichkeit sind Wasserstoffatome und in Poren eingelagerte Moleküle nicht abgebildet. Erstellt unter Zuhilfenahme veröffentlichter Einkristallstrukturdaten.^{[134]–[139]}
a: ZIF-8,^[134] $^3[\text{Zn}(\text{im})_2]$, im = 2-Methylimidazolat; **b:** MIL-101 bzw. MIL-101(Cr),^[135] $^3[\text{Cr}_3(\text{O})\text{X}(\text{BDC})_3(\text{H}_2\text{O})_2]$, X = F oder OH, BDC = Benzol-1,4-dicarboxylat (isotyp zu oben erwähntem MIL-101(Fe)); **c:** HKUST-1,^[136] $^3[\text{Cu}_3(\text{BTC})_2]$, BTC = Benzol-1,3,5-tricarboxylat; **d:** Zn-MOF-74,^[137] $^3[\text{Zn}_2(\text{DOBDC})(\text{DMF})_2]$, DOBDC = 2,5-Dioxidobenzol-1,4-dicarboxylat; **e:** $^2[\text{Sm}_2\text{Cl}_6(\text{Bipy})_3]\cdot 2\text{Bipy}$,^[138] Bipy = 4,4'-Bipyridin (isotyp zu oben erwähntem $^2[\text{Tb}_2\text{Cl}_6(\text{Bipy})_3]\cdot 2\text{Bipy}$); **f:** $^3[\text{Eu}_2(\text{BDC})_3]\cdot 2\text{H}_2\text{O}\cdot 2\text{DMF}$,^[139] DMF = *N,N*-Dimethylformamid.

Eine Kombination des MOFs HKUST-1 ($[\text{Cu}_3(\text{BTC})_2]$, BTC = Benzol-1,3,5-tricarboxylat, s. Abb. 8c) – welches sich als potentes Material für die Adsorption von Kohlenstoffdioxid herausgestellt hat – mit Citrat-stabilisierten SPIONs resultiert in einem magnetisch separierbaren und regenerierbaren Adsorbens für CO_2 .^[140] MFCs bestehend aus MOF-74 ($[\text{M}_2(\text{DOBDC})(\text{DMF}_2)]$, M = Mg, Mn, Co, Ni, Cu oder Zn; DOBDC = 2,5-Dioxidobenzol-1,4-dicarboxylat, s. Abb. 8c) und SPIONs zeigen katalytische Aktivität in Bezug auf die Veresterung von Lävulinsäure und Butanol.^[141] Dank der magnetischen Eigenschaften der genannten Komposite ist es möglich, nach erfolgter Anwendungen die Materialien zurückzugewinnen.

2.5.2 Magneto-optische Komposite

Magneto-optische Komposite stellen Materialien dar, in welchen die beiden Eigenschaften Magnetismus und Lumineszenz kombiniert sind. Um eine hohe Magnetisierung zu erreichen, wird häufig auf die kooperativen magnetischen Eigenschaften von Eisen- oder Eisenoxid-Partikel zurückgegriffen: Ferro- bzw. Ferrimagnetismus oder Superparamagnetismus (s. Kap. 9). Diese weisen im sichtbaren Bereich des elektromagnetischen Spektrums teils hohe Absorbanzen auf.^[142] Für angeregte Elektronen einer optisch aktiven Spezies in unmittelbarer Nähe zu den Magnetpartikeln existiert hierüber eine Vielzahl möglicher Pfade zur strahlungslosen Depopulation. Würden Lanthanoidionen mit Eisenoxiden in einem homogenen Material kombiniert werden, könnte die hohe Absorbanz der magnetischen Materialien auch in starke Konkurrenz zu den Lumineszenzprozessen treten. Studien haben gezeigt, dass sich beispielsweise Magnetit direkt mit Eu^{3+} dotieren lässt und ein magneto-optisches Material bildet. Jedoch wird die erreichte Sättigungsmagnetisierung durch einige Prozent an Eu^{3+} stark minimiert und in den Emissionsspektren ist nur der intensivste Übergang ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) erkennbar.^[143] Eine Kombination von Magnetismus und Lumineszenz kann auch durch sogenannte *single molecule magnets* (SSMs) auf Basis von Lanthanoiden erreicht werden.^[144] Diese weisen bisher jedoch eine *blocking temperature* (vgl. Kap. 2.2.3) von wenigen Kelvin im maximal zweistelligen Bereich auf. Bei Temperaturen darüber verlieren sie ihre starken magnetischen Eigenschaften,^[145] weswegen sie für viele alltägliche Applikationen ungeeignet sind.

Diese Umstände können durch einen heterogenen Kompositaufbau, in welchem die magnetische und die lumineszierende Komponente auf zwei separate, räumlich getrennte Materialien aufgeteilt wird, umgangen werden. Resultierende Materialkombinationen werden auch als magneto-optische oder luminomagnetische Komposite bezeichnet. In Analogie zu oben erwähnten Systemen, dienen auch für magneto-optische Komposite häufig partikuläre Metalloxide als magnetischer Teils des Kompositmaterials. Als Komponente mit optischen

Eigenschaften haben sich diverse Verbindungen als praktikabel erwiesen. So ist es möglich Glutathion, Diethylentriamin und Ammoniumeisencitrat zu einem luminomagnetischen Komposit bestehend aus Kohlenstoff-Quantenpunkten (QDs^y) als fluoreszierendem Material in Kombination mit Fe₃O₄-Partikeln als magnetischer Komponente zu generieren. Dieses magneto-optische Komposit kann genutzt werden, um aus wässrigen Medien Hg²⁺ zu adsorbieren, über Fluoreszenzlöschung zu detektieren und sogar magnetisch zu separieren.^[31] Durch eine Modifikation des Kohlenstoff-QD-Fe₃O₄-Komposits mit einer DNA-Sequenz, welche hochselektiv an das Fungizid Carbendazim binden kann, entsteht ein luminomagnetischer Sensor für die Detektion dieses Pflanzenschutzmittels.^[146] Weiterhin können lumineszierende CdSe@ZnS Quantenpunkte mit Fe₃O₄-Nanopartikeln – eingekapselt in polymeren Hybrid-Nanopartikeln – kombiniert werden. Durch verschiedene Gehalte an CdSe und ZnS kann die Chromatizität von Grün, über Gelb, bis hin zu Rot eingestellt werden. Entsprechende Komposite wurden bereits erfolgreich auf die Verwendung für konfokal-mikroskopische und magnetresonanztomografische Untersuchungen von Tumorzellen erprobt.^[29]

Anstelle von Quantenpunkten kann auch auf Lanthanoid-dotierte Verbindungen zurückgegriffen werden, wie beispielsweise bei dem Komposit Fe₃O₄/Gd₂O₃:Tb³⁺@SiO_x gezeigt, welches zur Lumineszenz-basierten Zellmaskierung und als MRT-Kontrastmittel Anwendung finden kann.^[147] Als potenzielles Material für die Tumorbildgebung und optisch geführte Hyperthermie zur Krebstherapie hat sich das Komposit Fe₃O₄@SiO₂@GdPO₄:Tb³⁺,Ce³⁺ herausgestellt. Ce³⁺ fungiert hier als Sensitizer für die Lanthanoid-Lumineszenz von Tb³⁺-dotiertem GdPO₄.^[30] Auch die Kombination von SPIONs und Y₂O₂S:Eu³⁺ resultiert in einem magneto-optischen Komposit. Fe₃O₄@Y₂O₂S:Eu³⁺ kann von ferromagnetischen Bauteilen mit Materialdefekten aufgrund von Inhomogenitäten der magnetischen Flussdichte an diesen und der darauf basierenden Akkumulation der Kompositpartikel, zur nicht-destruktiven Materialuntersuchung genutzt werden.^[148] Dieses Komposit stellt – neben beispielsweise den Systemen β-NaY_{0.8}Eu_{0.2}F₄@γ-Fe₂O₃^[149] und Eu-NaYF₄@PMAA@Fe₃O₄^[150] – einen der seltenen Fälle von magneto-optischen Kern-Satellit-Kompositen dar, bei welchen die lumineszierende Komponente als Kernmaterial vorliegt.

Als optische Komponente magneto-optischer Komposite können ebenso Koordinationsverbindungen dienen. Ein Beispiel hierfür stellt die Kombination des Lanthanoid-basierten MOF $2[\text{Tb}_2\text{Cl}_6(\text{Bipy})_3] \cdot 2\text{Bipy}$ (Bipy = 4,4'-Bipyridin), welches isotyp zu $2[\text{Sm}_2\text{Cl}_6(\text{Bipy})_3] \cdot 2\text{Bipy}$ (s. Abb. 8e) ist, und der Gerüstverbindung $3[\text{Eu}_2(\text{BDC})_3] \cdot 2\text{DMF} \cdot 2\text{H}_2\text{O}$ (DMF = *N,N*-Dimethylformamid, s. Abb. 8f) mit Fe₃O₄/SiO₂-Mikropartikeln dar. Dieses Komposit wurde erfolgreich zur ratiometrischen Wassergehaltsbestimmung mit einem Detektionslimit von ca. 0.03% H₂O in organischen Solvenzien getestet.^[32] Weiterhin ist das Ln-basierte MOF

^y von engl. *quantum dots*

${}^3\text{[Eu}_2(\text{BDC})_3\text{]}\cdot 2\text{DMF}\cdot 2\text{H}_2\text{O}$ mit anisotropen, superparamagnetischen Fe_3O_4 -Mikrostäben vereinbar, wodurch ein Komposit geschaffen wurde, dessen optische Eigenschaften durch ein externes Magnetfeld schaltbar sind.^[151] Für das Komposit $\text{Fe}_3\text{O}_4@\text{Eu}(\text{BDC})$ wurde eine sensorische Reaktion auf Metronidazol und Levofloxacin nachgewiesen, wodurch eine Applikation als magnetisch separierbarer Sensor für Antibiotika denkbar wird.^[152]

2.5.3 Synthesestrategien für MOF-SPION-Komposite und deren Aufbau

Für die Präparation von MOF-SPION-Kompositen wird zwischen verschiedenen Synthesestrategien anhand der zugrundeliegenden, ablaufenden Mechanismen und des resultierenden Aufbaus unterschieden. So wird zwischen *in situ* Methoden – zu welchen die Einbettungsmethode, das *layer-by-layer*-Verfahren, oder die Verkapselung zählen – und Vermischung differenziert.^{[153]–[155]} Im Rahmen der *in situ* Verfahren werden magnetische Partikel mit MOF-Präkursoren zur Reaktion gebracht, wohingegen bei der Vermischung beide Kompositpartner vor der Kombination separat präpariert werden.^[155]

Bei der Einbettungsmethode werden magnetische Partikel mit MOF-Präkursoren gemischt und zur Reaktion gebracht, bei welcher sowohl das MOF als auch unmittelbar das Komposit gebildet werden.^{[154],[156],[157]} Es ergeben sich häufig MOF-Schalen, welche einen magnetischen Kern einschließen (sog. *core-shell*^z Struktur).^{[156],[157]} Auch eine Umkehr der Kern-Schale-Rollen und somit eine Einbettung eines MOF-Kerns in eine Schicht von SPIONs ist möglich.^[158] Ebenso können im Rahmen der Einbettungsmethode Nanopartikel in die Kavitäten von MOFs eingelagert werden.^[159] Über die Verkapselungsmethode wird zwischen magnetischen Partikeln und MOFs eine Pufferschicht eingebaut, welche das Wachstum der MOF-Schicht auf dem eingekapselten magnetischen Kernmaterial begünstigen kann.^{[153],[154]} Die resultierenden Nanomaterialien werden anschließend dem Reaktionsgemisch der MOF-Synthese zugesetzt.^[160] Als Pufferschicht werden typischerweise Materialien wie Silica,^[161] organische Polymere,^[162] oder dem Linker des MOFs ähnelnde Moleküle^[163] genutzt. Eine *layer-by-layer* Synthese beinhaltet das sequenzielle Wachstum von Schichten der MOF-Bestandteile (Metallionen und Linker) auf magnetischen Partikeln, teilweise auch in mehreren Zyklen.^[164] Auch hier resultiert in der Regel ein *core-shell* Aufbau. Eine weitere Variante für die Synthese von MFCs stellt die Vermischungsmethode dar, bei welcher die im Vorfeld hergestellten Kompositpartner MOF und SPIONs mechanisch vermischt werden.^[165] Durch die separate Synthese der einzelnen Komponenten kann die Bildung von Nebenprodukten, welche bei den *in situ* Synthesen entstehen können, verhindert werden.

^z Zu beachten ist, dass für einen derartigen Aufbau die Nomenklatur Schale@Kern angewendet wird, obgleich die Bezeichnung *core-shell* und somit Kern-Schale lautet

3 Forschungsziele

Die synergistische Fusion mehrerer Materialien in einem Kompositsystem stellt eine elegante Möglichkeit zur Kombination der intrinsischen Eigenschaften der Kompositpartner dar. Aufgrund der Vielzahl der Eigenschaften, welche Koordinationspolymeren und Metall-organischen Gerüststrukturen inhärent ist, sind Komposite auf deren Basis besonders vielversprechende Materialien für verschiedenste Anwendungen.^{[155],[166]} Insbesondere die Kombination von Metall-organischen Gerüstverbindungen (MOFs) und Koordinationspolymeren (CPs) mit magnetischen Materialien ermöglicht einen nachhaltigen Einsatz der Koordinationsverbindungen. So können magnetische MOF-basierte Komposite (MFCs) gezielt zu gewünschten Einsatzorten bewegt werden oder nach erfolgtem Einsatz magnetisch zurückgewonnen werden. Hierdurch kann die für den jeweiligen Einsatz benötigte Menge an MOFs bzw. CPs reduziert werden, wodurch die zur Herstellung benötigten Ressourcen geschont werden. MFCs haben sich in diesem Zusammenhang als potente Materialien für diverse Applikationen erwiesen.^{[132],[133],[140],[141],[167]} Lanthanoid-haltige MFCs, welche Photolumineszenz aufweisen und als magneto-optische oder luminomagnetische Komposite bezeichnet werden, stehen im Hinblick auf den Einsatz als Sensormaterialien für diverse Stimuli^{[32],[168],[169]} oder auch als Fälschungsschutz^[169] ebenso im Fokus der Wissenschaft. Aus diesem Grund ist das Ziel der vorliegenden Arbeit die Herstellung und Untersuchung von neuartigen magneto-optischen Kompositsystemen, in welchen die optischen Eigenschaften von Koordinationsverbindungen mit den magnetischen Eigenschaften von Eisen- bzw. Eisenoxidpartikeln kombiniert werden. Dies beinhaltet auch die Herstellung und Untersuchung von neuartigen Koordinationsverbindungen mit optischen Eigenschaften, welche sich potenziell zu luminomagnetischen Kompositen weiterverarbeiten lassen.

Für Anwendungen opto-magnetischer Komposite, wie die Verwendung als lumineszierende Farbanstriche oder versteckte Fälschungssicherungsmerkmale, ist das dunkle Erscheinungsbild partikulärer magnetischer Materialien häufig kontraproduktiv. Aus diesem Grund wurde die in Kap. 4.1 beschriebene Generierung eines Kompositmaterials angestrebt, welches nicht nur ein weißes Erscheinungsbild aufweist, sondern zudem noch weiß luminesziert und somit eine Bezeichnung als *All White Magnet* rechtfertigt. Ein Weißlichtemitter sendet Wellenlängen im gesamten Bereich des sichtbaren elektromagnetischen Spektrums aus. Prädestiniert hierfür sind Materialien, welche über mehrere lumineszierende Spezies verfügen, deren Farben sich additiv bis hin zu Weiß mischen. Daher wird auf die Koordinationsverbindung EuTb@IFP-1 als Emitter zurückgegriffen, welche unter UV-Bestrahlung simultan rote (Eu^{3+}), grüne (Tb^{3+}) und blaue (IFP-1-Ligand) Lumineszenz aufweist. Essenziell für ein weißes Erscheinungsbild des Komposits ist ebenfalls eine bereits „weiße Farbe“ der verwendeten Magnetpartikel auf mikroskopischer Skala, welche durch das

Einbetten der Partikel in eine Licht brechende Hülle erreicht wird. Durch die Kombination dieser beiden Komponenten, Emitter und Magnetpartikel, entsteht ein Komposit, welches die bisher einmalige Eigenschaftskombination von starkem Ferro- bzw. Ferrimagnetismus, „weißer“ Farbe und Weißlichtemission aufweist.

Ein typischer Aufbau für MFCs ist ein *core-shell* Aufbau mit einem magnetischen Kern und einer ihn umgebenden lumineszierenden MOF-Hülle. Dieser Aufbau hat zur Folge, dass mit zunehmendem MOF-Gehalt die Magnetisierbarkeit sinkt, die Lumineszenz jedoch nur bis zu einem Sättigungswert ansteigt. Ein umgekehrter Aufbau mit einem lumineszierenden Kern und einer dichten, magnetischen Hülle hätte zur Folge, dass sowohl einfallendes als auch emittiertes Licht stark absorbiert würde und die Lumineszenz entsprechender Komposite bereits bei geringen Gehalten magnetischen Materials kaum noch beobachtbar wäre. Über einen Kern-Satellit-Aufbau – wie er in Kap. 4.2 dargestellt wird – mit lumineszierendem Kern und einer Hülle von magnetischen Satellit-Partikeln hingegen ist eine Lichtemission des Kerns weiterhin möglich. Ein nanopartikulärer Aufbau der magnetischen Partikel ist ursächlich dafür, dass die lumineszierenden Kerne nicht von einer dichten Schicht magnetischen Materials umgeben werden und somit eine Propagation von Licht möglich ist. Weiterhin ist die Dispergierbarkeit entsprechender Partikel abhängig von den funktionellen Gruppen der Magnet-Satellitpartikel und hierüber von deren Gehalt. Aus diesem Grund sollte der Kern-Satellit-Aufbau mit lumineszierendem Kern und magnetischer Satellit-Partikelschale untersucht werden. Dies beinhaltet auch den Einfluss des Verhältnisses zwischen lumineszierender und magnetischer Komponente auf die magneto-optischen Eigenschaften des Komposits.

Die Suche nach neuen Verbindungen mit optischen Eigenschaften ist ebenso ein wichtiger Bestandteil der Forschung an magneto-optischen Kompositen wie die Charakterisierung neuartiger Komposite aus bekannten Verbindungen. Auch Übergangsmetall-basierte Koordinationsverbindungen können über optische Eigenschaften verfügen, welche sie für die Generierung magneto-optischer Komposite zu attraktiven Kandidaten macht. Zudem kann über das Einbringen von Lanthanoiden in das Porensystem von Übergangsmetall-basierten MOFs die Lumineszenz der Lanthanoide (Ln) zu deren Eigenschaften hinzugefügt werden. Durch den hier üblicherweise geringeren Gehalt an Lanthanoiden im Vergleich zu Ln-basierten MOFs wird so auch der Bedarf an Selten-Erd-Elementen reduziert. In Kap. 4.3 wird die Herstellung und Charakterisierung ebensolcher, bisher unbekannter Koordinationsverbindungen aufgezeigt. Da der Ligand 2-(1,2,1*H*-Triazol-3-yl)pyridin (Hpt) bzw. dessen deprotonierte Spezies 3-(Pyridin-2-yl)-1,2,4-triazolat (pt) dafür genutzt werden kann, Lanthanoidionen mittels des Antenneneffekts zur Lumineszenz anzuregen, stellt er einen idealen Kandidaten zur Synthese neuer Koordinationspolymere dar, in deren Poren

Lanthanoide eingelagert und anschließend zur Photolumineszenz angeregt werden. Doch nicht nur Photolumineszenz stellt eine Eigenschaft dar, die für magnetische Komposite mit optischen Eigenschaften genutzt werden kann. Auch beispielsweise ein thermochromes Verhalten könnte synergistisch mit Magnetismus verknüpft werden, um einen magnetisch steuerbaren Temperatursensor zu bilden. Aus diesem Grund sollte die Forschung an neuen Koordinationspolymeren mit optischen Eigenschaften nicht allein auf photolumineszierende Verbindungen beschränkt werden.

Insgesamt ist das Ziel dieser Arbeit die Entwicklung und Charakterisierung von sowohl neuartigen magneto-optischen Kompositen auf Basis von lumineszierenden Koordinationsverbindungen als auch die Erforschung neuartiger Koordinationsverbindungen mit potenziellem Einsatz in magnetischen Kompositen mit zusätzlichen, optischen Eigenschaften.

4 Ergebnisse

4.1 An all white magnet by combination of electronic properties of a white light emitting MOF with strong magnetic particle systems

Im Rahmen der ersten Publikation dieser Arbeit wird ein magneto-optisches Komposit präsentiert, welches sowohl unter Tageslicht weiß erscheint, als auch unter UV-Bestrahlung weiß luminesziert, weshalb das Komposit als *All White Magnet* bezeichnet werden kann.

Als ferro- bzw. ferrimagnetische Komponente dienen weichmagnetische α -Fe- bzw. hartmagnetische Fe_3O_4 -Partikel. Um eine weiße „Farbe“ dieser sonst schwarzen bzw. braunen Partikel zu erreichen, sind die Magnetpartikel mit einer Hülle aus Titandioxid-Partikeln mithilfe eines Styrol-Butadien-Copolymers als Bindemittel beschichtet. Ein klassischer *core-shell* Aufbau mit magnetischem Kern und einer dichten Hülle an TiO_2 sowie eine statistische Mischung von Magnet- und Titandioxid-Partikeln hat nur eine geringfügige Aufhellung der Magnetpartikel zur Folge. Essenziell für ein weißes Erscheinungsbild ist eine Anordnung von TiO_2 -Partikeln mit einer Größe entsprechend etwa der halben Wellenlänge des eingestrahlten Lichts um den magnetischen Kern herum, wodurch eine diffuse Lichtstreuung und Lichtbrechung garantiert wird. Dieser Aufbau wird über einen zweiphasigen Co-Sprühtrocknungsprozess erreicht. Anhand der *CIE L*a*b**-Farbkoordinaten der Mikromagnete wird ihr weißer Charakter deutlich. Über lasergranulometrische Untersuchungen ergab sich eine Größe von ca. 10 μm für die weißen Magnet-Suprapartikel.

Als lumineszierende Komponente dient die mit Eu^{3+} und Tb^{3+} *in situ* kodotierte, Metallorganische Gerüstverbindung IFP-1 (s. Abb. 5). Sie enthält eingelagerte Lanthanoidionen, welche mit UV-Licht über den Liganden 4-Amido-5-imidato-2-methylimidazolat des IFP-1 mittels des Antenneneffekts zur Lumineszenz angeregt werden können. Die Kombination der blauen, Ligand-basierten IFP-1-Lumineszenz und der charakteristischen roten (Eu^{3+}) bzw. grünen (Tb^{3+}) Lanthanoid-Lumineszenz ergibt nach dem RGB-Konzept einen Weißlichtemitter.

Diese beiden Komponenten werden über solvothermale Umsetzung zu *All White Magnet* Suprapartikeln kombiniert. Durch das Vorhandensein der Reflexe von EuTb@IFP-1 , TiO_2 und α -Fe bzw. Fe_3O_4 im Pulverdiffraktogramm der erhaltenen Komposite zeigt sich, dass alle eingesetzten Komponenten ohne kristalline Nebenprodukte vorliegen. Über die Lumineszenzspektren der *All White Magnet* Komposite und die Bestimmung der *CIE*-xy-Farbkoordinaten des emittierten Lichtes wird weiterhin ersichtlich, dass – unabhängig von der Kombination mit den weißen Mikromagneten – die Weißlichtemission erhalten bleibt. In Kombination mit der beobachteten Magnetisierbarkeit der erhaltenen Produkte wird eine erfolgreiche, synergistische Fusion der Magnetpartikel und des MOF evident. Weiterhin zeigt

sich anhand der rasterelektronenmikroskopischen Untersuchungen, dass die Strukturierung der *All White Magnet* Komposite abhängig von der Kontaktzeit der Reaktionspartner während der Solvothermalsynthese ist. Durch Variation der Reaktionszeit kann der Beschichtungsmodus von 1 – 3 μm großen MOF-Partikeln, welche in die TiO_2 -Partikelhülle eingebaut werden, bis hin zu magnetischen Satellitpartikeln auf den Oberflächen von 50 – 70 μm großen EuTb@IFP-1 -Kristalliten variiert werden. Durch das weiße Erscheinungsbild und die weiße Lumineszenz mit charakteristischen Banden, sowie die Magnetisierbarkeit ist eine Anwendung der *All White Magnet* Komposite als magnetisch steuerbare Weißlichtquelle oder als verstecktes, schwer zu kopierendes Fälschungssicherheitsmerkmal denkbar.

Entscheidend für die erfolgreiche Eigenschaftskombination der Aufbau der Suprapartikel. Neben der erforderlichen, partikulären TiO_2 -Beschichtung der Magnetpartikel ermöglicht die Zugabe des lumineszierenden MOF zur äußeren Schicht der Komposite bzw. einen Kern-Satellit-Aufbau bei längeren Kontaktzeiten erst die Beobachtung der Lanthanoidlumineszenz. Eine Beschichtung der Magnetpartikel mit EuTb@IFP-1 und anschließender Ummantelung mit TiO_2 -Partikeln würde die Lichtausbeute aufgrund der diffusen Streuung und Brechung einfallenden Lichtes drastisch mindern. Das vollständige Umhüllen des lumineszierenden Kerns mit den magnetischen, TiO_2 -Partikel-beschichteten Mikromagneten würde ebenso die Propagation einfallenden und emittierten Lichtes hemmen. Nur der dargestellte, suprapartikulären Aufbau mit Magnetpartikeln als Kern, umgeben von einer partikulären TiO_2 -Schicht und der lumineszierenden MOF-Komponente bzw. der Kern-Satellit-Aufbau kann in einem *All White Magnet* resultieren.

Die Erstautorenschaft dieser Publikation ist zu gleichen Anteilen zwischen *M. T. Seuffert* und *Dr. S. Wintzheimer* aufgeteilt. Die Experimente im Rahmen dieser Publikation wurden unter der Betreuung von *Prof. Dr. K. Mandel* und *Prof. Dr. K. Müller-Buschbaum* entwickelt und durchgeführt. Die Planung und Umsetzung der Synthesen der *All White Magnet* Kompositpartikel wurde von *M. T. Seuffert* vollzogen. Die pulverdiffraktometrische Charakterisierung verwendeter und erhaltener Substanzen, die Bestimmung der Lumineszenzeigenschaften, sowie die Untersuchungen zum Einfluss verschiedener Kontaktzeiten auf den Aufbau der Komposite wurden von *M. T. Seuffert* durchgeführt. Die Herstellung der weißen magnetischen Partikel und die Bestimmung der Eigenschaften derer wurde von *Dr. S. Wintzheimer*, *M. Oppmann*, *T. Granath* und *J. Prieschl* vorgenommen. Die Synthese des Weißlichtemitters EuTb@IFP-1 wurde von *A. Alrefai* unter Betreuung von *Prof. Dr. H.-J. Holdt* durchgeführt. Das Manuskript wurde von den beiden Erstautoren verfasst und von allen Koautoren bearbeitet. Ergänzende Informationen (*supporting information*) zu dieser Publikation sind in Kap. 7.1 festgehalten.

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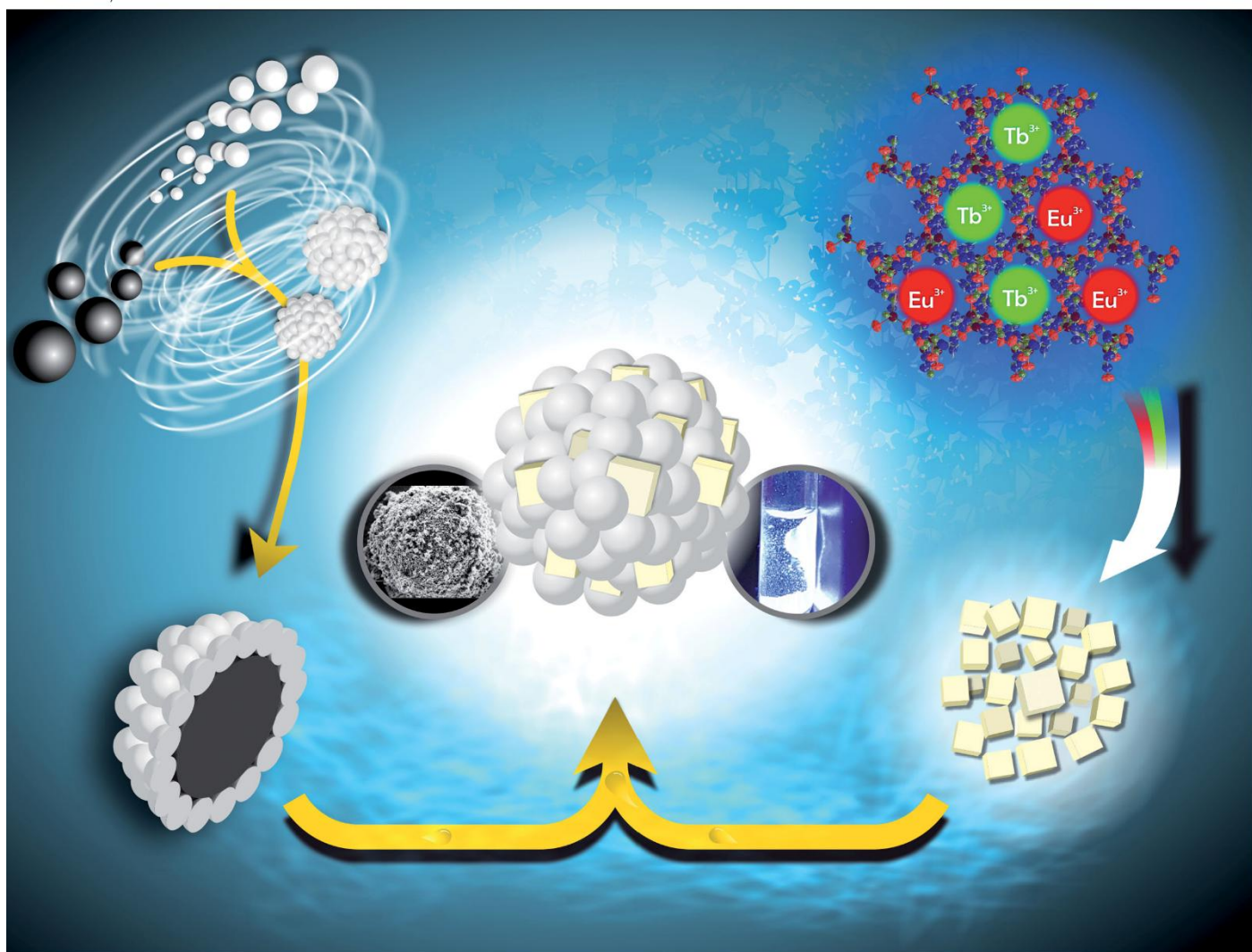
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An all white magnet by combination of electronic properties of a white light emitting MOF with strong magnetic particle systems†

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A multi-component particle system was developed that combines the properties of white color, white light emission and strong magnetism on the macroscopic and microscopic scale. The system is constituted by combination of an inorganic white core with either hard or soft magnetic properties and a white light emitting MOF. The key towards this achievement is the supraparticle character constituted by a magnetic core, of either magnetite or α -Fe, surrounded by titania and silica nanoparticles of a certain size in a loose structural shell-arrangement as white components and finally the white light emitting metal-organic framework (MOF) EuTb@IFP-1 as building blocks of a core-shell structure. The supraparticles are created by forced assembly of the inorganic compounds and by combining spray-drying and postsynthetic modification by solvothermal chemistry. Thereby, the gap is bridged that homogenous compounds are either strongly magnetic, white in appearance or white light emitting. The composites presented herein inherit these properties intrinsically as electronic properties. The white characteristics are based on all optical properties that enable white: light reflection, refraction, and light emission. This work shifts the paradigm that strong magnetic materials are always expected to be intrinsically dark.

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Introduction

In the recent years, luminescent metal-organic frameworks (MOFs) have been in the focus of research due to their high chemical variability and excellent photoluminescence efficiency, with the design of white light emitters and optical sensing being major routes of development.^{1–11} In addition, composite systems with other chemical components attracted attention to generate multifunctional systems by combination of the individual component properties.^{12–21} Thereby, also the microscopic combination of luminescence and magnetism can be achieved,

as shown for the functionalization of magnetic particles with luminescent compounds in PB@SiO₂@BTC@Ln (PB = Prussian blue, BTC = benzene-1,3,5-tricarboxylate, Ln = Tb³⁺/Eu³⁺)²¹ or for silica-stabilized magnetite particles functionalized with the luminescent MOFs ³[Eu₂(BDC)₃]·2H₂O·2DMF (BDC = benzene-1,4-dicarboxylate) or ²[Ln₂Cl₆(bipy)₃]·2bipy (Ln = Tb³⁺, Eu³⁺, bipy = 4,4'-bipyridine).^{22–24} Such MOF-particle composites chemically enlarge this rare combination of properties, which is otherwise only known for composites of magnetic particles with luminescent quantum dots^{25–28} and lanthanide-doped oxides.^{29–31}

As common expectation, strong magnets are dark; typically even black. It is generally accepted that strong magnetism, such as ferro- or ferrimagnetism, always enforces this appearance neither coinciding with white and especially not with the emission of white light. From theory, the necessary but not sufficient condition for magnetism is the presence of unpaired electron spins^{32,33} and their ordering in a magnetic solid, so that an overall magnetic moment and different types of magnetism in the solid result.^{34,35} Strongly magnetic materials typically absorb a broad range of visible light based on excitation of electrons close to the Fermi level resulting in their dark appearance, which is typically not accompanied by the

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emission of radiation.^{36,37} In contrast, typical white character requires light reflection instead of total absorption. Light emission is based on the emission of photons from an excited state resulting in a chromaticity of certain color coordinates, typically, without pathways of radiation-less decay.^{38–40}

Previously, it was shown that a coating layer containing reflecting materials, such as silver, or refractive materials naturally appearing white, such as titanium dioxide (titania), around a magnetic black body particle are suitable to microscopically brighten up a black system. Indeed, such approaches yield remarkable results, yet, the layer of reflective oxides lighten the system without yielding a real white magnetic material.^{41–43}

Looking into the science of technical paints, it can be found that the “perfect white” of a wall is achieved by inorganic paints containing semiconductor particles such as titania in the size range of 200 to 250 nm, *i.e.*, roughly $\lambda/2$ of the visible light.^{44–46} It is important that the particles are only loosely agglomerated in a way that they form a porous coating layer.^{44,46,47} The key property, which is achieved thereby, is diffuse scattering of light, hindering incoming light to propagate through this layer;^{44,48} thus this layer acts like a reflector and consequently also diffuses light. This insight was adapted herein to create a white magnetic particle.

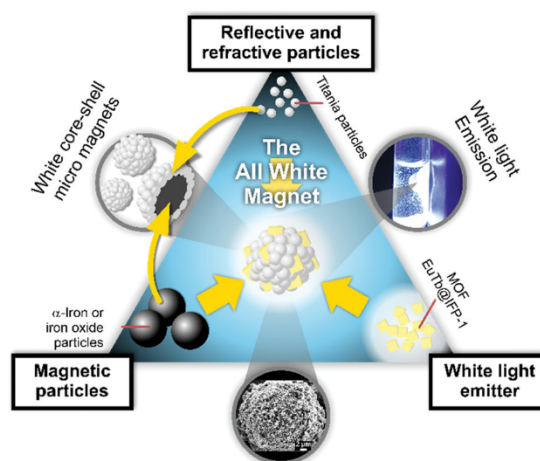
In order to design a device defined as all white in nature and not only white in appearance, also the emission of white light is an additional and highly beneficial property.

Combining these concepts, we have now challenged the paradigm of dark, non-emissive magnets in order to head for the direct opposite, namely a magnet being intrinsically white and in addition even being able to emit white light despite the possible correlation of magnetic ordering, excitation of states close to the Fermi level and possible pathways of radiation-less decay in the electronic system. We focused on a combinatorial materials science approach and utilized small particles for intrinsic properties on a microscopic scale of strong magnetism, such as α -Fe or Fe_3O_4 , reflective TiO_2 , and a luminescent MOF. For the latter, the white light emitting MOF EuTb@IFP-1 (Imidazolate Framework Potsdam 1)^{8,49} was chosen as emissive functionalization of the already white magnetic particles.

Results and discussion

In this work, magnetic white as well as white light emitting particles have been generated by a complex particulate system that consists of a strong magnetic core, a non-dense light reflective and refractive coating layer and an additional luminescent outer shell. All are connected to one composite system combining magnetism (either soft or hard magnetic) and optical properties that enable the impression of white, *viz.* optimizing light reflection and refraction as well as enable processes of excitation and white light emission (see Scheme 1).

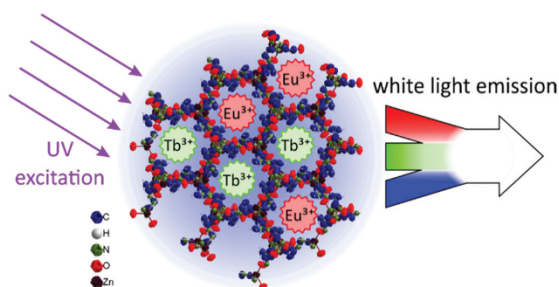
In order to achieve such a composite, combination of several processes maintaining all relevant properties was required. One step includes the achievement of microscopically white



Scheme 1 α -Iron or nanostructured iron oxide microparticles are spray-dried in combination with titania pigments, yielding white, magnetic core-shell particles. After functionalization with a white light emitting metal organic framework, namely (EuTb@IFP-1), the all white magnet is obtained. A photograph under UV light excitation ($\lambda = 365 \text{ nm}$) and a scanning electron micrograph of it are shown as insets.

magnetic particles, the other the deposition of a white light emitting MOF on the surface of these particles, while maintaining all optical and magnetic properties.

For step one, a loose coating layer of titania particles was generated around a magnetic core of soft magnetic highly pure iron metal (α -iron) microparticles or hysteretic/hard ferromagnetic nanostructured iron oxide (magnetite, Fe_3O_4) microparticles. Moreover, for a subsequent modification of the magnetic particles the white light emitting metal-organic framework (MOF) EuTb@IFP-1 (Imidazolate Framework Potsdam 1⁴⁹ with Eu^{3+} and Tb^{3+} ions in the pore system) was selected, which possesses luminescence properties with white light emission of the quality of a three color emitter according to the RGB concept (red-green-blue, see Scheme 2).⁵ By combination of both constituents, the semiconductor particle coating layer and the MOF ideally cause (a) reflection and refraction of incoming visible light and (b) white luminescence upon the MOF being



Scheme 2 White light emission of EuTb@IFP-1^8 according to the RGB concept by simultaneous emission of red (Eu^{3+}), green (Tb^{3+}) and blue (IFP-1) light upon UV excitation.

excited with UV-light (principle of the particle setup: Scheme 1). In general, such complex, so-called supraparticles,⁵⁰ are known to enable a great variety of intriguing, often novel, combinations of properties.^{50,51}

Other than for a dense coating layer on a particle, for which very well-established wet chemical approaches exist,^{52,53} creating a shell of loosely connected particles on a core particle is challenging. Herein, a method was chosen to create such a supraparticle made of particle building blocks based on forced assembly *via* external confinement, namely spray-drying (see Fig. S1 in the ESI† for a principle scheme of the synthesis setup and for the details on the syntheses). Prior to forming a loose shell of titania particles on magnetic core particles, optionally, reflecting or other “primer” layers can be coated on the magnetic component by means of wet chemistry. In fact, the choice of these pre-treatment steps and the spray-drying parameters lead to an enormous variety in terms of color appearance of the particles (see Fig. S2, ESI† for a selected, exemplary overview on such variations). Selection of unsuitable parameters yields brownish or greyish particles that do not achieve the goal of obtaining the “color” white. While dense “primer” layers on the magnetic core particle have not shown significant whitening of the samples for all cases, the use of particles in the size range of roughly $\lambda/2$ of the visible light^{44–46} had more influence on the color of the samples due to more efficient light scattering. Furthermore, the arrangement of dark and light scattering particles within the microparticle was crucial. A statistic mixing of both particle types did not yield significant

whitening of the samples. In contrast, the coating of a dark magnetic core with loosely agglomerated light scattering particles results in white micromagnets as this coating hinders incoming light to propagate through it.

Thus, by careful optimization of the precursor materials and their arrangement within the spray-dried microparticles, white magnetic particles can be obtained (Fig. 1). In this case, white magnetic particles were prepared by repeated spray-drying of α -iron or magnetite particles (of around 5 μm), serving as core particles, with titania particles (of 80 to 400 nm in diameter), forming a coating around the core particles, and a styrene butadiene copolymer binder (see methods section and Fig. S3 in the ESI†).

The resulting white magnetic particles are hereafter referred to as WI (White magnet containing Iron) and WO (White magnet containing iron Oxide). The two-fold spray-drying process was chosen (Fig. S1, ESI†) in order to guarantee a closed coating of the magnetic core particles as holes within this light diffusing layer would allow the light to propagate to the dark core material, leading to a less white macroscopic color impression. The styrene butadiene copolymer binder was needed in order to achieve a sufficient mechanical stability of the loose nanoparticle-based coating layer and its connection to the core material, while not influencing the optical properties of the microparticle.

Scanning electron micrographs (SEM image inset Fig. 1a, d and Fig. S4a, b, e and f, ESI†) in combination with energy dispersive X-ray spectroscopy (EDX, Fig. S4c, d, g and h, ESI†)

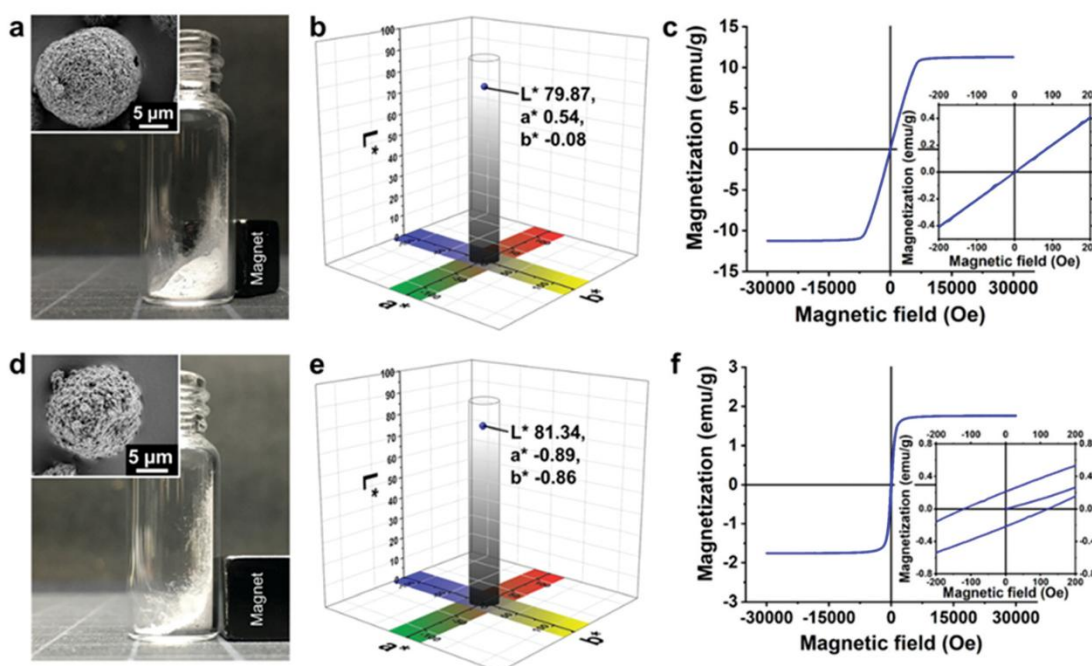


Fig. 1 Photographs and scanning electron micrographs as insets (a and d), as well as CIE $L^*a^*b^*$ color values (b and e) and magnetization measurements (c and f) of either white magnets, WI (a–c) or WO (d–f).

confirm the particle structure suggested in Scheme 1. This means, the core of around 5 μm of the particles is constituted by the magnetic material, whereas the other components form a shell around this core, as proven for spherical and anisotropic core/shell structures in our work on Ln-MOF@Fe₃O₄/SiO₂ particles^{22,24} and smart optical composite materials of MOF@superparamagnetic microrods.²³

A shell of approximately 2.5 μm thickness of loosely connected titania particles was assembled (for particle size determinations see Fig. S5a, ESI[†]), being responsible for light reflection and refraction. Besides their obvious white appearance (Fig. 1a, b, d and e), the particles still provide magnetic properties of the core material. Further magnetization and color characterizations of the white micromagnet components are shown in the ESI[†] (Fig. 1c, f, Fig. S5b, c and S6, ESI[†]). Concerning the magnetization decrease (in emu per g) of the magnetic microparticle samples after the spray-drying cycles (Fig. S6, ESI[†]), the overall amount of non-magnetic material (titania) within the sample is significantly increased by each spray-drying cycle, whereas the amount of core material remains the same, leading to a lower magnetization value per gram sample without a change in the magnetization of the magnetic core itself. The whiteness is given in CIE (Comission Internationale de l'Éclairage) $L^*a^*b^*$ values (Fig. 1b and e). CIE $L^*a^*b^*$ is a non-uniform color space with 3 dimensions: L^* for lightness and a^* and b^* for the color-opponents.⁵⁴ While this color space defines the coordinates $L^* 100 a^* 0 b^* 0$ as the white point,⁵⁵ perceived whiteness of an object is a psychophysical sensation and therefore not only influenced by the lightness L^* but also by its luminous reflectance, and thus the illumination source, by its material, gloss and texture, as well as by the color education of the observer.^{54,56–58} Furthermore, due to the non-uniformity of the CIE $L^*a^*b^*$ space, the closer a color is to the white point, the larger is the observers L^* tolerance. This may justify why the WI and WO are perceived as white while the measured L^* values differ slightly from the white point. The powder X-ray diffractograms of the synthesized magnetic particles WI and WO mainly show the reflections of titania. The most intense reflections of the diffraction patterns of the

contained magnetic material (WI: α -iron; WO: magnetite) are also observable as reflections of low intensity (Fig. S7a and b, ESI[†]).

The white magnetic particles were subsequently modified with the white luminescent metal–organic framework EuTb@IFP-1 as additional shell component. The functionalization of WI and WO was achieved by a solvothermal reaction of the particles with EuTb@IFP-1 (see hereafter) and yielded composite materials exhibiting both luminescence of white light and magnetism. These materials are referred to as Luminescent White magnets containing Iron (LWI) in case of composite materials containing WI as magnetic component, and Luminescent White magnets containing iron Oxide (LWO) in case of composite materials containing WO as magnetic component. For the property combination of white appearance, white luminescence and strong magnetism, the titania coating on the magnetic particles does not only act as substrate for the MOF but most importantly as functional reflective surface in the all white magnets. It causes light reflection and refraction and is also shielding the lanthanide containing luminescent MOF from the magnetic core materials, which are capable of quenching the luminescence. Thereby, a non-beneficial electronic interaction of the magnetic core and the luminescent shell is prevented, with both properties intrinsically coinciding on the microscopic level.

The MOF IFP-1 consists of zinc cations three-dimensionally connected by 2-methylimidazole-4-amide-5-imidate as organic linker.⁴⁹ It exhibits hexagonal channels (see Fig. S8, ESI[†]) in which Eu³⁺ and Tb³⁺ are intercalated yielding the white light emitting hybrid material EuTb@IFP-1.⁵ The luminescence of EuTb@IFP-1 is constituted by a blue fluorescence of the metal–organic framework and red and green emission of Eu³⁺ and Tb³⁺ intercalated into the MOF pores and excited *via* an antenna effect of organic linker (2-methylimidazole-4-amide-5-imidate) contained in the IFP-1 structure (see Scheme 2, Fig. S9a and b, ESI[†]).^{5,49} Hence, the absorption of UV light leads to a simultaneous emission of light of three colors (red, green, and blue), which overall adds up to an almost ideal white light emission of the synthesized luminescent, magnetic composites (Fig. 2). To depict the interpretation of the luminescence color by the human eye, the color coordinates

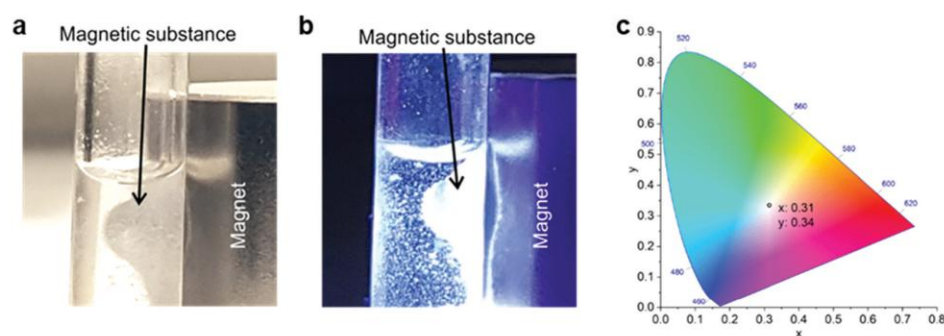


Fig. 2 Photograph of white magnet particles containing α -iron (WI), functionalized with white luminescent EuTb@IFP-1 (LWI), attracted by a magnet under visible light (a), under UV light excitation ($\lambda = 365 \text{ nm}$) (b) and the chromaticity diagram (c) with chromaticity coordinates calculated from the photoluminescence emission spectrum of the all white magnet LWI (Fig. S9a–c, ESI[†]).

according to the CIE system are used, in which the luminescence chromaticity is described by the tristimulus values XYZ of a standard.^{59,60} A comparison of the calculated chromaticity coordinates of the all white magnet material (*e.g.*, $x = 0.31$, $y = 0.34$, see Fig. 2c) with the values for ideal white light emission ($x = 0.333$, $y = 0.333$) confirms a nearly perfect white light emission of the synthesized material. Investigation of the luminescence lifetime by overall process decay time determination reveals two luminescence lifetimes for the most intense emission bands, as described for EuTb@IFP-1⁵ ($\lambda_{\text{exc}} = 360$ nm, $\lambda_{\text{em}} = 470$ nm, $\tau_1 = 0.13(1)$ ns, $\tau_2 = 4.22(14)$ ns) for the background MOF fluorescence, ($\lambda_{\text{exc}} = 360$ nm, $\lambda_{\text{em}} = 543$ nm, $\tau_1 = 580(33)$ μ s, $\tau_2 = 1062(60)$ μ s for Tb³⁺ Tb@IFP-1) and ($\lambda_{\text{exc}} = 360$ nm, $\lambda_{\text{em}} = 615$ nm, $\tau_1 = 314(3)$ μ s, $\tau_2 = 1337(115)$ μ s for Eu³⁺).

For the functionalization of the herein reported white magnetic particles with a white light emitting MOF, the pore system of IFP-1 was initially loaded with 0.5 equivalents of both europium and terbium, each. Contact of particles and MOF was achieved under solvothermal conditions in dry hexane as non-coordinating solvent. A detailed synthesis description is given in the experimental section. By heating a mixture of the white magnetic particles (WI or WO) and the white light emitting metal-organic framework EuTb@IFP-1 in hexane, luminescent, magnetic composite materials with iron (LWI) or iron oxide (LWO) as magnetic components can be obtained, which are not only of a white color, but also exhibit white light emission under UV excitation (Fig. 2b). Contact time of the white magnet particles and the EuTb@IFP-1 steer the size of the MOF crystallites with small MOF particles of a diameter of 1–3 μ m on the particle surface at start (see Fig. S10a–d, ESI†) and ending at larger MOF crystals (50–70 μ m in diameter, see Fig. S10e–h, ESI†) being functionalized by the particles. In addition, the luminescence becomes more intense the more emitting MOF is deposited (see Fig. S13, ESI†). As mentioned before, also the addition of the paramagnetic MOF material to the composite system leads to a decrease of the overall magnetization. Nonetheless, the synthesized all white magnet composite particles show a strong magnetism, which is why they can be attracted by a neodymium magnet (see Scheme 1 and Fig. 2). The composition of magnetic particles combined with the MOF also becomes evident in the powder X-ray diffraction pattern of the all white magnet. The reflections of the crystalline MOF IFP-1, as well as the reflections of titania of the particles can be clearly identified (Fig. S7c and d, ESI†).

In corroboration with the original MOF luminescence, the luminescence emission spectra show the bands expected for the emission of EuTb@IFP-1⁵ – exemplarily shown for LWI (Fig. S9, ESI†). The excitation spectra for the most intense luminescence bands of each emitting component (IFP-1: $\lambda_{\text{em}} = 433$ nm, Tb³⁺: $\lambda_{\text{em}} = 544$ nm, Eu³⁺: $\lambda_{\text{em}} = 617$ nm) reveal that the white light emission can be excited at two wavelengths: 354 nm and 360 nm. The lower wavelength causes higher intensity of the blue emission of the luminescent MOF. The higher excitation wavelength causes a more intense yellowish emission occurring from the lanthanide ions (Fig. S9a and b, ESI†)

Accordingly, the luminescence color of the composite material is further tunable from cold white light (chromaticity coordinates: $x = 0.30$, $y = 0.31$) to warm white light ($x = 0.31$, $y = 0.34$) by just varying the excitation wavelength (Fig. S11, ESI†).

For LWO (containing magnetite (WO) as magnetic component), the emission spectra also contain the luminescence bands expected for IFP-1⁵ (Fig. S12a and b, ESI†). Analogous to LWI, the luminescence can be excited at two wavelengths, namely 350 and 375 nm. The overall luminescence is shifted hypsochromically in comparison to LWI (Fig. S11b and S12b, ESI†).

Altogether, the obtained composite particle systems WI and WO can be considered as white micro magnets. The functionalization with a white light emitting metal-organic framework leads to the formation of white magnetic composite materials with additional white luminescence. Its light emission is almost ideal white for LWI with a color temperature that can be tuned by appropriate selection of the excitation wavelength.

The composites presented herein enable numerous, especially “decorative” applications that are not available to dark magnets. Possible applications range, *e.g.* from magnetic, white objects such as paper or rubber, sophisticated hidden magnetic anti-counterfeiting labels to white magnetic ink, and magnetically moveable white light emitting objects. To illustrate this, magnetic components incorporated into bank notes nowadays are a state-of-the-art security feature, their presence being obvious, as there are metallic stripes or regions clearly visible in the bank note. The presented magnetic supraparticles carry a unique ID increasing the options for anti-counterfeit protection. As white objects, the white MOF@particle composites enable hiding such features at any place in any white paper material while they are still identifiable by means of magnetic particle spectroscopy⁶¹ and photoluminescence.

Experimental

Synthetic procedures

Materials. Titania pigment BILLIONS[®] BLR-699 (of 80 to 400 nm in diameter, determined *via* SEM) was purchased from Lomon Billions. Carbonyl iron CIP-HS (of 4.9 ± 1.7 μ m in diameter, determined *via* laser diffraction) and iron(II/III) oxide nanopowder (of 50 to 100 nm in diameter, determined *via* SEM) were obtained from BASF and Sigma Aldrich. Styrene butadiene copolymer binder PSBR-100 was provided by Targray. Eu(NO₃)₃·5H₂O (99.99% trace metals basis) and Tb(NO₃)₃·5H₂O (99.9% trace metals basis) were purchased from Sigma Aldrich. DMF was purchased from VWR International. Extra dry hexane (97%) was purchased from Acros Organics and used without any further purification. Water was deionized before use.

Synthesis of iron oxide core for the hard magnetic white micro magnet. While the soft magnetic α -iron core was commercially purchased, the nanostructured iron oxide supraparticles as hard magnetic core material were obtained *via* spray-drying an aqueous iron oxide nanoparticle dispersion with a concentration of 0.01 g mL^{−1} with a “B-290” mini spray dryer (Büchi). The inlet

air temperature was chosen to be 140 °C and the outlet temperature was 60–65 °C during the spray-drying process.

Synthesis of soft and hard magnetic white micro magnets.

In the following, synthesis protocols leading to the successful preparation of white micromagnets are described. The basis for these protocols were diverse, precedent synthesis approaches including the coating of α -iron particles with a titanium dioxide and a silver shell, as well as coating iron oxide nanoparticles with a silica shell and spray-drying these variants in order to cover them with silica or/and titania nanoparticles. Their composition and visual appearance are listed in Fig. S2 (ESI[†]). For the successful synthesis of white micromagnets, either the α -iron or the iron oxide core (2.76 g) were intermixed with titania pigment (23.46 g) and styrene butadiene copolymer binder (13.80 g) in a ratio of 1:8.5:5 and dispersed in water (200 ml) with the help of ultra-sonication yielding a dispersion with 20% solid content. This mixture was spray-dried with a “B-290” mini spray dryer (Büchi). The inlet air temperature was chosen to be 140 °C and the outlet temperature was 60–65 °C during the spray-drying process. Purification was carried out by dispersing the obtained powder in ethanol *via* stirring and subsequent magnetic separation of the desired product. This washing cycle was repeated 5 times. The obtained particles are denoted as semi-White micro magnet containing either α -Iron or iron Oxide (sWI or sWO) in the following. For a second spray-drying cycle, this purified magnetic powders (0.65 g) were intermixed with titania pigment (0.89 g) and styrene butadiene copolymer binder (1.38 g) in a ratio of 1:3:2.11 and dispersed in water (20 ml) with the help of ultra-sonication yielding a dispersion with 20% solid content. For subsequent spray-drying the inlet air temperature was chosen to be 140 °C and the outlet temperature was 60–65 °C. The obtained powder was purified again *via* 5 washing cycles and dried. The resulting white, magnetic particles are hereafter referred to as WI in case of α -iron particle containing system or WO as iron oxide containing system.

Synthesis of the white light emitting metal–organic framework EuTb@IFP-1. The white light emitter EuTb@IFP-1 was synthesized according to the literature procedure by dissolving 0.76 mmol (198 mg) $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.38 mmol (163 mg) $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.38 mmol (165 mg) $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and 0.76 mmol (100 mg) 4,5-dicyano-2-methylimidazole in 6 mL DMF. The mixture was transferred into a sealed tube, heated up to 110 °C for three days and cooled to room temperature. The resulting, crystalline product was obtained by filtration from the reaction mixture.⁵

Functionalization of soft and hard magnetic all white micro magnets with metal–organic frameworks. The functionalization of the white magnetic particles WI and WO with the metal–organic framework EuTb@IFP-1 was achieved by a solvothermal reaction. In a typical reaction, the white micro magnet and EuTb@IFP-1 were mixed in an agate mortar under inert atmosphere in a mass ratio of 2.16:1. After transferring the mixture into a Duran[®] glass ampoule and adding dry hexane, the solvent was degassed by freezing the mixture, evacuating the ampoule and allowing the mixture to thaw again. This procedure

was repeated one more time followed by freezing the reaction mixture, evacuating the ampoule and closing it by melting. The reaction mixture was allowed to warm up to room temperature and was homogenized in an ultrasonic bath for three minutes. Subsequently, the ampoule was placed in a corundum oven and heated to 90 °C for 72 h. After the solvent was removed manually under inert atmosphere, the product was dried in vacuum. Subsequent to synthesis, the magnetic composite was magnetically separated from excess non-magnetic reactants. For a more detailed synthesis description, see supplementary information and Table S1 (ESI[†]).

Analytical investigations

SEM/EDX. Scanning electron micrographs (Fig. 1a, d, Fig. S4a, b, e and f, ESI[†]) were acquired using a Zeiss Supra 25 SEM at 3 keV. Energy dispersive X-ray analyses (EDX, Fig. S4c, d, g and h, ESI[†]) were done with 15 keV at a working distance of 8 mm.

Magnetization investigation. Magnetic properties were investigated using a vibrating sample magnetometer VersaLabTM 3T from Quantum Design. Magnetization measurements (Fig. 1c, f, Fig. S6, ESI[†]) were performed at 300 K by cycling the applied field from –30 kOe to +30 kOe for two times with a step rate of 100 Oe s^{–1} at 20 °C.

Size determination. Laser diffraction measurements (Fig. S5a, ESI[†]) were carried out on a Microtrak Bluewave using FLEX version 11.0.0.3 as analysis software.

Colorimetry. CIE $L^*a^*b^*$ values and reflectance (Fig. 1b, e, Fig. S5b and c, ESI[†]) were obtained with a BYK-Gardner spectro-guide 45/0 gloss.

Powder X-ray diffraction. Powder X-ray diffraction patterns (Fig. S7, ESI[†]) were measured using a Bruker D8 Discover DaVinci diffractometer with focusing Göbel mirrors and a linear LynxEye detector in a parallel beam geometry in transmission mode using $\text{CuK}\alpha$ radiation ($\lambda = 154.056$ pm). PXRD samples were finely grounded and filled in Lindemann glass capillaries with 0.3 or 0.5 mm diameter under inert gas atmosphere.

Photoluminescence spectroscopy. Photoluminescence spectra (Fig. S9 and S12, ESI[†]) were recorded using a Jobin Yvon Fluorolog 3 (Horiba) with a 450 W Xe short-arc lamp (USHIO), double-grated excitation and emission monochromators, and a photomultiplier tube (R928P) using FluorEssence™ software. Corrections of the recorded spectra with regard to the monochromators and the detector were done using corrections provided by the manufacturer. In addition the excitation spectra were corrected for the spectral distribution of the Xe lamp using a photodiode reference detector. All luminescence spectra were collected without using an edge filter. This was done in order to prevent a loss of information due to truncation of the emission spectra in the blue region of the electromagnetic spectrum where the luminescence of the IFP-1 network is observable. Hence, the emission spectra could only be measured to a wavelength below twice the wavelength of the excitation light (720 nm in case of an excitation wavelength of 360 nm). The rearmost emission band of europium (around 700 nm) was therefore approximated with a

Gaussian profile (Fig. S9c, ESI†) based on a Gaussian fit of an emission spectrum measured with an edge filter (Fig. S9d, ESI†). A comparison of the CIE chromaticity coordinates calculated from the emission spectrum as measured, corrected using a Gaussian approximation for the rearmost europium emission band shows, that this band does not affect the chromaticity coordinates (Fig. S11a, ESI†).

Conclusions

Supraparticle systems constituted from magnetic cores of α -Fe or Fe_3O_4 together with TiO_2 and the white light emitting MOF EuTb@IFP-1 have been generated. They can be called all white as they combine hard as well as soft magnetic properties with the character of real white appearance and even white light emission as electronic properties on the microscale. This combination of optical and magnetic properties is exceptional. Typically, it cannot be observed together for homogenous matter due to a correlation of magnetic ordering, excitation of states close to the Fermi level and possible pathways of decay in the electronic system that prevent the presence of all properties at once. The white nature of the composite systems unites all possible relevant optical properties including light reflection, refraction, excitation, and emission. The optical properties and thus the character of white can even be switched between the “color” white and white light emission. Via a minimization of electronic interaction between the magnetic core and the MOF shell material, suppression of total absorption and quenching of the luminescence by the magnetic constituents is achieved, which is otherwise typical for one homogenous magnetic compound or metal. The synthetic procedure is based on forced assembly of the particle building blocks to supraparticles via spray-drying, followed by post-synthetic modification with the white light emitting MOF EuTb@IFP-1 . Different from macroscopically painting a magnet white, the composites presented herein enable “decorative” applications that were impossible up to now: magnetically moveable white light emitting objects, magnetic, white paper or rubber, white magnetic ink, and sophisticated hidden anti-counterfeiting labels. Beyond application, the current work ends a long existing paradigm, namely that magnets are always dark or even black and would hence absorb most of the visible light.

Conflicts of interest

There are no conflicts to declare.

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4.2 Tuning Magnetic and Photophysical Properties of Luminomagnetic Metal-Organic Framework Composites in an Inverse Core-Satellite Structure

Im Rahmen der zweiten Publikation wurde der Beschichtungsmodus, welcher sich bei dem *All White Magnet* bereits für MOF-Kristallite gezeigt hat, aufgegriffen, um ein Komposit zu generieren, welches nicht der klassischen Rollenverteilung magneto-optischer Komposite mit einer lumineszierenden MOF-Schale auf magnetischen Kernen folgt, sondern eine Kern-Satellit-Strukturierung mit Lanthanoid-MOF-Kern und superparamagnetischen, Citrat-stabilisierten Fe_3O_4 -Satellitpartikeln aufweist.

Die inversen *core-satellite* Komposite beinhalten Kristallite der Lanthanoid-basierten MOFs ${}^3[\text{Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ ($\text{Ln} = \text{Eu}, \text{Tb}$) mit einer Größe von ca. 250 nm als Kernmaterial, deren Oberflächen von superparamagnetischen Eisenoxid-Nanopartikeln (SPIONs) funktionalisiert sind. Über lasergranulometrische Messungen wurde eine hydrodynamische Partikelgröße der SPIONs zu ca. 20 nm bestimmt. Diese Größenverteilung ist notwendig, um die inverse Kern-Satellit-Strukturierung zu erreichen. Größere Magnetpartikel in Relation zu MOF-Kristalliten hätte einen Aufbau mit magnetischem Kern und lumineszierenden Satelliten bzw. Schale zur Folge. Die Kristallite der nasschemisch synthetisierten MOFs ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ und ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ werden solvothermal mit den über Kopräzipitation hergestellten SPIONs kombiniert. Über mehrere Analysenmethoden wird die erfolgreiche Synthese magneto-optischer Komposite nachgewiesen. In den Pulverdiffraktogrammen der Komposite sind die Reflexe von sowohl Fe_3O_4 als auch ${}^3[\text{Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ ($\text{Ln} = \text{Eu}, \text{Tb}$) zu beobachten. Die quantifizierte Magnetisierbarkeit ohne Vorhandensein einer Hysterese weist den Superparamagnetismus der Produkte nach. Die beobachteten Banden in den Lumineszenzspektren sowie das Vorhandensein charakteristischer Banden für funktionelle Gruppen des MOFs, Citrats und der SPIONs in den Infrarotspektren der Produkte untermauern den kompositären Charakter zusätzlich.

Durch die Kern-Satellit-Strukturierung mit lumineszierendem Kernmaterial und magnetischen Satellit-Partikeln wird eine präzise Einstellung der Eigenschaften möglich, welche mit einem konventionellen Kern-Schale-Aufbau nicht erreichbar wäre. Bei der Verwendung eines magnetischen Kernels und einer dichten, lumineszierenden Schale würde durch die Variation des MOF:SPION-Verhältnisses eine Minderung der magnetischen Eigenschaften mit steigendem MOF-Gehalt eintreten. Die massenbezogene Lumineszenzintensität entsprechender Komposite würde bis zu einer Sättigungsintensität steigen, ab welcher nur noch eine sinkende Magnetisierung mit steigendem MOF-Gehalt beobachtbar wäre. Im Falle eines Kern-Schale-Aufbaus mit lumineszierendem Kern und dichter,

magnetischer Schale wären bereits bei geringen gehalten an magnetischer Komponente erhebliche Einbußen in Bezug auf Lumineszenzintensität zu verbuchen. Ein Abzielen auf eine niedrige Magnetisierbarkeit bei hoher Lumineszenzintensität wäre bei konventionellen *core-shell* Partikeln mit magnetischem Kern nur durch hohe Gehalte an lumineszierender Hülle möglich, was die Partikelgröße und Dispergierbarkeit negativ beeinflussen könnte. Durch das Aufbringen einer nicht dichten Schicht magnetischer Nanopartikel auf lumineszierende MOF-Kristallite werden diese Effekte umgangen. Eine nicht vollständige Satellit-Beschichtung der Kristallitoberflächen resultiert in der für die Lanthanoidionen charakteristischen Lumineszenz bei zeitgleich niedriger Magnetisierbarkeit. Durch den partikulären Charakter der SPIONs kann bei einer vollständigeren Beschichtung dennoch eine Propagation von Licht durch die magnetische Partikelhülle erfolgen, wodurch hohe Magnetisierbarkeit und trotzdem mit dem bloßen Auge erkennbare Lumineszenz erreicht werden.

Durch die Citrat-Stabilisierung der SPIONs wird nicht nur die Agglomeration und Aggregation der Magnetpartikel verhindert, wodurch der Superparamagnetismus verloren ginge. Auch stehen bei der Bildung der Komposite viele funktionelle Gruppen zur Verfügung, welche eine starke Bindung der Kompositpartner zur Folge haben. Dies zeigt sich auch anschaulich durch die Stabilität erhaltener Komposite. Selbst durch mehrmaliges Ultraschall-assistiertes Dispergieren und anschließende magnetische Separation sind die Kompositpartner nicht voneinander zu trennen, was anhand konstant bleibender Magnetisierbarkeit evident wird. Dies zeigt die bemerkenswerte Stabilität der *core-satellite* Komposite. Die Entstehung von Kern-Satellit-Kompositen ist weiterhin sowohl unabhängig vom gewählten pH-Wert während der Stabilisierung der SPIONs und somit vom Deprotonierungsgrad der Citrat-Funktionalitäten als auch vom gewählten Lösungsmittel zur Synthese. Ferner wird durch den Kern-Satelliten-Aufbau mit Citrat-stabilisierten SPIONs auf der Oberfläche von MOF-Kristalliten eine gute Dispergierbarkeit der Komposite erreicht. Durch Verwendung kleiner Mengen an Komposit kann eine kolloidale Dispersion hergestellt werden, welche trotz der geringen Kompositgehalte intensiv luminesziert (s. Abb. 9).

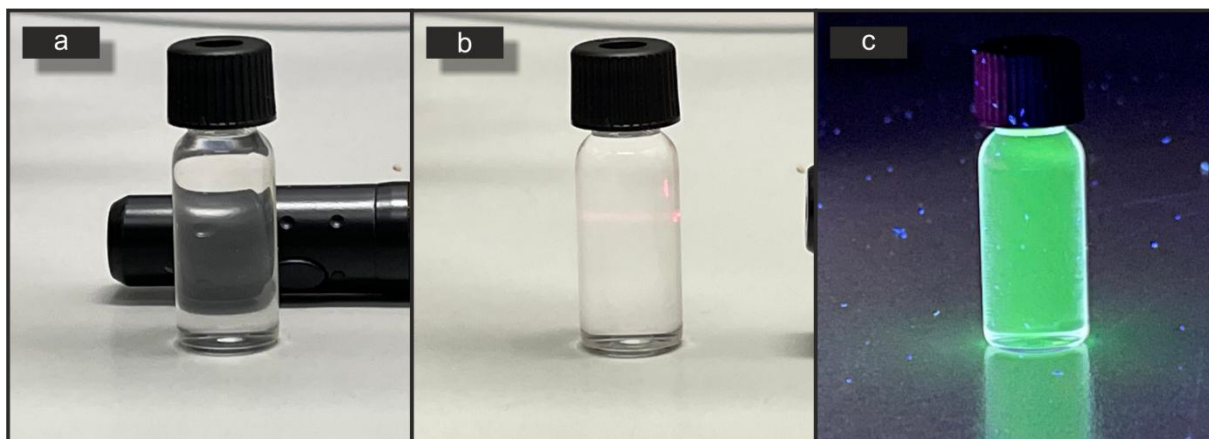


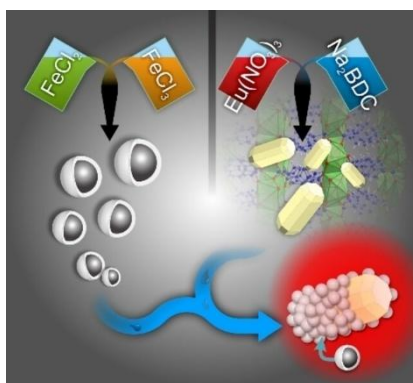
Abb. 9. Fotografien einer kolloidalen Dispersion des Komposits SPIONs@TbMOF (s. Kap. 4.2) bei Normallicht (a), mit Einstrahlung von Laserlicht zum Nachweis des Tyndall-Effektes (b) sowie unter UV-Bestrahlung ($\lambda = 302 \text{ nm}$) zum Nachweis der Photolumineszenz (c).

Die Sättigungsmagnetisierung der Komposite ist über einen linearen Zusammenhang mit dem MOF:SPION-Verhältnis verknüpft. Die Lumineszenzintensität ist exponentiell proportional zum MOF-Anteil in den Kompositen. Für den exponentiellen Zusammengang wird der Anteil der SPIONs, die wellenlängenabhängige Absorbanz der SPIONs sowie die MOF-Lumineszenzquantenausbeute berücksichtigt, worüber sich die massenbezogene Lumineszenzintensität vorhersagen lässt. Die Chromatizität des Komposits kann weiterhin in Abhängigkeit des im MOF enthaltenen Lanthanoids variiert werden, wobei eine Mischung beider MOFs ${}^3[\text{Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ ($\text{Ln} = \text{Eu}, \text{Tb}$) in gelber Lichtemission resultiert. Tb-haltige Komposite zeigen eine Rotverschiebung der Emissionsfarbe relativ zur zu erwartenden Chromatizität. Dies ist auf die Wellenlängen-abhängige Absorbanz der SPIONs zurückzuführen, welche mathematisch korrigiert werden kann.

Die Erstautorenschaft liegt bei *M. T. Seuffert*. Die Synthese der lumineszierenden Koordinationspolymere sowie der Komposite und deren Charakterisierungen über Pulverdiffraktometrie, Rasterelektronenmikroskopie, energiedispersive Röntgenspektroskopie und Lumineszenzspektroskopie wurden unter der Betreuung von *Prof. Dr. K. Müller-Buschbaum* von *M. T. Seuffert* geplant und in Zusammenarbeit mit *T. Kasper* und *R. Maile* durchgeführt. Die Darstellung und Untersuchung der SPIONs sowie die magnetische Charakterisierung der Komposite erfolgte durch *T. Granath*, *R. Pujales-Paradela*, *J. Prieschl* und *Dr. S. Wintzheimer* unter der Betreuung von *Prof. Dr. K. Mandel*. Das Manuskript wurde vom Erstautor verfasst und von allen Koautoren bearbeitet. Ergänzende Informationen (*supporting information*) zu dieser Publikation sind in Kap. 7.2 festgehalten.

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Tuning Magnetic and Photophysical Properties of Luminomagnetic Metal-Organic Framework Composites in an Inverse Core-Satellite Structure

Marcel T. Seuffert,^[a] Tim Granath,^[b] Thomas Kasper,^[a] Ruben Maile,^[a] Rosa Pujales-Paradela,^[b] Johannes Prieschl,^[b] Susanne Wintzheimer,^[b, c] Karl Mandel,^[b, c] and Klaus Müller-Buschbaum^{*[a, d]}

Luminomagnetic composites have been synthesized that allow for an individual tuning of luminescence intensity, chromaticity and magnetization by combination of superparamagnetic, citrate-stabilized iron oxide nanoparticles with the luminescent MOFs $^3\text{Ln}(\text{Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4)$ ($\text{Ln}=\text{Eu}, \text{Tb}$; BDC^{2-} =terephthalate). The components are arranged to a concept of inverse structuring compared to previous luminomagnetic composites with MOF@magnetic particle (shell@core) composition so that the luminescent MOF now acts as core and is covered by magnetic nanoparticles forming the satellite shell. Thereby, the

magnetic and photophysical properties are individually tunable between high emission intensity ($1.2 \cdot 10^6 \text{ cps mg}^{-1}$) plus low saturation magnetization (6 emu g^{-1}) and the direct opposite ($0.09 \cdot 10^6 \text{ cps mg}^{-1}$; 42 emu g^{-1}) by adjusting the particle coverage of the MOF. This is not achievable with a core-shell structure having a magnetic core and a dense MOF shell. The composition of the composites and the influence of different synthesis conditions on their properties were investigated by SEM/EDX, PXRD, magnetization measurements and photoluminescence spectroscopy.

Introduction

Multifunctional composites are compounds that enable a merging of inherent characteristics of multiple components into one system. This smart way of combining properties of multiple substances has gained growing interest in the recent years.^[1,2,3,4] Metal-organic frameworks (MOFs) have become composite partners, whose combination with various materials is of increasing scientific interest. By arranging MOFs together with e.g., magnetic substances, it is possible to synthesize

composite systems featuring magnetism in combination with characteristics arising from the MOF's intrinsic properties and structure. To obtain MOF containing composites, methods like embedding,^[5,6] layer-by-layer growth,^[7] encapsulation,^[8,9] or mixing^[10] have been developed.^[11,12] Examples for magnetic composites implying MOFs are systems containing ZIF-8^[13,14] or IRMOF-3,^[6] which are catalytically active. Utilizing the MOFs MIL-100^[15] or PCN-222,^[11] composites were reported being able to remove Cr(VI) or U(VI) from waste water. Furthermore, composites containing MIL-88A enable the application as drug carriers for medical purposes^[16] and $\text{NH}_2\text{-MIL-53(Al)}$ and NU-1000 for MOF crystal orientation.^[17] By utilizing metal-organic frameworks based on lanthanides, luminomagnetic composites were achieved and investigated, e.g. as luminescent sensors^[18,19] for different MOFs and magnetic materials. E.g., when titania coated iron or iron oxide particles are combined with the white-light emitting MOF EuTb@IFP-1 , a composite system is obtained, which is magnetic, white in appearance, and even white luminescent.^[20] In luminomagnetic examples, the MOF was arranged as shell at the outside and the magnetic material as core at the inside, the properties of the MOFs being important for potential applications, while the combination with magnetic components results in options either to separate the composite after usage, or to directly guide the materials to desired locations.

An example for constituents imparting magnetic properties to composites, are metallic iron or iron oxide nano- and microparticles.^[2,4,11,20] Small particles as composite component require a stabilization against aggregation and agglomeration, since a uniform dispersion of a solid in a liquid facilitate a behaviour of this heterogeneous materials close to being homogeneous.^[21] A way to achieve stabilization of e.g., iron

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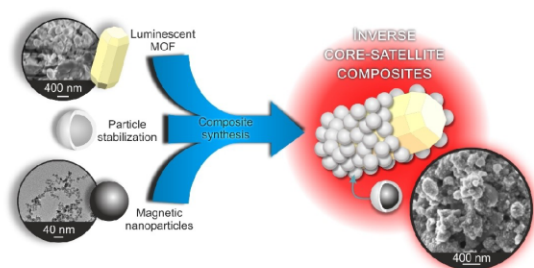
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oxide nanoparticles is a modification with alkyl phosphonates and phosphates,^[22] block-copolymers,^[23] or carboxylates, such as oleic acid, to bind to the surface of particles and to hinder aggregation sterically and/or electrostatically.^[24] Another commonly used carboxylate stabilizer for iron oxide particles is citric acid, which is capable of binding to the particle surface by hydrogen bonds, or one or two of its carboxylate functionalities.^[24,25,26] In addition, the remaining, non-bonding functional groups make the particles amenable of establishing chemical bonds to other substances.^[25]

For optimizing the luminescence intensity of the overall composite materials, the electronic exchange between the magnetic material and the luminescent compound needs to be minimized because of light absorption and luminescence quenching abilities of iron oxide.^[27] Typically this is achieved by coating the respective particles with inert oxides like silica^[4,18,19,28] or titania^[20] prior to the functionalization with luminescent MOFs. These mediator materials lower the magnetization of the magnetic particles, but, also enable a binding to the metal ions of a luminescent MOF to oxide surface defects, such as O–H groups.

Up to now, typically, composites containing magnetite particles and MOFs form core-shell structures with iron oxide functioning as core material covered by a MOF shell.^[4,6,9,13,19,28,29] There are only a few non-luminomagnetic examples, where roles are interchanged and MOFs, namely MIL-101^[10,30] or MOF-5,^[31] NH₂-MIL-53(Al) and NU-1000^[16] represent the core material covered by an iron oxide particle shell. An inversion of roles has been reported for a solid material with YO₄:Eu³⁺ cores surrounded by silica, functionalized with iron oxide nanoparticles^[32] and for β-NaY_{0.8}Eu_{0.2}F₄@γ-Fe₂O₃ core-satellite particles.^[33] Herein, we describe the synthesis, properties and tunability of properties of such inverse core-satellite composites for luminescent, lanthanide-based MOFs. This leads to core-satellite composites, in which magnetic citrate-stabilized iron oxide nanoparticles cover MOF crystallites of ³_∞[Ln₂(BDC)₃(H₂O)₄] (Ln=Eu, Tb) as satellite shell (see Scheme 1) leading to options for an individual tuning of luminescence and magnetism, which would not be achievable by the core-shell functionalization mode having magnetic particles as core material and luminescent MOF as outer shell.



Scheme 1. Inverse core-satellite concept of composite systems comprising magnetic nanoparticles on top of a luminescent MOF, allowing also for a core-satellite arrangement

Results and Discussion

In this work, luminomagnetic composite systems were generated that achieve the goal to individually grant fine-tuning options for both, luminescence properties and magnetization. This has been accomplished by solvothermally combining superparamagnetic iron oxide nanoparticles (SPIONs) and the luminescent (MOFs) ³_∞[Eu₂(BDC)₃(H₂O)₄] (Eu–BDC) or ³_∞[Tb₂(BDC)₃(H₂O)₄] (Tb–BDC). SPIONs were chosen due to the high dispersibility and strong superparamagnetism and the respective MOFs because of their chemical and structural stability, as well as the intense luminescence.

The prepared composite systems do not build a core-shell structure with a MOF shell being deposited on the surface of the magnetic particles. The obtained composites instead exhibit an inverse core-satellite modification mode with inversion of roles of “core” and “shell”, whereby MOF crystallites are covered to different extend by the magnetic satellite nanoparticles. Only this modification mode allows for the fine tunability of luminescence and magnetism.

In core-shell composites comprising a magnetic particle core and luminescent MOF shell, increasing the shell thickness leads to an increase in luminescence intensity while diminishing magnetization. From a certain layer thickness on, an increasing MOF amount would lower the magnetization further, while the luminescence intensity remains the same.

To the contrary, with an inverse core-shell modification mode, a dense magnetic shell would diminish the luminescence intensity. However, if the magnetic shell consists of nanoparticle satellites instead of a dense coating, the emitted light can propagate through the magnetic layer, resulting in the preservation of the photophysical properties of the luminescent MOF. Moreover, the luminescence intensity and the magnetization can be adjusted by varying the amount of magnetic particles covering the MOF. Additionally, since the magnetic particles function as outer shell, the dispersibility of the respective composites can be increased depending on the external functional groups of the particles.

To examine this tunability of properties of inverse core-satellite composites, differences in magnetization and luminescence properties were triggered and investigated in dependence of deliberate variation of the synthesis conditions. Thereby, the component ratio of iron oxide nanoparticles and MOF was adjusted to specific values, and the differences in photophysical and magnetic properties were examined in dependence of this ratio. Furthermore, the tunability of emission colour, and the stability of the inverse core-satellite composites against washing assisted by ultrasonication and synthesis in different solvents were examined.

Tunability of Emission Intensity and Saturation Magnetization of Inverse Core-Satellite Composites

To obtain luminomagnetic composites, the two solid components ³_∞[Ln₂(BDC)₃(H₂O)₄] (Ln–BDC, Ln=Eu, Tb) and superparamagnetic iron oxide nanoparticles (SPIONs, citrate-stabilized at

a pH of 2.1) were synthesized separately (see experimental section). The applied luminescent MOFs Ln-BDC contain trivalent lanthanide ions, which are eight-coordinate by oxygen atoms. Six of these oxygen atoms belong to carboxylate functions of terephthalate ligands, and two belong to coordinating water molecules (see Figure S1).^[34] The identity and purity of the synthesized metal-organic framework was confirmed by powder X-Ray diffraction (PXRD, see Figure S2) and elemental analysis (see experimental section). The obtained crystallites of $^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ are 255 nm (± 170 nm) in size (hydrodynamic particle diameter), as shown by dynamic light scattering. The hydrodynamic diameter of crystallites of $^3_{\infty}[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ were determined as 220 nm (± 177 nm; see Figure S3). The magnetic nanoparticles consist of iron oxide in the magnetite structure, proven by PXRD (see Figure S4), and are approximately 10 nm in size according to transmission electron micrographs (see Figure S5), wherefore they are considered as nanoparticles. By dynamic light scattering a hydrodynamic particle diameter of 21 ± 10 nm was determined (see Figure S3). Considering the formation of a solvent shell, this corresponds with the results of TEM investigations. To prohibit agglomeration and aggregation, the nanoparticles were stabilized with citric acid. Hence, in the IR spectra of the stabilized particles, bands are present, which can be assigned to the functional groups of citric acid and Fe–O vibrations (see Figure S6).

To investigate the influence of the component ratio MOF:SPIONs on the properties of resulting composites, the amounts of MOF and SPIONs were adjusted to specific values. The resulting MOF:SPIONs weight ratio as well as the designation of the obtained composites are listed in Table 1. The composites are hereafter referred to as SPIONs@EuMOF-*x*, whereby *x* corresponds to the mass equivalents of MOF used for the synthesis. Powder diffraction patterns of the synthesized composites show reflections of both, $^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (which is isotopic to $^3_{\infty}[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$) and magnetite/maghemite ($\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$, the latter being a defective form of magnetite, which is hardly distinguishable for nanoparticles by PXRD) (see Figure 1). In the powder diffractograms, the intensity of the most intense reflection of $^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ ($2\theta = 9.1^\circ$) increases with a rising amount of MOF. Accordingly, the intensity of the most intense reflection of magnetite/maghemite ($2\theta = 35.5^\circ$) is reduced with decreasing iron oxide content. Due to the low amount of SPIONs within the composites SPIONs@EuMOF-8 and SPIONs@EuMOF-10 (11 wt% and 9 wt%, respectively), this

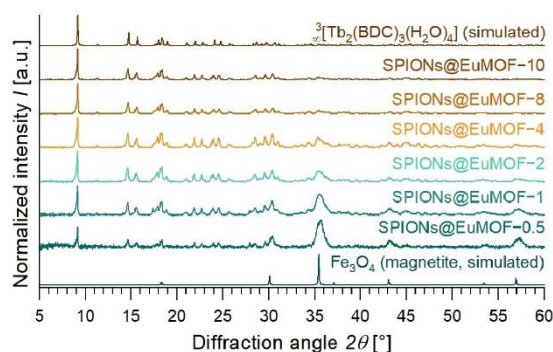


Figure 1. Powder X-ray diffractograms of synthesized composite systems SPIONs@EuMOF-*x* (containing SPIONs citrate-stabilized at pH 2.1) with different MOF:SPIONs weight ratios in comparison to the diffractograms of magnetite (Fe_3O_4)^[37] and $^3_{\infty}[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$,^[34] both simulated from respective single crystal diffraction data.

reflection has low intensity in the corresponding diffractograms. This proves, that both constituents are present within the obtained products and the used component weight ratios are directly associated with the ratio of luminescent and magnetic compounds within the composite.

Electron micrographs of the synthesized composites show that they consist of crystallites, which are covered by smaller satellite particles, indicating the inverse core-satellite character. The coverage of crystallites by satellite particles gets more clear by comparison of electron micrographs of synthesized composites (e.g., SPIONs@EuMOF-2) and pure $^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (see Figure 2) equally treated to the synthesis procedure of the composites. The previously smooth surfaces of the MOF crystallites become coarse in appearance like the shape of “roasted almonds”, when covered by iron oxide particles (see Figure 2). This morphology of the crystallite surfaces gradually increases with rising SPIONs amount (see Figure S7), being in good agreement with the inverse core-satellite functionalization mode with core-satellite character. This type of functionalization is further confirmed by transmission electron microscopy (TEM) of e.g., isolated SPIONs@EuMOF-4 composites (see Figure 3) indicating the combination of $^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ and SPIONs on the nanometer scale. Thereby, the interaction of SPIONs with the MOF crystallite surfaces can be expected established

Table 1. Investigated weight ratio of MOF:SPIONs, amount of stabilized iron oxide nanoparticles in the product composites and composite designations.

Weight ratio MOF:SPIONs	Amount of iron oxide [wt%]	Composite designation
0.5:1	67	SPIONs@EuMOF-0.5
1:1	50	SPIONs@EuMOF-1
2:1	33	SPIONs@EuMOF-2
4:1	20	SPIONs@EuMOF-4
8:1	11	SPIONs@EuMOF-8
10:1	9	SPIONs@EuMOF-10

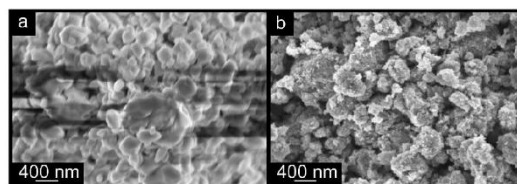


Figure 2. Scanning electron micrographs of a sample of pure $^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Eu-BDC, a) in comparison to the composite SPIONs@EuMOF-2 (b).

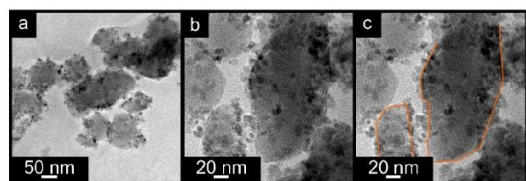


Figure 3. Transmission electron micrographs of isolated SPIONs@EuMOF-4 composites (a, b); a micrograph with surfaces of $^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ highlighted, the surface coverage with SPION particles is imminent (c).

via C–O–Eu bonds between the citrate stabilization and the lanthanide ions.

The hydrodynamic particle size of the composites was determined and is, e.g., 390 ± 350 nm for SPIONs@EuMOF-4 (see Figure S8).

Energy dispersive X-ray spectra reveal that both, europium and iron are detectable near the surfaces of the coated crystals. Thereby, with decreasing amount of SPIONs, the signal strength and amount of detected aerial pixels, representing detected X-ray radiation characteristic for europium, increases, whereas, in case of iron, a drop in pixel density is observable (see Figure S9).

Besides these indications for co-localization of Eu–BDC and SPIONs, the presence of both constituents becomes evident by the magnetizability and, at the same time, homogeneous red-light emission upon UV excitation (see Figure 4) of the synthesized composites. The former arises from contained iron oxide nanoparticles. The latter appears due to the excitation of

the photoluminescent compound $^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ by irradiation with UV light.

The observed red emission is ion-specific for the lanthanide ion Eu^{3+} . This phenomenon upon UV irradiation is well known for lanthanide-containing coordination compounds and arises from a sensitizer effect of the ligand (in this case the BDC^{2-} ligand, which is responsible for light uptake). Energy transfer is finally followed by radiative decay^[35,36] and red emission for the Eu^{3+} containing MOF.

Due to the described inverse core-satellite mode, the intensity of the light emission strongly depends on the selected MOF:SPIONs weight ratio with light emission intensity of the composite strongly increasing from SPIONs@EuMOF-0.5 (MOF:SPIONs=0.5:1) to a MOF:SPIONs weight ratio of 10:1 (SPIONs@EuMOF-10, see Figure 4).

Excitation spectra of the synthesized substances (Figure 5) show a broad excitation band at 317 nm and red emission by intra-4f-transitions of Eu^{3+} in the emission spectra.^[38] This complies with an energy transfer and antenna effect. Additionally, for pure Eu–BDC direct 4f–4f excitation bands are observable. They are hardly present for the composites, which can be explained by the absorbing nature of iron oxide^[39] (see Figure S10). The emission spectra of synthesized compounds all show the characteristic emission bands for Eu^{3+} ions^[38] (see Figure 5) resulting in red emission colour. Assignments of the observed transitions involved in the photoluminescence process are given in detail in Figure S11.

The chromaticity coordinates of SPIONs@EuMOF-x composites according to the CIE (Commission Internationale de l'Éclairage) xy colour space^[40] are listed in Table S1. The

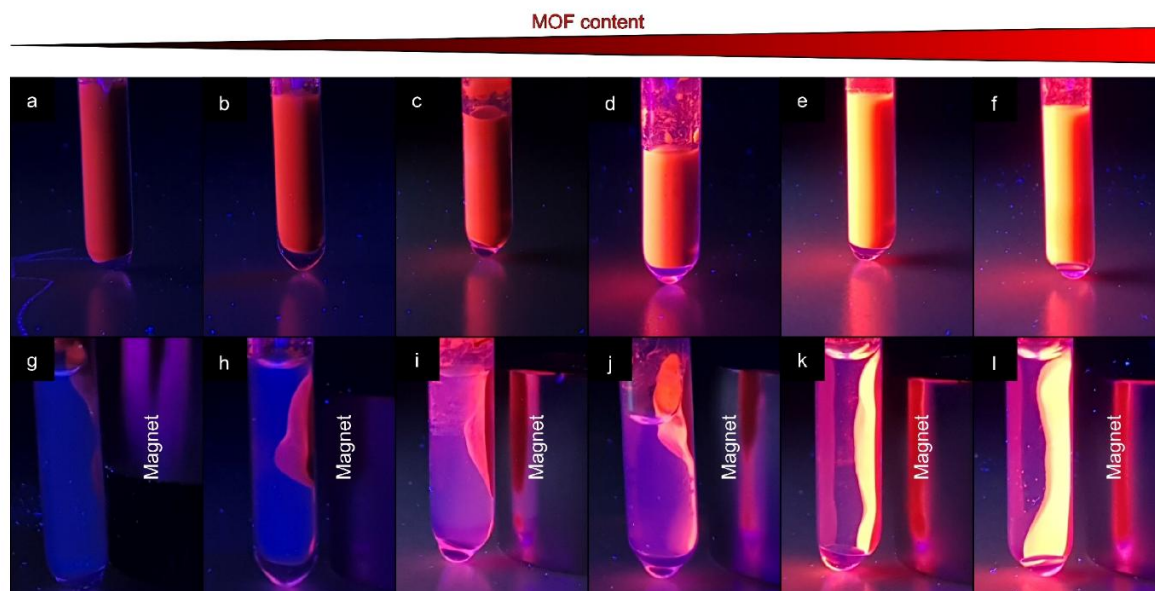


Figure 4. The synthesized composites SPIONs@EuMOF-x under UV excitation ($\lambda_{\text{exc}} = 302$ nm) without (a–f) and with (g–l) applying an external magnetic field for a growing MOF content for the MOF:SPIONs weight ratios listed in Table 1. a, g: SPIONs@EuMOF-0.5; b, h: SPIONs@EuMOF-1; c, i: SPIONs@EuMOF-2; d, j: SPIONs@EuMOF-4; e, k: SPIONs@EuMOF-8; f, l: SPIONs@EuMOF-10.

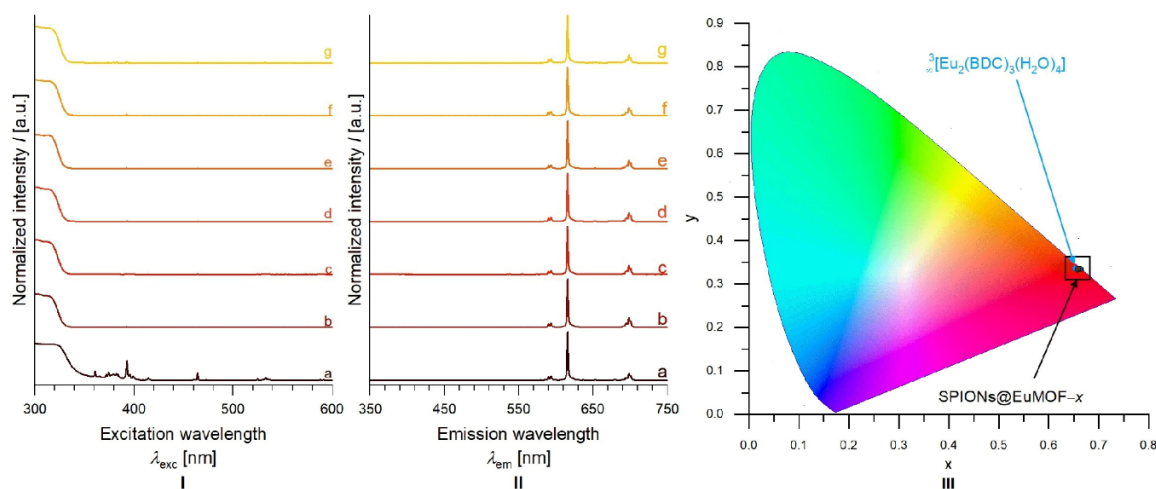


Figure 5. Normalized photoluminescence excitation (I) and emission spectra (II), as well as CIE chromaticity diagram with inserted chromaticity coordinates xy (III) of synthesized composites SPIONs@EuMOF- x in defined MOF:SPIONs weight ratios (see Table 1 and Table S1). a: pure MOF $^3\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4$; b: SPIONs@EuMOF-0.5; c: SPIONs@EuMOF-1; d: SPIONs@EuMOF-2; e: SPIONs@EuMOF-4; f: SPIONs@EuMOF-8; g: SPIONs@EuMOF-10. Emission spectra were recorded at $\lambda_{\text{exc}} = 317$ nm. Excitation spectra were recorded for $\lambda_{\text{em}} = 616$ nm. Assignments of the transitions observed are given in Figure S11.

determined chromaticity for all is in good accordance to the chromaticity determined for pure Eu-BDC.

To quantify the observed gradual change in luminescence intensity, the mass-related emission intensity I_M of the synthesized substances was determined. Recorded emission intensities are listed in Table S2. The change in the luminescence intensity in dependence of the SPIONs content is not only influenced by a simple “dilution” of the luminescent compound with non-luminescent nanoparticles. The absorbing nature of iron oxide at both, the excitation and emission wavelengths of the luminescent MOF, also affects the emission intensity. Considering all these mechanisms the mass-related intensities I_M of the most intense emission band (at $\lambda_{\text{exc}} = 317$ nm) can be described according to

$$I_M = I_{\text{max}} \cdot (1 - p(\text{SPIONs})) \cdot \left(A_1 \cdot 10^{-A_1 p(\text{SPIONs})} + A_2 \cdot 10^{-\frac{A_2}{\Phi} p(\text{SPIONs})} \right) \cdot \frac{1}{\sum_{i=1}^2 A_i} \quad (1)$$

with I_{max} as mass-related emission intensity I_M of pure Eu-BDC ($3.6(2) \cdot 10^6 \text{ cps} \cdot \text{mg}^{-1}$), $p(\text{SPIONs})$ as applied weight percentage of SPIONs (citrate-stabilized at pH=2.1), A_1 as absorbance A of the iron oxide nanoparticles at $\lambda = 616$ nm (0.912) and A_2 as absorbance A at $\lambda = 317$ nm (1.779), and Φ as quantum yield of pure Eu-BDC ($\Phi = 0.126(2)$ for $\lambda_{\text{exc}} = 317$ nm, $\lambda_{\text{em}} = 550$ – 725 nm). The first, linear term of Equation 1 $I_M \cdot (1 - p(\text{SPIONs}))$ can be assigned to a “dilution” of a luminescent substance with a non-luminescent compound. This term is multiplied with a correction factor concerning the absorbance A of the non-luminescent compound at both, the emission (A_1) and the excitation wavelength (A_2). In addition to the absorbance, the quantum yield Φ influences the mass-related emission intensity and is added as a quotient in the exponent of the latter

correction factor. Furthermore, the two absorption corrections are weighted with the respective absorbances A_1 and A_2 , enforcing a normalization by $\Sigma A = A_1 + A_2$. The recorded mass-related emission intensities, a simulated curve of Equation 1, and a fit of Equation 1 to the recorded data is shown in Figure 6.

While fitting I_M , the quantum yield Φ of pure MOF was held constant at 0.126, while the other parameters (I_{max} , A_1 , A_2) were refined freely. An adjusted coefficient of determination (COD) of 0.984 was reached, which confirms the accuracy of Equation 1 already apparent in Figure 6. The refined besides the determined parameters are listed in Table 2.

The quantum yields of the synthesized compounds decrease gradually with reducing the MOF content, as well. The decrease can thereby be described with an exponential decay function. However, due to the already described intensity influencing mechanisms, the quantum yield of the pure MOF exceeds the value expected according to the fit function, as it does not encompass the additional absorber (see Figure S12). For the pure MOF a quantum yield of 0.13(2) is reached, which is in good accordance to the published value of 0.14.^[41] According to the exponential trend, the quantum yield for the pure MOF should reach a value of approximately 0.09(2).

Table 2. Determined and refined parameters of Equation 1. A simulated curve and fitted curve, as well as recorded mass related intensities I_M of the synthesized substances are depicted in Figure 6.

Parameter	Determined	Refined
$I_{\text{max}} [10^6 \text{ cps} \cdot \text{mg}^{-1}]$	3.6(2)	3.6(4)
A_1	0.91	1.3(2)
A_2	1.80	1.7(3)

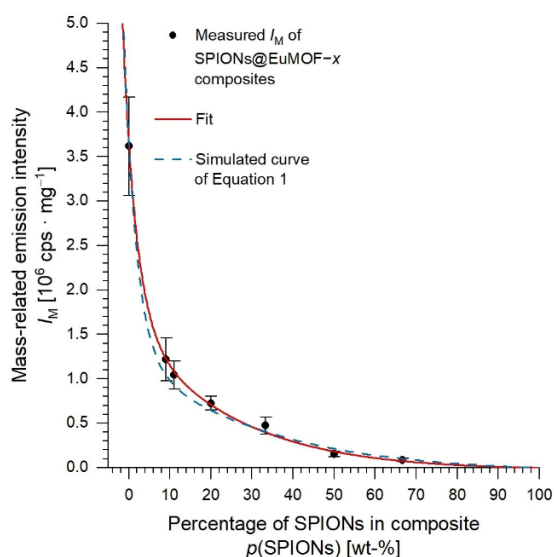


Figure 6. Determined mass-related emission intensities I_M ($\lambda_{em} = 616$ nm, $\lambda_{exc} = 317$ nm) of the composites SPIONs@EuMOF- x in dependence of the amount of SPIONs p (SPIONs) used for the synthesis of the composites (see Table S2), as well as a fit of Equation 1 besides a simulated curve of Equation 1. All variables except for the quantum yield Φ of the pure MOF were refined during the fit. Depicted error bars correspond to 3σ . The refined parameters are listed in Table 2. The adjusted coefficient of determination (COD) was 0.984.

In addition, the luminescence lifetime of the synthesized compounds was also investigated. The luminescence intensity decay of a sample of pure ${}^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Eu-BDC) treated analogously to the synthesis procedure of the composites (mortaring and solvothermal treatment, without addition of iron oxide nanoparticles) can be described with a monoexponential decay. The luminescence lifetime was determined as 0.4380(3) ms. For all composites comprising of Eu-BDC and iron oxide nanoparticles, the determined luminescence lifetimes are in the same range of approximately 0.4 ms (see Table S3). All these determined luminescence lifetimes match well the published value for ${}^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ of 0.40(4) ms.^[41] Therefore, neither the solvothermal treatment in water, nor the presence of iron oxide nanoparticles on the crystallite surfaces of the luminescent lanthanide MOF influences the luminescence mechanism of the MOF other than light absorption. As a result, the electronic systems of the iron oxide nanoparticle part of the composites and of the MOF part do not interact.

Direct influence of the selected component ratio is also observed for the magnetization of the composites (see Figure 7). All composites show superparamagnetic behaviour, since no hysteresis is observed for the magnetization. This indicates the presence of magnetic *nanoparticles* as individual magnetic domains within the composites. The mass-related saturation magnetization M_s thereby increases for rising nanoparticle content and accordingly for decreasing MOF content.

Indeed, the saturation magnetization in dependence of the applied wt% of SPIONs and can be well described by a linear function. This indicates that the MOF:SPIONs ratios selected for syntheses match with the ratios in the respective products. The

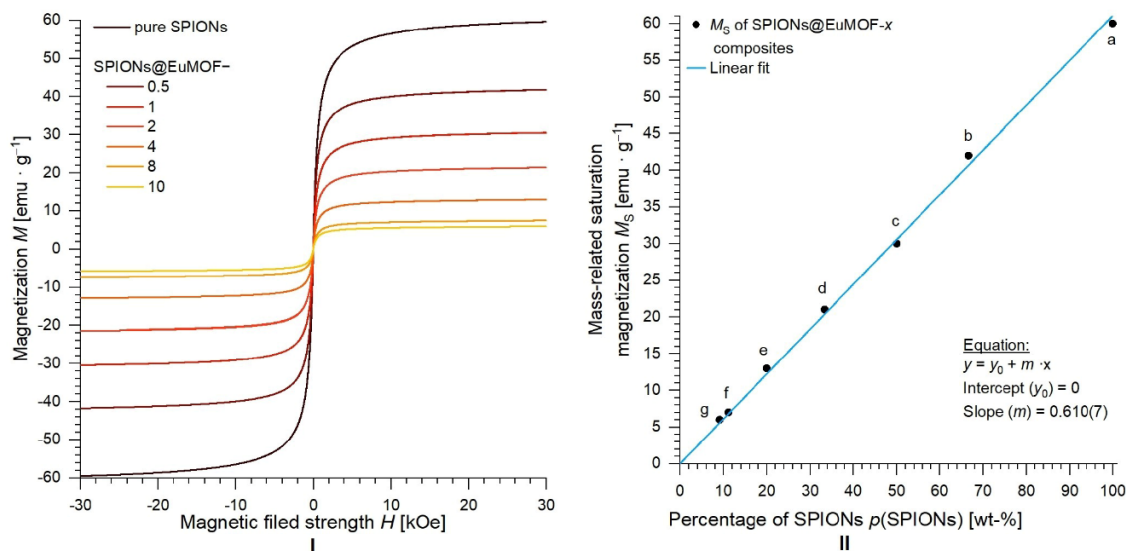


Figure 7. Magnetization curves of the composites SPIONs@EuMOF- x comprising ${}^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ and SPIONs, (citrate stabilized at pH = 2.1); with different MOF:SPIONs weight ratios (I) and mass-related saturation magnetizations M_s (see Table S2) of these composites in dependence of selected weight percentages p (SPIONs) of iron oxide nanoparticles (II). a: pure citrate-stabilized (pH = 2.1) iron oxide nanoparticles ($p(\text{NP}) = 100$ wt%); b: SPIONs@EuMOF-0.5 ($p(\text{NP}) = 66.67$ wt%); c: SPIONs@EuMOF-1 ($p(\text{NP}) = 50.00$ wt%); d: SPIONs@EuMOF-2 ($p(\text{NP}) = 33.33$ wt%); e: SPIONs@EuMOF-4 ($p(\text{NP}) = 20.00$ wt%); f: SPIONs@EuMOF-8 ($p(\text{NP}) = 11.11$ wt%); g: SPIONs@EuMOF-10 ($p(\text{NP}) = 9.09$ wt%).

linear approximation with an adjusted coefficient of determination of 0.999 shows, how accurate and precise the magnetization can be adjusted by choosing a defined component ratio. Therefore, the selected MOF:SPIONs ratio corresponds very well to the mass ratio of the two components in the product. Determined saturation magnetizations are listed in Table S2.

The presence of both components within the composites is further substantiated by the recorded IR spectra of the composites SPIONs@Eu-BDC, which show characteristic bands of the ligands (terephthalate and water) of the MOF,^[34] as well as of citrate and iron oxide (see Figure S13). Additionally, the composition comprising Eu-BDC and SPIONs gets evident in the absorption spectra as well. Pure iron oxide particles absorb light in the entire visible range with rising absorbance for decreasing wavelength. The absorption spectrum of pure Eu-BDC MOF contains several narrow peaks low in intensity, which are assigned to $4f-4f$ transitions, and a broad, intense absorption band at approximately 310 nm, which can be assigned to the light absorption of the ligand within the MOF (see Figure S10 and Figure S11). These characteristics of both compounds are also present in the absorption spectra of the composites SPIONs@EuBDC, in which the absorption band at 310 nm becomes more dominant with increasing MOF content (see Figure S10).

Altogether, the combination of the performed analyses clearly indicates the tunability of both, saturation magnetization and emission intensity of the composite materials. An analogously deliberate tunability of properties would not be achievable with a core-shell structuring of a magnetic core and a MOF shell. In such a composite, the luminescence intensity would just increase with increasing MOF content to a saturation value, from which on additional MOF content would only lower the magnetization of the composites further and no significant influence on luminescence intensity would be further observable.

Tunability of Emission Chromaticity of the Inverse Core-Satellite Composites

Since the MOF $^3_{\text{Eu}}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ is isotypic to the respective terbium-containing structure, the possibility of a composite containing other lanthanide containing MOFs of the constitution $^3_{\text{Ln}}[\text{Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$, such as $^3_{\text{Tb}}[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Tb-BDC) or a combination of MOFs, can be utilized to tune the chromaticity of light emission in addition to the intensity. Hence, a synthesis analogous to the preparation of SPIONs@Eu-MOF-4 with a MOF:SPIONs weight ratio of 4:1 and SPIONs citrate-stabilized at pH=2.1 was performed using Tb-BDC, as well as a 1:1 weight mixture of Tb-BDC and Eu-BDC. The obtained composite systems again exhibit magnetizability and intense luminescence (see Figure 8).

The composition and structuring of the composites were again investigated and confirmed by PXRD (see Figure S14), SEM/EDX (see Figure S15), and TEM (see Figure S16). These prove the simultaneous presence of crystallites of the MOF(s) and iron oxide particles deposited on their surfaces building the

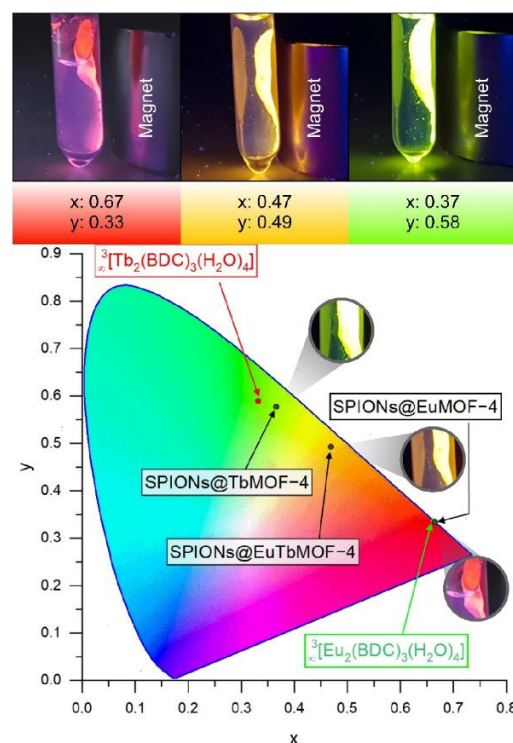


Figure 8. Composites SPIONs@EuMOF-4 (top left), SPIONs@EuTbMOF-4 (top center), and SPIONs@TbMOF-4 (top right), as well as corresponding CIE chromaticity coordinates xy (see Table S1) and a CIE chromaticity diagram with xy inserted as points (bottom). All composites contain SPIONs citrate-stabilized at pH=2.1 (MOF(s):SPIONs weight ratio 4:1).

inverse core-satellite structuring with core-satellite character, and a homogeneous distribution of Tb, Eu and Fe analogously to the already described systems. The photoluminescence spectra of the composite containing both lanthanide MOFs (SPIONs@EuTbMOF-4) show the characteristic transitions of both lanthanide ions,^[38,42] Eu^{3+} and Tb^{3+} , while the spectra of SPIONs@TbMOF-4 show characteristic bands of Tb^{3+} only (see Figure S17 and Figure S11). Accordingly, the colour of the light emission can be tuned by the selection of the ratio of Eu and Tb. In case of Tb containing composites, light absorption of the SPIONs needs to be considered when quantitatively evaluating the chromaticity because of the absorbance of SPIONs being increased in the green region of the visible spectrum.

Therefore, the emitted light of SPIONs@EuTbMOF-4 has a yellow colour, which arises from the mixture of the red emission of Eu^{3+} and the green emission of Tb^{3+} (see Figure 6). The determined chromaticity coordinates of the synthesized composites are listed in Table S1. The particle diameter according to dynamic light scattering of SPIONs@TbMOF-4 was determined to 115 ± 55 nm (see Figure S7).

The chromaticity of the composite SPIONs@TbMOF-4 differs from the pure MOF. While the CIE coordinates xy of pure Tb-BDC are located in the green region of the respective colour

space, the chromaticity coordinates of the composite containing both, iron oxide nanoparticles and Tb–BDC, are shifted towards red in comparison to pure Tb–BDC resulting in a yellowish-green emission colour (see Figure S18). This can be explained by light absorption by the iron oxide nanoparticles in the visible range (see Figure S10). Since the absorbance at low wavelengths is higher compared to the absorbance at high wavelengths, blue and green light is absorbed to a greater extent compared to red light. Therefore, the chromaticity of a composite containing Tb–BDC is shifted towards red in comparison to pure Tb–BDC. The emission spectra can be corrected by

$$I_0(\lambda) = I(\lambda) \cdot 10^{A(\lambda)} \quad (2)$$

with $I(\lambda)$ being the recorded emission intensity I at a certain wavelength λ , $A(\lambda)$ as the corresponding absorbance A of SPIONs at λ , and $I_0(\lambda)$ being the resulting corrected emission intensity at λ . The maximum absorbance of iron oxide nanoparticles was thereby normalized to 1. Subsequently – since the qualitative luminescence spectra were normalized to the most intense emission band ($\lambda = 545$ nm for SPIONs@TbMOF-4) – the normalized absorbance was adjusted to be 0 at the respective wavelength. Applying this correction, the spectral differences between SPIONs@TbMOF-4 and pure Tb–BDC diminish and the chromaticity coordinates converge (see Figure 9). Since the absorbance of iron oxide is low in the red region of visible spectrum (see Figure S10), the chromaticity of SPIONs@EuMOF-x composites does not require adjustment but already matches with the chromaticity of pure Eu–BDC and remains almost unaffected by the correction (see Figure S18).

A comparison of all determined chromaticity coordinates with and without applied absorption correction is listed in Table S4. This confirms the assumption the involved luminescence processes are not mechanistically affected by the presence of iron oxide nanoparticles except by light absorption.

Stability of the Inverse Core-Satellite Composites

To determine their stability, the synthesized SPIONs@EuMOF-4 composites were synthesised in different solvents (water, EtOH and cyclohexane) and washed several times (see experimental section). A change in ratio of constituents due to washing would be directly observable in magnetization of resulting substances. When comparing the magnetizations of SPIONs@EuMOF-4, without washing and after washing three, five, and eight times, no significant difference is observable, which proves the remarkable stability of inverse core-satellite composites and the inherent contact of the two components (see Figure 10).

Besides water, analogous syntheses of SPIONs@EuMOF-4 were performed in ethanol and cyclohexane to investigate the influence of different solvent polarities and hence dispersibility of iron oxide nanoparticles. Again, inverse core-satellite composites with a core-satellite character were obtained (see Figure S19), which consist of iron oxide nanoparticles and the MOF $^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (see Figure S20). The composite materials again exhibit strong magnetism and intense luminescence (see Figure 11). No significant differences, neither in SEM/EDX (see Figure S19), PXRD (see Figure S20), nor in magnetization investigations (see Figure S21) can be observed. Additionally, only minor influences on photoluminescent properties (see

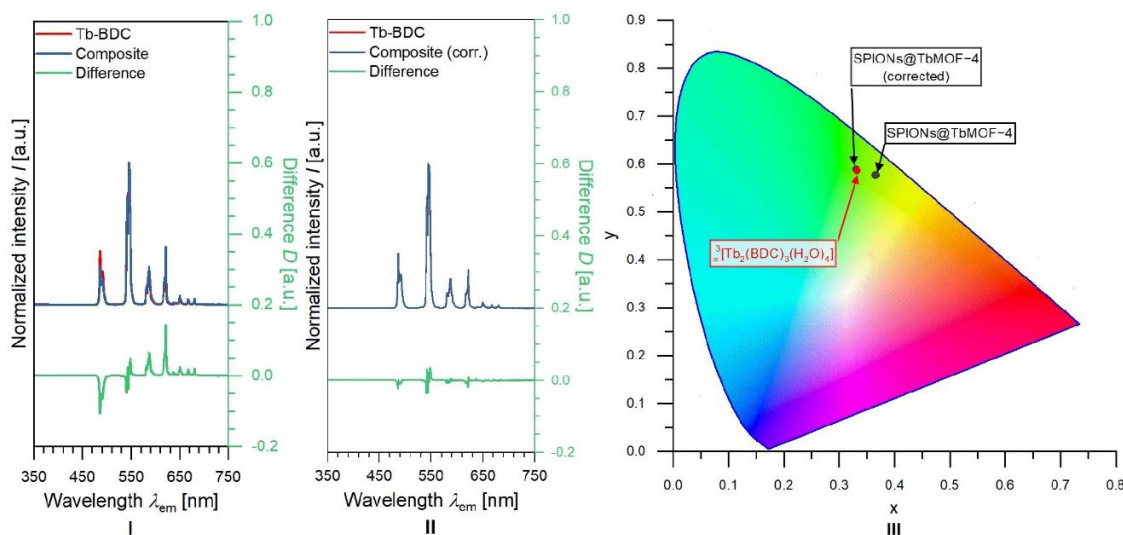


Figure 9. Emission spectra of TbMOF-4@NP (blue) and pure $^3_{\infty}[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Tb–BDC, red) and the intensity difference of those (green) (I); Emission spectrum of TbMOF-4@NP (blue) corrected for the absorption of iron oxide nanoparticles (see Figure S6), emission spectrum of pure Tb–BDC (red) and the difference of those (green) (II); Chromaticity diagram according to CIE of TbMOF-4@NP (corrected for the absorption of iron oxide and as recorded) and of pure Tb–BDC (III). The intensity difference was calculated using $I(\text{TbMOF-4@NP}) - I(\text{Tb–BDC})$.

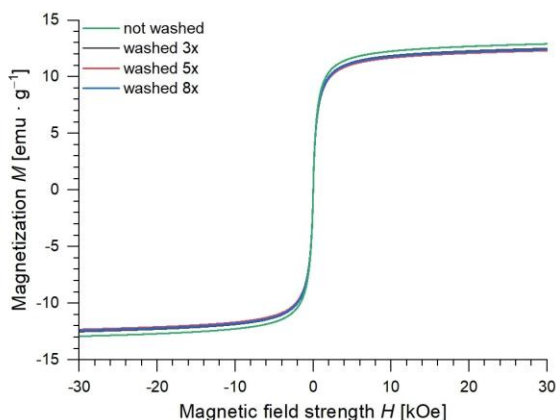


Figure 10. Magnetization of washed SPIONs@EuMOF-4 composites in comparison to the magnetization of as-synthesised SPIONs@EuMOF-4. The magnetization is almost identical for all samples.

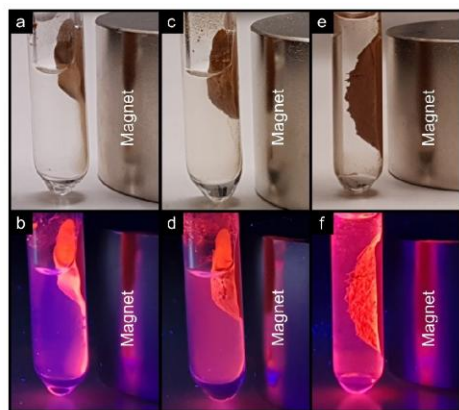


Figure 11. SPIONs@EuMOF-4 composites synthesized in water (a, b), ethanol (c, d), and cyclohexane (e, f) under visible (a, c, e) and UV light ($\lambda_{\text{exc}} = 302 \text{ nm}$, b, d, f).

Figure S22) are observable. This shows that the formation of the inverse core-satellite structuring is independent of the selected solvent and that the composites are stable in different solvents.

Further Investigations on Property Dependencies

Additionally, investigations on the influence of the deprotonation grade of the citric acid stabilization were performed. No significant differences in magnetic and photophysical properties were observed when the stabilization pH value was adjusted to 4.0, 5.6 or 7.5 instead of 2.1. Accordingly, the formation of the inverse core-satellite composites is independent of the deprotonation grade of citric acid. Detailed information on the investigations are provided in the supporting information.

Conclusion

Strongly luminescent Ln-based metal-organic frameworks $^3[\text{Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Ln=Eu, Tb; BDC^{2-} =terephthalate) were successfully combined with superparamagnetic, citrate-stabilized iron oxide nanoparticles (SPIONs) to composites according to an inverse core-satellite functionalization mode with core-satellite character. Within, luminescent MOF crystallites act as core material partly covered by magnetic satellite nanoparticles. The inverse functionalization mode allows for a finetuning of the inherent properties of both components, magnetism and luminescence, by means of magnetization and emission intensity. Such defined and quantitative steering of properties, especially of the luminescence intensity, is not achievable for the previously reported core-shell composites with a luminescent MOF as closed shell around a magnetic core. In the inverse concept, the MOF crystallites can be only partly coated with the iron oxide nanoparticles. As a result, the luminescence intensity is not only influenced by simple "dilution" of the luminescent MOF within the non-luminescent material but also by the light-absorbing nature of iron oxide itself. Thereby, the luminescence mechanisms themselves are not influenced by the magnetic satellite nanoparticle shell apart from light absorption, as proven by lifetime determinations. Thereby, the luminescence intensity becomes tuneable through the amount of magnetic material. In addition, also the colour of the emitted light can be tuned by selecting different ratios of different lanthanide MOFs, such as Eu/Tb-BDC-MOFs. The chromaticity can be mathematically corrected regarding the absorption of iron oxide nanoparticles leading to a quantitative approach towards chromaticity differences.

The saturation magnetization can be directly adjusted linearly by a defined weight ratio of the components, $^3[\text{Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Ln=Tb, Eu) and citrate-stabilized Fe_3O_4 nanoparticles. Thereby, the selected component weight ratio corresponds to the weight ratio of the constituents in the composite.

Furthermore, the constituents are not separable by washing, ultrasonication and magnetic separation and can be synthesized in different solvents, indicating a remarkable stability of the synthesized composites.

In addition to the steering character of photophysical and magnetic properties, the new luminomagnetic inverse core-satellite SPIONs@MOF composites offer options for a utilization as luminescent, magnetic ink or anticounterfeiting protection. Thereby, the mutual dependence of saturation magnetization and luminescence intensity allows e.g. producing a forgery protection that has the characteristics of a specific ID with defined saturation magnetization and luminescence intensity. This could reach from a barely visible but instrumentally detectable photoluminescence of a specific colour combined with a high saturation magnetization to the direct opposite. Not only the structure and stability, but also the tunability of properties, which would not be achievable with core-shell particles imparting a magnetic core and a MOF shell, of the presented composites allows for multiple options of adjustment

to the respective needs beyond the previously reported MOF containing composites.

Experimental Section

Detailed information on the analytical methods is provided in the supporting information.

Materials: Europium(III) nitrate hexahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9% (REO), abcr GmbH), terbium(III) nitrate hexahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9% (REO), abcr GmbH), terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$, 98%, abcr GmbH), sodium hydroxide (NaOH, 98% (p.a.), Grüssing GmbH), iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99%, Sigma-Aldrich), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%, Sigma-Aldrich), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, $\geq 99\%$, Sigma-Aldrich), ammonia solution ($\text{NH}_3(\text{aq})$, 28–30%, Roth), and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 97%, Stockmeier Chemie GmbH & Co. KG) were used as purchased and without further purification.

Synthesis of citrate-stabilized Fe_3O_4 nanoparticles (SPIONs): Superparamagnetic iron oxide nanoparticles (SPIONs) were synthesized via the established method of co-precipitation.^[44] 2.16 g (8.00 mmol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 795 mg (4.00 mmol) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in deionized water (100 mL) and precipitated with 5 mL ammonia solution (28–30 wt%) under stirring. Afterwards the obtained precipitate was washed with water until reaching a neutral pH. Subsequently, for stabilization purposes, 100 mL of a 50 mM citric acid solution was added, whose pH was adjusted to 2.1, 4.0, 5.6, or 7.5 with aqueous ammonia solution. Afterwards, the obtained nanoparticles were washed several times to remove the excess of citric acid and finally vacuum dried at 70 °C. The obtained particles were investigated by TEM revealing an approximate size of 10 nm (see Figure S5). The hydrodynamic particle diameter of SPIONs was determined to 21 nm (± 10 nm), 23 nm (± 11 nm), 23 nm (± 10 nm), and 24 nm (± 11 nm) for SPIONs citrate-stabilized at 2.1, 4.0, 5.6, and 7.5 (Figure S29). Considering the formation of a solvent shell around the particles, this corresponds with the particle size by observed TEM. PXRD analysis evinces the particles containing iron oxide in the magnetite structure (see Figure S4 and Figure S25). IR spectra show characteristic bands of citrate and iron oxide and therefore confirm the nanoparticles composition comprising of iron oxide and citrate (see Figure S6 and Figure S26).

Synthesis of Na_2BDC : Disodium terephthalate (Na_2BDC) was synthesized according to the literature^[45] with slight adaptations. Briefly, 4.98 g (30.0 mmol) of terephthalic acid (H_2BDC) and 3.59 g (90.0 mmol) of sodium hydroxide (NaOH) were mixed with 60 mL deionized water and heated under reflux and stirring for one hour resulting in a clear solution. Subsequently, 30 mL ethanol were added to the boiling solution leading to the formation of a white precipitate. The mixture was filtered hot over a sintered glass filter funnel and the obtained colourless solid was dried in vacuum. Phase purity was confirmed by NMR spectroscopy and elemental analysis. The yield was 42% based on terephthalic acid. ^1H NMR (400 MHz, D_2O , δ): 4.79 (s, D_2O), 7.89 (s, H, Ar H); Anal. calcd. for $\text{C}_8\text{H}_4\text{Na}_2\text{O}_4$: C 45.75, H 1.92, N, 0.00; found: C 45.04; H 1.80; N 0.00.

Synthesis of $^3\text{[Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$: The synthesis of $^3\text{[Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (BDC = benzene-1,4-dicarboxylate) was performed in an adapted synthesis based on a synthesis procedure for $^3\text{[Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ reported in the literature.^[36] In a typical synthesis 892 mg (2.00 mmol) of europium nitrate hexahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and 840 mg (4.00 mmol) of previously synthesized disodium terephthalate (Na_2BDC) were separately dissolved in 10 mL deionized water, each. The solutions were combined and stirred overnight leading to the formation of a white precipitate.

The solid was separated by filtration over a sintered glass filter funnel, washed thrice with 20 mL of deionized water each, and dried in vacuum. The identity and phase purity of $^3\text{[Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ were confirmed by powder X-ray diffraction (see Figure S2) and elemental analysis. SEM investigations reveal a crystallite size of approximately 50–500 nm (see Figure 2) corresponding with the particle diameter of 255 nm (± 170 nm) determined by dynamic light scattering (see Figure S3). The yield was 64% based on Eu. IR (KBr): ν = 3464 (br), 3066 (w), 1609 (m), 1587 (m), 1545 (s), 1506 (s), 1420 (s), 1407 (s), 1310 (m), 1163 (w), 1139 (w), 1099 (w), 1021 (w), 884 (w), 829 (w), 762 (m), 751 (m), 586 (m), 558 (m), 530 (m), 510 (m), 437 cm^{-1} (w). Anal. calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_{16}\text{Eu}_2$: C 33.20, H 2.32, N 0.00; found: C 32.92, H 2.28, N, 0.00.

Synthesis of $^3\text{[Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$: The synthesis of $^3\text{[Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ was performed analogously to $^3\text{[Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ in an adapted synthesis based on the procedure reported for $^3\text{[Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ ^[36] using $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ instead of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The identity and phase purity of $^3\text{[Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ were confirmed by powder X-ray diffraction (see Figure S2) and elemental analysis. The yield was 90% based on Tb. Anal. calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_{16}\text{Tb}_2$: C 32.67, H 2.28, N: 0.00; found: C 32.30, H 2.31, N 0.00.

Synthesis of the composites SPIONs@LnMOF-x: To prepare the composites SPIONs@LnMOF-x (Ln=Eu, Tb), the synthesized, citrate-stabilized iron oxide nanoparticles (SPIONs) and the luminescent MOF $^3\text{[Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ or $^3\text{[Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ were combined in defined MOF:SPIONs weight ratios. The luminescent compound(s) and iron oxide nanoparticles were finely grounded in an agate mortar for five minutes. The obtained homogeneous mixture was transferred into a Duran® glass ampoule and a solvent (water, cyclohexane, or ethanol) was added. The ratio of the solid components and the solvent was thereby adjusted to 1:16 (solid:solvent, e.g. for synthesis of SPIONs@EuMOF-4: 40 mg $^3\text{[Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$, 10 mg SPIONs, 0.8 mL water; For applied component masses and solvent amount see Table S5). The resulting mixture was degassed by freezing in liquid nitrogen, evacuating the ampoule and letting the mixture thaw again. This procedure was repeated once more. Afterwards, the mixture was frozen and the ampoule was evacuated and sealed. The reaction mixture then was homogenized in an ultrasonic bath for three minutes. The ampoule was shaken and placed in a corundum oven, which was heated up within five hours to a temperature approximately 10 °C above the boiling point of the used solvent (110 °C for water, 90 °C for ethanol and cyclohexane), held at this temperature for five hours, followed by cooling down to room temperature in five hours. After the synthesis, the ampoule was opened, the resulting luminomagnetic composite material was magnetically separated from the liquid phase, and subsequently dried in vacuum (0.001 mbar) for one hour. The composite character of the resulting products was confirmed by powder X-ray diffraction and SEM/EDX, as well as TEM investigations and stability tests. Additionally, the luminescence and magnetic properties were investigated.

Synthesis of the composite SPIONs@EuTbMOF-4: Citrate-stabilized superparamagnetic iron oxide nanoparticles (SPIONs), $^3\text{[Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Eu–BDC) and $^3\text{[Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Tb–BDC) in a Tb–BDC:Eu–BDC:SPIONs weight ratio of 2:2:1 were mixed in an agate mortar and solvothermally treated analogously to the described synthesis procedure of SPIONs@LnMOF-x. Applied amounts of the constituents are listed in Table S5.

Washing procedure for SPIONs@EuMOF-4 composites: Three samples of SPIONs@EuMOF-4 were separately synthesized according to the synthesis procedure described above. After solvother-

mal treatment, the resulting reaction mixtures were transferred into a 10 mL screw cap glass and filled to 5 mL each, followed by treating with ultrasound for five minutes. Subsequently, the screw cap vessels were placed beside a neodymium magnet for five minutes followed by a rotation by 180°. This step was repeated three times, followed by a magnetic separation of the composites for five minutes, again. The liquid phases were removed and 5 mL deionized water were added in each vessel. The whole washing procedure was repeated two, four, or seven times, followed by drying in vacuum, resulting in SPIONs@EuMOF-4 composites, which were washed three, five or eight times in whole with almost unchanged magnetization (see Figure 10).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: composites · core-shell nanostructures · luminescence · magnetism · metal-organic frameworks

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4.3 Homoleptic coordination polymers and complexes of transition metals with 2-(1,2,4-1H-triazol-3-yl)pyridine and tuning towards white-light emission

Im Rahmen der dritten Publikation wurden neuartige Koordinationsverbindungen auf Basis von Übergangsmetallionen und dem Liganden 2-(1,2,4-1H-Triazol-3-yl)pyridin (Hpt) mit dem Ziel der Herstellung von Substanzen mit optischen Eigenschaften untersucht. Auf Basis der porösen Struktur des erhaltenen Koordinationspolymers (CP) $[\text{Zn}(\text{pt})_2]$ und dessen Photolumineszenzeigenschaften konnte ein Weißlichtemitter generiert werden, welcher als Alternative zu dem im *All White Magnet* verwendeten IFP-1 anwendbar sein könnte (s. Kap. 4). Im Gegensatz zu IFP-1 wird das eindimensionale Koordinationspolymer $[\text{Zn}(\text{pt})_2]$ nicht *in situ* sondern postsynthetisch mit Lanthanoidionen beladen, wodurch während der Synthese keine potenziell störenden Fremdionen präsent sind.

Das solvothermal synthetisierte Koordinationspolymer $[\text{Zn}(\text{pt})_2]$, welches Hpt in seiner deprotonierten Form zeigt unter UV-Bestrahlung Ligand-basierte, blaue Lumineszenz. Unter Einbeziehung der C—H $\cdots$ N Wasserstoffbrückenbindungen weist $[\text{Zn}(\text{pt})_2]$ eine supermolekular dreidimensionale, polymere Struktur mit quadratischen Porenkanälen auf, was die Möglichkeit einer Beladung mit Lanthanoidionen mit sich bringt. Nach erfolgreicher Imprägnierung des CPs mit den Lanthanoid-Ionen Eu^{3+} und Tb^{3+} ist in Analogie zu EuTb@IFP-1 entsprechend des RGB-Konzeptes Weißlichtemission unter UV-Bestrahlung mit einer Quantenausbeute von 24% beobachtbar. Die Anregung der Lanthanoidionen erfolgt hierbei aufgrund des Antenneneffekts über den Liganden des Koordinationspolymers, wie sich über lumineszenzspektroskopische Untersuchungen zeigt.

Neben dem CP $[\text{Zn}(\text{pt})_2]$ konnten 19 weitere Verbindungen synthetisiert und charakterisiert werden. Hierzu zählen auch die zu $[\text{Zn}(\text{pt})_2]$ isotypen Koordinationspolymere $[\text{M}(\text{pt})_2]$ (M = Mn, Fe, Co, Ni, Cu, Cd), welche in Abhängigkeit des enthaltenen Übergangsmetallions unterschiedliche, optische Eigenschaften aufweisen. Dies beinhaltet eine intensive Farbe im Fall von $[\text{M}(\text{pt})_2]$ (M = Fe, Co, Ni, Cu), sowie einen thermochromen Effekt, welcher für $[\text{Fe}(\text{pt})_2]$ beobachtet und untersucht wurde. Die Koordinationspolymere sind über eine Umsetzung der jeweiligen Übergangsmetallacetate und des Liganden Hpt in Pyridin zugänglich. Hierbei wird im Fall von $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (OAc = Acetat) zunächst das Koordinationspolymer $[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (Py = Pyridin) erhalten, welches das gleiche Strukturmotiv wie $[\text{Zn}(\text{pt})_2]$ aufweist und in dessen Poren Pyridinmoleküle in kristallographisch geordneter Weise eingeschlossen sind. Anhand pulverdiffraktometrischer Untersuchungen zeigte sich eine Umwandlung zu $[\text{Cu}(\text{pt})_2]$ ohne kristallographisch geordnete Lösungsmittelmoleküle,

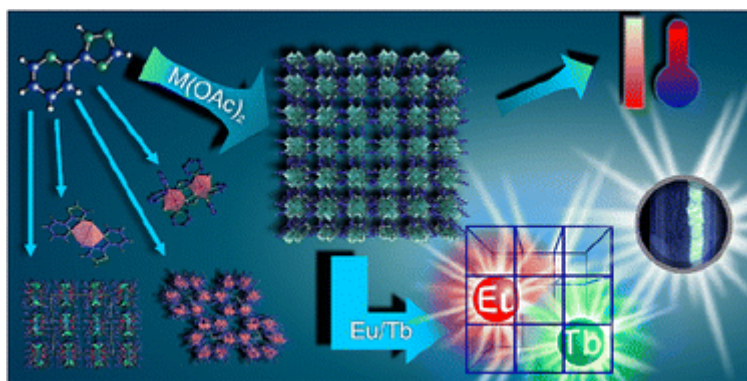
welches isotyp zu $^1[\text{Zn}(\text{pt})_2]$ ist. Die sukzessive Abgabe eingeschlossener Lösungsmittelmoleküle weist auf eine mögliche Aktivierung der Koordinationspolymere hin, was eine Imprägnierung mit Lanthanoiden möglich macht. Dies steht im Einklang mit den bestimmten inneren Oberflächen von $^1[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Fe}, \text{Co}, \text{Zn}$), welche $217 \text{ m}^2 \cdot \text{g}^{-1}$ ($^1[\text{Fe}(\text{pt})_2]$), $181 \text{ m}^2 \cdot \text{g}^{-1}$ ($^1[\text{Co}(\text{pt})_2]$) bzw. $160 \text{ m}^2 \cdot \text{g}^{-1}$ ($^1[\text{Zn}(\text{pt})_2]$) betragen.

Beim Übergang von Acetaten zu Halogeniden wird im Fall von MnCl_2 , FeCl_2 , CoCl_2 und CoBr_2 die Bildung von mononuklearen Komplexen mit der Summenformel $[\text{MX}_2(\text{Hpt})_2]$ ($\text{MX}_2 = \text{MnCl}_2, \text{FeCl}_2, \text{CoCl}_2, \text{CoBr}_2$) beobachtet. In diesen liegt der Ligand – im Gegensatz zu den CPs $^1[\text{M}(\text{pt})_2]$ – nicht deprotoniert vor, weshalb keine polymere Verknüpfung stattfindet. Durch Variation der Syntheseparameter entstehen weiterhin Koordinationsverbindungen von mononuklearen und dinuklearen Komplexen, über eindimensionale CPs bis hin zu zweidimensionalen Koordinationspolymeren, welche einkristallröntgendiffraktometrisch charakterisiert sind. Diese bisher unbekannten Verbindungen umfassen den homoleptischen Komplex $[\text{Zr}(\text{pt})_4]$, den Komplex $[\text{ZnCl}_2(\text{Hpt})_2]$, welcher isotyp zu beispielsweise $[\text{MnCl}_2(\text{Hpt})_2]$ ist, die dinuklearen Komplexe $[\text{Fe}_2\text{X}_2(\text{pt})_2(\text{Py})_4]$ ($\text{X} = \text{Cl}, \text{Br}$), die eindimensionalen CPs $^1[\text{MnCl}(\text{bpt})]$ ($\text{bpt} = 3,5\text{-bis}(2\text{-Pyridyl})\text{-}1,2,4\text{-triazolat}$), bei welchem der Ligand *in situ* gebildet wird, sowie $^1[\text{Co}_2\text{Cl}_3(\text{pt})(\text{H}_2\text{O})_2] \cdot 4\text{CyOH}$ ($\text{CyOH} = \text{Cyclohexanol}$) neben den zweidimensionalen Koordinationspolymeren $^2[\text{Cu}_2\text{Cl}(\text{pt})]$ und $^2[\text{Co}_2\text{Br}_2(\text{pt})_2]$. Die große Anzahl an identifizierbaren Verbindungen zeigt die Vielfalt an potenziell neuen Koordinationsverbindungen unterschiedlicher polymerer Dimensionalität, welche den Liganden Hpt bzw. dessen deprotonierte Spezies pt oder dessen Derivate enthalten.

Die Erstautorenschaft liegt bei *M. T. Seuffert*. Die Entwicklung und Durchführung der Experimente erfolgten von *M. T. Seuffert* unter der Betreuung von *Prof. Dr. K. Müller-Buschbaum*. Die Charakterisierungen erhaltener Verbindungen wurden vom Erstautor in Zusammenarbeit mit *A. E. Sedykh*, *T. C. Schäfer* und *Dr. J. Becker* durchgeführt. Das Manuskript wurde von *M. T. Seuffert* erstellt und von *A. E. Sedykh* und *Prof. Dr. K. Müller-Buschbaum* bearbeitet. Ergänzende Informationen (*supporting information*) zu dieser Publikation sind in Kap. 7.3 festgehalten.

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5075Homoleptic coordination polymers and complexes
of transition metals with 2-(1,2,4-1*H*-triazol-3-yl)
pyridine and tuning towards white-light emission†Marcel T. Seuffert,^a Alexander E. Sedykh,^{id} ^a Thomas C. Schäfer,^a Jonathan Becker^a
and Klaus Müller-Buschbaum ^{id} ^{*,a,b}

Twelve coordination compounds ranging from polymers to complexes based on divalent ions of the 3d-transition metals Mn to Zn, and Cd together with the ligand 2-(1,2,4-1*H*-triazol-3-yl)pyridine (Hpt) were synthesised and fully characterised. The main products are homoleptic, one-dimensional coordination polymers $\frac{1}{n}[\text{M}(\text{pt})_2]$ (M = Mn–Zn, and Cd, pt = 3-(pyridin-2-yl)-1,2,4-triazolate), $\frac{1}{n}[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$, besides complexes $[\text{MX}_2(\text{Hpt})_2]$ from MnCl_2 , FeCl_2 , CoCl_2 , CoBr_2 , ZnCl_2 , and Hpt = 2-(1,2,4-1*H*-triazol-3-yl)pyridine. In addition to these series, single crystalline by-products of the reactions were identified and their structures determined. The obtained products were investigated with single-crystal (SCXRD) and powder X-ray diffraction (PXRD), including temperature-dependent PXRD, physisorption experiments, UV-Vis, IR, and photoluminescence spectroscopy (PL), simultaneous thermal analysis, and elemental analysis. Based on $\frac{1}{n}[\text{Zn}(\text{pt})_2]$, it was possible to generate a white light-emitting compound by addition of Eu^{3+} and Tb^{3+} . It follows the RGB concept with blue ligand-based emission of the coordination polymer and red/green emission of lanthanide ions and shows excitation dependent tuneable character of emission colour from blue to practically perfect white.

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Introduction

Coordination compounds and complexes have been under extensive chemical investigation and have multiple applications *e.g.*, functioning as catalysts¹ as well as for medical and biochemical purposes.² This includes *e.g.*, various zinc-based coordination compounds acting as anticancer agents,³ or complexes based on the tridentate Schiff base ligand, 4-(2-((1*E*,2*E*)-1-(2-(*p*-tolyl)hydrazineylidene)-propan-2-ylidene)-hydrazineyl) with anticancer or antimicrobial activities depending on contained metals.⁴ Complexes of Fe(III), and Co(II) with Isatin-hydrazone derivatives were reported showing anti-inflammatory properties.⁵ Besides, coordination complexes can be utilised as sensor materials for various analytes by luminescence moni-

toring. For example, the formation of a complex and thereon fluorescence quenching of a 2-pyridinecarbonyl substituted 8-aminoquinoline derivative was reported being applicable to quantify Cu^{2+} in water and food.⁶ A complex based on Pd(II) and a hydrazone derived Schiff base was found to be capable of ratio-metric detection of F^- .⁷ The compound $[(\text{ppy})_2\text{Ir}(\text{IPP})]\text{PF}_6$ (ppy = 2-phenylpyridine, IPP = 1-(1*H*-imidazo[4,5-*f*][1,10]phenatrolin-2-yl)phenol) was reported being applicable as a “turn-off” fluorescence sensor for Ni^{2+} .⁸ This shows the numerous potential applications, coordination complexes possess.

By usage of multidentate ligands and depending on the ligand structure, it is possible to obtain polymeric coordination compounds, namely coordination polymers (CPs) and metal-organic frameworks (MOFs). These groups of coordination compounds were intensively studied over the recent years.^{9–12,13} The properties of CPs and MOFs depend on their structure and containing building blocks – often metal ions and ligands – leading to various possible applications, such as electrochemical properties¹⁴ resulting in energy storage implementations,^{11,15} catalytic utilisation,^{16,17} medical purposes,^{9,12,18,19} and environmental protection applications.^{10,16,20}

One of the most fascinating properties of manifold MOFs is photoluminescence, leading to applications like sensing,²¹ bioimaging,^{9,18,22} optoelectronic devices,²³ and aesthetical or anti-counterfeiting applications.^{24,25} Investigated photoluminescent coordination compounds often contain multiple

^aInstitute of Inorganic and Analytical Chemistry, Justus Liebig University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany. E-mail: kmbac@uni-giessen.de^bCenter for Materials Research (LAMA), Justus Liebig University Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany† Electronic supplementary information (ESI) available: Analytical methods as well as 50 figures and 39 tables showing the crystallographic data, powder X-ray diffractograms, photoluminescence spectra, luminescence intensity decays and corresponding lifetimes, absorption spectra, IR spectra, thermal properties, and physisorption properties. CCDC 2347927, 2347920, 2347949, 2347948, 2347938, 2347937, 2347952, 2347953, 2347947, 2347946, 2347951, 2347925, 2347917 and 2347950. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4dt03149k>

chromophores, leading to the possibility of tuning the emission colour. This can be achieved *e.g.*, by functionalisation of MOFs with lanthanide ions.^{26,27,28–31} White light emission is a frequently desired property of alike compounds, attained by utilising additive colour mixing according to the RGB concept.^{25,28,32} Thereby, white light emitting CPs and MOFs as solid-state light sources are a more environment-friendly alternative to *e.g.* mercury containing fluorescent lights.^{33,34} This makes them promising candidates for lighting technologies or anti-counterfeiting applications.³⁵ As a matrix material for such luminescent compounds, transition metal coordination polymers can be exploited, as it was shown for ZIF-8,^{29,31} MOF-5,²⁶ or $\{[\text{Zn}_3(\text{bdc})_3(\text{EtOH})_2] \cdot (\text{EtOH})_{0.6}\}$ (bdc = benzene dicarboxylate).³⁰ Moreover, by intercalation of Eu^{3+} and Tb^{3+} to MIL-124, a white light emitter was created, which potentially can be utilised in luminescent devices like displays, or for lighting.³³ Furthermore, a coordination polymer gel obtained by reaction of europium acetate and terbium acetate with 5,5',5''-(benzene-1,3,5-tricarboxyl)tris(azanedi-yl)trisophthalic acid featuring white light emission was published, which is applicable as invisible anti-counterfeit ink.³⁶ By coating of UV-LEDs with a composite comprising carbon dots, and the MOF $[\text{Eu}_{1.22}\text{Tb}_{0.78}(1,4\text{-phda})_3(\text{H}_2\text{O})](\text{H}_2\text{O})$ it was possible to generate a white LED.³⁷

There are several examples of CPs containing transition metals and 1,2,4-*H*-triazole (TzH), or rather 1,2,4-triazolate (Tz), as ligand.³⁸ It was shown, that those compounds can exhibit guest-sensitive luminescence.³⁹ Therefore, also derivatives of triazoles are of increasing scientific interest as potential ligands for CPs with photoluminescent properties. A ligand, which was recently used for this purpose, is 2-(1,2,4-*H*-triazol-3-yl)pyridine (Hpt)^{40–42,43–47} or derivatives of it.^{46,48,49} Numerous compounds based on these ligands in combination with transition metals were reported, such as coordination polymers, like the isotopic, homoleptic compounds $[\text{Ni}(\text{pt})_2] \cdot 1.5\text{H}_2\text{O}$ ⁴⁰ and $[\text{Cu}(\text{pt})_2] \cdot \text{H}_2\text{O}$,⁴¹ as well as the heteroleptic polymers $[\text{Cu}_2\text{I}(\text{pt})_2]$,⁵⁰ and $[\text{Cu}(\text{pt})(\text{OAc})]$.⁵¹ They all exhibit a one-dimensional polymeric structure with $\eta^2\text{-}\mu_2$ -coordination mode of the deprotonated pt ligand. Also, compounds containing derivatives of Hpt were published, such as $[\text{Cu}(\text{H-2py-trz-pba})_2]$ (H-2py-trz-pba = 4-(3-(pyridin-2-yl)-4*H*-1,2,4-triazol-4-yl)benzoate),⁵² $[\text{Mn}_2(\text{bpt})_2(\text{SCN})_2(\text{H}_2\text{O})_2]$ (containing the Hpt derivative bpt = 3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole),⁴⁶ and $[\text{Zn}(\text{5-nipa})(\text{L}^{22})(\text{H}_2\text{O})]$ (5-nipa = 5-nitroisophthalate, L^{22} = 2,2'-(4*H*-1,2,4-triazole-3,4-diyl)dipyridine).⁴⁹

Various reported compounds also feature additional properties, like $[\text{Fe}(\text{Hpt})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$, which shows a temperature-dependent spin crossover of $\text{Fe}(\text{II})$.⁴³ Also, the d^{10} transition metal ion $\text{Cu}(\text{I})$ forms complexes with Hpt derivatives, such as $[\text{Cu}(\text{bptzH})(\text{PPh}_3)_2](\text{ClO}_4)$ (bptzH = 2-(3-*tert*-butyl-1,2,4-*H*-triazol-5-yl)pyridine), $[\text{Cu}(\text{fptzH})(\text{PPh}_3)_2](\text{ClO}_4)$ (fptzH = 2-(3-trifluoromethyl-1,2,4-*H*-triazol-5-yl)pyridine), and $[\text{Cu}(\text{bptzH})(\text{dppe})](\text{ClO}_4)$ (dppe = 1,2-bis(diphenylphosphino)ethane), which all show intense, luminescence in the solid state with emission colours from blue to green.⁵³ This shows the potential of coordination compounds based on Hpt and its derivatives with regard to optical properties.

In this work, we extend the number of coordination compounds based on Hpt and present the structures and properties of new compounds with 3-(pyridin-2-yl)-1,2,4-triazolate (pt) as ligand, namely the polymers $[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Mn}$ (1), Fe (2), Co (3), Ni (4), Cu (5), Zn (6), Cd (7)), and $[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (8), besides the complexes $[\text{MX}_2(\text{Hpt})_2]$ ($\text{MX}_2 = \text{MnCl}_2$ (9), FeCl_2 (10), CoCl_2 (11), CoBr_2 (12)) containing 2-(1,2,4-*H*-triazol-3-yl)pyridine (Hpt). Depending on the contained transition metal ion, the synthesised CPs can exhibit photophysical properties and – in case of a zinc-containing CP – can even be used as blue component of a RGB-type white light-emitter.

The obtained compounds were investigated with regard to structure, photophysical properties and thermal properties, which is described hereafter.

Results and discussion

The compounds $[\text{Zn}(\text{pt})_2]$ (6), $[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (8), $[\text{MnCl}_2(\text{Hpt})_2]$ (9), $[\text{FeCl}_2(\text{Hpt})_2]$ (10), $[\text{CoCl}_2(\text{Hpt})_2]$ (11), $[\text{CoBr}_2(\text{Hpt})_2]$ (12), and $[\text{ZnCl}_2(\text{Hpt})_2]$ (13) were obtained as single crystals suitable for SCXRD. Therefore, the crystal structures were determined for these compounds based on SCXRD data, isostructural or even isotopic character of further elements of the series of compounds were determined by PXRD.

Syntheses of and crystal structure investigations on $[\text{M}(\text{pt})_2]$ (1–7)

Based on single crystal X-ray data, the crystal structure of this series of compounds was determined for the homoleptic, one-dimensional coordination polymer (CP) $[\text{Zn}(\text{pt})_2]$ (6). Crystals of 6 suitable for single crystal X-ray diffraction investigations were obtained by reaction of water-free ZnCl_2 , 2-(1,2,4-*H*-triazol-3-yl)pyridine (Hpt), and benzylamine in a mixture of toluene and pyridine. CP 6 crystallises in the tetragonal crystal system in the space group $I4_1/acd$. The CP contains distorted, zinc-based octahedra, in which Zn^{2+} is coordinated by four deprotonated, 3-(pyridin-2-yl)-1,2,4-triazolate (pt) ligand molecules. Two $\eta^2\text{-pt}$ ligands coordinate *via* N1 of the pyridine ring and N2 of the triazole ring. The other two η^1 ligand molecules coordinate *via* N3 of the triazole ring to Zn. Thereby, each pt ligand coordinates to two zinc ions. This results in octahedra which are interconnected by two neighbouring nitrogen atoms of the triazole rings (here N2 and N3). The consequential, one-dimensional polymeric strands screw about the crystallographic *c* axis and are stacked within the unit cell, forming square-shaped pore channels.

Detailed crystallographic data is listed in Table S1† A depiction of the crystal structure is given in Fig. 1. Considering weak C–H...N interactions,⁵⁴ each pt ligand establishes two hydrogen bonds to ligand molecules of a neighbouring polymeric strand. This results in a supermolecular three-dimensional polymeric structure (Fig. S1†).

The interatomic Zn–N distances in CP 6 were determined to be within the range of 207(5) pm to 232(4) pm (Table S2†). These distances match with published values for *e.g.* $[\text{Zn}(\text{H-2py-trz-ia})] \cdot 5.25\text{H}_2\text{O}$ (H-2py-trz-ia = 5-(3-pyridyl)-1,2,4-triazol-



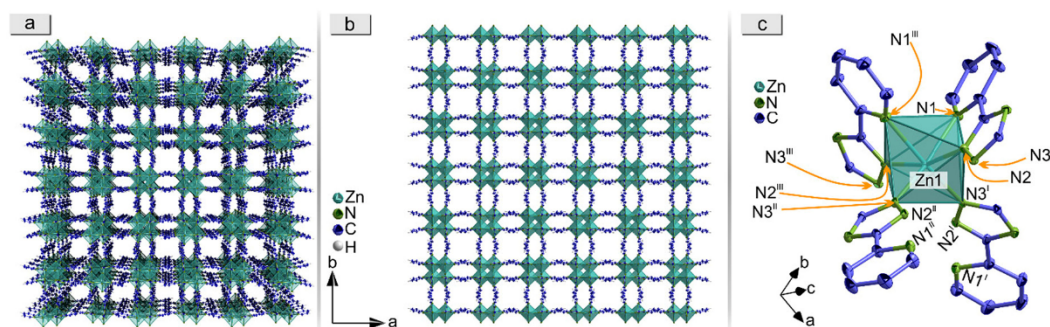


Fig. 1 Depiction of the crystal structure of $\frac{1}{\infty}[\text{Zn}(\text{pt})_2]$ (**6**). Presented are: A three-dimensional depiction of the square-shaped pore channels along the crystallographic c axis (a), an excerpt of the crystal structure along the crystallographic c axis in parallel projection (b), and the extended coordination of Zn^{2+} (c, hydrogen atoms are omitted). Polyhedra around Zn are highlighted dark cyan. Displayed thermal ellipsoids correspond to 50% probability level of the atoms. For clarity, only one of the two disorders of the ligand molecule is depicted. Crystallographic data is summarised in Table S1† Symmetry operations: I = $1/4 + y, 1/4 - x, -1/4 + z$; II = $x, -y, 1/2 - z$; III = $1/4 - y, 1/4 - x, 1/4 - z$.

4-yl)iso-phthalate), which contains fivefold coordinated Zn^{2+} interconnected three-dimensionally by H-2py-z-ia, and for which corresponding distances in a range of 212–221 pm are reported.⁴⁷

The distances in **6** are also in good agreement with distances in $\frac{1}{\infty}[\text{Zn}(\text{5-nipa})(\text{L}^{22})(\text{H}_2\text{O})]$ (5-nipa = 5-nitro-isophthalate, L^{22} = 2,2'-(4H-1,2,4-triazole-3,4-diyl)dipyridine),⁴⁹ which contains octahedrally coordinated Zn^{2+} and for which Zn–N distances of 214–235 pm are reported.

By comparison of the reported sum formulas, CP **6** is closely related to reported compounds $\frac{1}{\infty}[\text{Ni}(\text{pt})_2] \cdot 1.5\text{H}_2\text{O}$,⁴⁰ and $\frac{1}{\infty}[\text{Cu}(\text{pt})_2] \cdot \text{H}_2\text{O}$,⁴¹ which also feature octahedral coordination of the metal ions by $\eta^2\text{-}\mu_2$ -coordinating pt ligands and one-dimensional polymeric structures. Within these two CPs, polymeric zig-zag chains with two different orientations within the unit cell are formed, rather than screwing strands as observed for **6**. This leads to a denser packing within the unit cell for the already reported compounds in comparison to **6**. For the single crystal structure of CP **6**, a residual electron density of 215 electrons per unit cell located in the square-shaped channels were found, indicating solvent molecules being intercalated there.

PXRD investigations on $\frac{1}{\infty}[\text{M}(\text{pt})_2]$

Bulk materials of $\frac{1}{\infty}[\text{M}(\text{pt})_2]$ (**1–7**) were obtained by solvothermally reacting stoichiometric amounts of the metal acetate (hydrates) $\text{M}(\text{OAc})_2 \cdot x\text{H}_2\text{O}$, $\text{M} = \text{Mn–Zn, Cd}$, and the ligand Hpt in pyridine (see Experimental section). Subsequent to washing with fresh solvent and drying in vacuum, the homoleptic compounds $\frac{1}{\infty}[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Mn}$ (**1**), Fe (**2**), Co (**3**), Ni (**4**), Cu (**5**), Zn (**6**), Cd (**7**)) are obtained, which are isotypic, and can be synthesised phase-pure, as proven by powder diffractograms (Fig. 2). The isotypic character of the CPs **1–7** was confirmed by Pawley refinements (see Fig. S4, and Table S15†). By these, the cell constants of **1–7** were determined to the values listed in Table S27.†

It is noteworthy, that CP **5** ($\frac{1}{\infty}[\text{Cu}(\text{pt})_2]$) differs from the already reported compound $\frac{1}{\infty}[\text{Cu}(\text{pt})_2] \cdot \text{H}_2\text{O}$ ⁴¹ although having

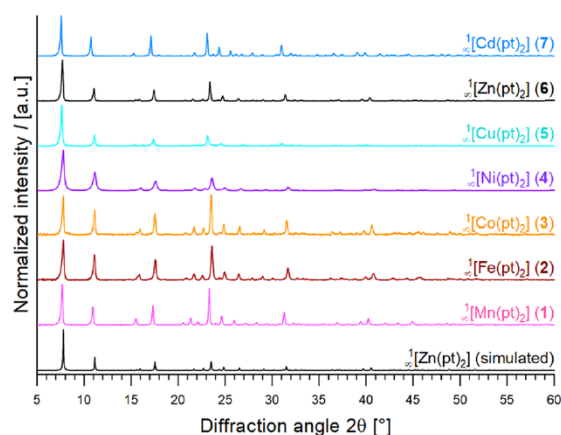


Fig. 2 PXRD patterns of $\frac{1}{\infty}[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Mn}$ (**1**), Fe (**2**), Co (**3**), Ni (**4**), Cu (**5**), Zn (**6**), Cd (**7**)), in comparison to a pattern of **6** simulated from SCXRD data.

the same polymer sum formula. Indeed, **5** is isotypic to $\frac{1}{\infty}[\text{Zn}(\text{pt})_2]$ (**6**) as proven by PXRD and Pawley refinement utilizing SCXRD data of **6** (see Fig. 2, Fig. S4, and Table S15†). Hence, **5** also crystallises in the tetragonal crystal system in a body-centred Bravais lattice and exhibits polymeric strands screwing about crystallographic c axis, as described above. Contrary, $\frac{1}{\infty}[\text{Cu}(\text{pt})_2] \cdot \text{H}_2\text{O}$ ⁴¹ contains polymeric zig-zag chains with two different orientations within the unit cell crystallizing in a primitive Bravais lattice.⁴¹

Temperature-dependent PXRD investigations on $\frac{1}{\infty}[\text{M}(\text{pt})_2]$

The effect of intercalated solvents is further noticeable. Differences in reflection intensities between recorded patterns and the simulated pattern of $\frac{1}{\infty}[\text{Zn}(\text{pt})_2]$ (**6**), which are observable within Fig. 2, can be explained by solvent molecules being intercalated within the square-shaped pore channels. An influ-



ence on reflection intensities is a known effect of guests being present in pore systems.⁵⁵ Furthermore, different constituting metal ions and the tendency of these CPs to crystallise with a needle-shaped habitus leading to preferred orientation effects with regard to PXRD influence the reflection intensities, as well.

To investigate the differences and changes of reflection intensities more intensively, temperature-dependent PXRD recordings were performed. When analysing respective patterns of $[\text{Zn}(\text{pt})_2]$ (**6**) (Fig. 3), the intensity of the (2 0 0) reflection at approx. 7.8° in 2θ shows the largest detectable variation in intensity in dependence of temperature T and increases upon heating (between 30°C and 405°C). Since related lattice

planes intersect the square-shaped pore channels (Fig. 4), the intensity of this reflection is possibly influenced by guest molecules intercalated in the pores. With increasing temperature, the differences in intensities between recorded and simulated patterns of **6** diminish with solvent molecules leaving the pores. The powder pattern of **6** can be identified up to a temperature of 430°C , while the intensities of observed reflections start to decrease above 405°C , as shown for the four most intense reflections in Fig. S6.† Additionally, the broad reflections that are assigned to the formation of ZnCN_2 , begin to emerge. At 455°C , the coordination polymer is decomposed completely, and the majority phase is identified as ZnCN_2 (Fig. 3).

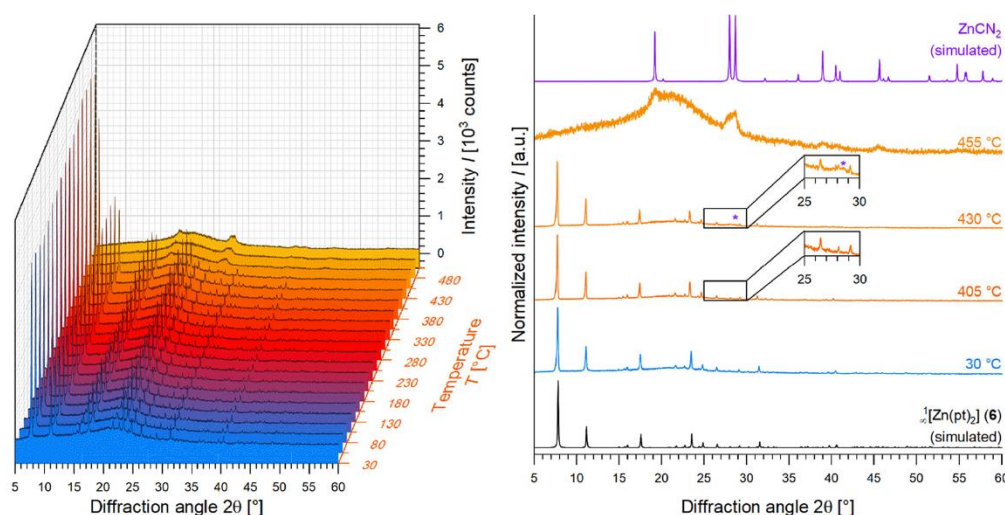


Fig. 3 Temperature-dependent powder X-ray diffractograms of $[\text{Zn}(\text{pt})_2]$ (**6**) reaching from 30°C to 505°C in steps of 25°C (left) besides recorded diffractograms of **6** at 30°C , 405°C and 430°C in comparison to diffractograms CP **6**, and ZnCN_2 ,⁶¹ both simulated from respective SCXRD data (right).

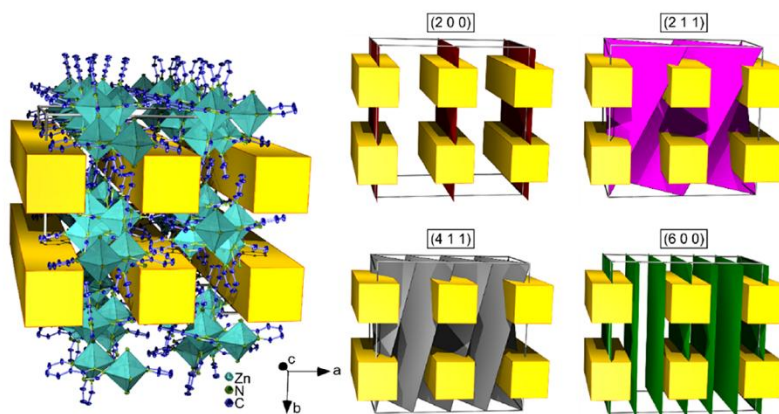


Fig. 4 3D depiction of the crystal structure of $[\text{Zn}(\text{pt})_2]$ (**6**) with square-shaped pore channels marked as yellow cuboids, as well as 3D depictions of the unit cell without atoms and inserted lattice planes. Lattice planes corresponding to the most intense PXRD reflections observed are inserted as coloured planes: red = (200), pink = (211), grey = (411), green = (600).



Analogous temperature-dependent PXRD investigations were performed for $^1_\infty[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Mn}$ (1), Fe (2), Co (3), Ni (4), Cu (5), Cd (7)) leading to comparable results.

For $^1_\infty[\text{Mn}(\text{pt})_2]$ (1), the formation of unknown phase(s) is observable. $^1_\infty[\text{Fe}(\text{pt})_2]$ (2) converts to a high pressure phase of magnetite,⁵⁶ followed by transition to magnetite⁵⁷ at 480 °C and finally to hematite⁵⁸ at 505 °C. $^1_\infty[\text{Co}(\text{pt})_2]$ (3) and $^1_\infty[\text{Cu}(\text{pt})_2]$ (5) decompose to amorphous compounds. Temperature-dependent PXRD investigations on $^1_\infty[\text{Ni}(\text{pt})_2]$ (4) show the formation of Ni_3C ⁵⁹ above 280 °C. In analogy to the high-temperature behaviour of $^1_\infty[\text{Zn}(\text{pt})_2]$ (6) described above, CP 7 ($^1_\infty[\text{Cd}(\text{pt})_2]$) decomposes to CdCN_2 ⁴⁸ above 405 °C, at first, which subsequently converts to CdO ⁶⁰ at 505 °C. Temperature-dependent PXRD investigation results are summarised in Table 1. Corresponding PXRD patterns are given within the ESI (Fig. S6–S18†), besides Fig. 3. This shows that the solvents can

be removed from square-shaped pore channels by thermal treatment.

Crystal structure of the one-dimensional, homoleptic coordination polymer $^1_\infty[\text{Cu}(\text{pt})_2]\cdot 0.5\text{Py}$ (8)

A structure which is closely related to CP 6, was found for the coordination polymer $^1_\infty[\text{Cu}(\text{pt})_2]\cdot 0.5\text{Py}$ (8, Fig. 5). This compound crystallises in the orthorhombic crystal system in the space group *Ibca*. The same structural motif of $^1_\infty[\text{Zn}(\text{pt})_2]$ (6) is present in CP 8. It contains distorted, copper-ion-based octahedra, in which Cu^{2+} is coordinated by four deprotonated pt molecules, two η^2 - and two η^1 -pt, in analogy to CP 6.

Solvent molecules (pyridine) are intercalated in the rectangular pore channels in a *crystallographically ordered* manner, resulting in a change of the crystal system from tetragonal to orthorhombic in comparison to $^1_\infty[\text{Zn}(\text{pt})_2]$ (6).

Excerpts of the crystal structure of CP 8 are given in Fig. 5 and Fig. S2.† Detailed crystallographic information is given in Table S3.† Interatomic Cu–N distances ranging from 198(3) pm to 260(2) pm (Table S4†) coincide with distances reported for the one-dimensional coordination polymer $^1_\infty[\text{Cu}(\text{pt})_2]\cdot \text{H}_2\text{O}$, which consist of pt-linked, $\text{Cu}(\text{II})$ -based octahedra. Interatomic Cu–N distances for this compound are ranging from 197 pm to 254 pm.⁴¹

PXRD investigations on $^1_\infty[\text{Cu}(\text{pt})_2]\cdot 0.5\text{Py}$ (8)

As mentioned above, the CPs $^1_\infty[\text{M}(\text{pt})_2]$ can be obtained as bulk material by solvothermal reaction of metal acetates and Hpt in pyridine. However, due to the porosity of these substances, solvent molecules are intercalated. Accordingly, drying is essential to achieve $^1_\infty[\text{Cu}(\text{pt})_2]$ (5). The product initially obtained by reaction of $\text{Cu}(\text{OAc})_2\cdot \text{H}_2\text{O}$ and Hpt in pyridine (without washing and vacuum drying), contained both, single crystals of $^1_\infty[\text{Cu}(\text{pt})_2]\cdot 0.5\text{Py}$ (8) and reflections of 8 in the powder diffractogram, only. This means, the as-synthesised, still damp product of the reaction of $\text{Cu}(\text{OAc})_2\cdot \text{H}_2\text{O}$ and Hpt

Table 1 Sum formula and temperature, up to which the compound is stable (T_{st}), the compound is identifiable by PXRD (T_{max}), temperature, at which reflections of the coordination polymer are no longer observable by PXRD (T_{dec}), as well as the resulting majority phase

Compound	Sum formula	T_{st} ^a [°C]	T_{max} [°C]	T_{dec} [°C]	Majority phase at T_{dec}
1	$^1_\infty[\text{Mn}(\text{pt})_2]^b$	330	430	455	Unknown phase
2	$^1_\infty[\text{Fe}(\text{pt})_2]^b$	305	430	455	Fe_3O_4 (magnetite) ^{d,56}
3	$^1_\infty[\text{Co}(\text{pt})_2]^b$	455	455	480	Amorphous
4	$^1_\infty[\text{Ni}(\text{pt})_2]^b$	280	480	505	Ni_3C ⁵⁹
5	$^1_\infty[\text{Cu}(\text{pt})_2]^b$	305	330	330	Amorphous
6	$^1_\infty[\text{Zn}(\text{pt})_2]^c$	405	430	455	ZnCN_2 ⁶¹
7	$^1_\infty[\text{Cd}(\text{pt})_2]^b$	405	430	455	CdCN_2 ^{e62}

^a The temperature stability was evaluated by investigation of reflection intensities in temperature-dependent PXRD. As soon as a drop in intensity of the reflections is observed, the beginning decomposition of the crystalline structure is assumed. ^b See also Fig. S7–S18.† ^c See Fig. 3, and Fig. S6.† ^d High-pressure crystal structure of magnetite⁵⁸ at 250 kPa. It converts to magnetite⁵⁷ at 455 °C and finally to hematite⁵⁸ at 505 °C. ^e Transition to CdO ⁶⁰ is observed at 505 °C.

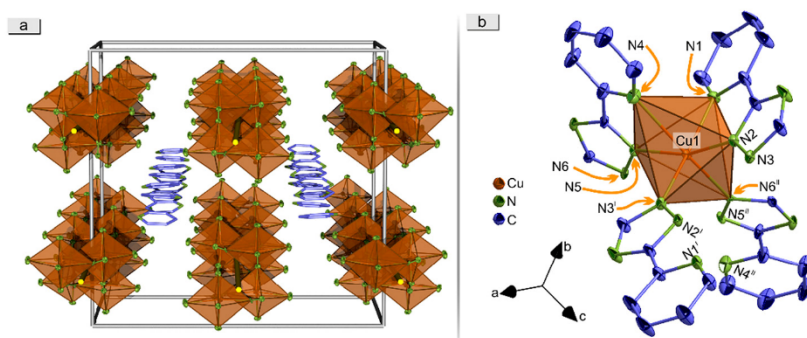


Fig. 5 Depiction of the crystal structure of $^1_\infty[\text{Cu}(\text{pt})_2]\cdot 0.5\text{Py}$ (8). Presented are: An enlarged 3D illustration of the rectangular channels within the elemental cell with depiction of both disorders of trapped pyridine molecules (a; for simplification, only Cu atoms and coordinating N atoms of the CP are depicted and pyridine molecules are shown in wire stick representation), as well as the extended coordination of Cu^{2+} (b; hydrogen atoms are omitted). Polyhedra around Cu are highlighted in orange. Displayed thermal ellipsoids correspond to 50% probability level of the atoms. Crystallographic data is summarised in Table S3.† Symmetry operations: I = $1 - x, 3/2 - y, z$; II = $3/2 - x, y, 1 - z$.



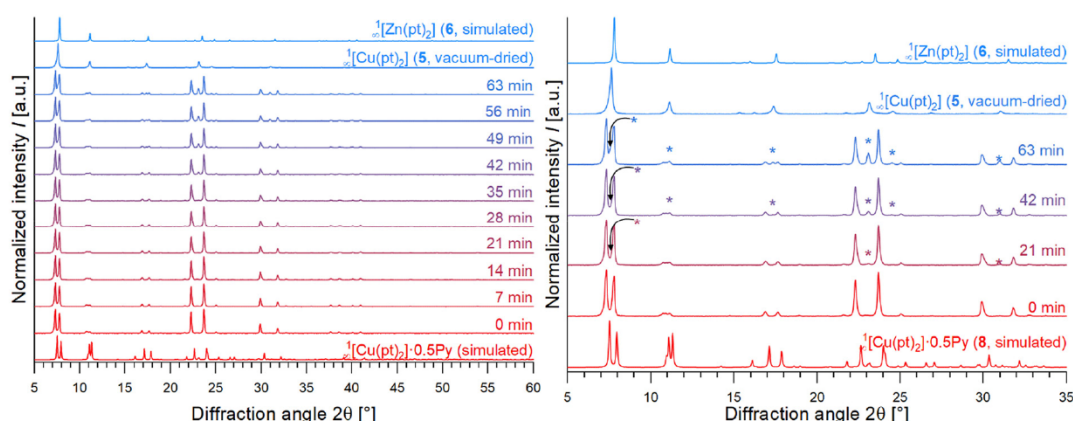


Fig. 6 Powder X-ray diffractograms of the reaction product of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and Hpt in pyridine after air-drying for given durations as well as a pattern of the vacuum-dried product in comparison to patterns of $1/\infty[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (CP 8) and $1/\infty[\text{Zn}(\text{pt})_2]$ (CP 6), both simulated from respective SCXRD data. Upon air-drying, the reflections of CP 5 appear. After vacuum-drying, the pattern of the product shows reflections of 5, only.

contains $1/\infty[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (8) as majority phase instead of 5. However, CP 8 is only stable in the presence of pyridine and converts completely into $1/\infty[\text{Cu}(\text{pt})_2]$ (5) upon drying, which was proven by comparison of recorded PXRD patterns after several minutes of air-drying and complete vacuum-drying (Fig. 6, reflections corresponding to 5 are marked with*). The pattern of a freshly synthesised, still damp product shows reflections of CP 8, only. Upon drying, the reflections of CP 5 begin to appear. The vacuum-dried product exhibits reflections of 5, only (Fig. 6). This shows the direct effect of crystallographically ordered solvent molecules within the structure, leading to the reduction of the symmetry as described above.

Photophysical properties of selected compounds

Photoluminescence properties of impregnated $1/\infty[\text{Zn}(\text{pt})_2]$.

Due to constituting metal atoms, the synthesised compounds feature conspicuous optical properties, like intense colour for compounds containing ions of iron, cobalt, nickel, or copper. The coordination polymers $1/\infty[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Mn}$ (1), Zn (6)) are colourless (determined according to $L^*a^*b^*$ scatter diagrams, see Fig. 7, Fig. S20 and Table S16†).

Considering potential luminescence application, these two candidates are therefore appropriate due to their white appearance and, hence, low absorption of visible light. Upon UV excitation, 6 exhibits blue luminescence. Since both, incoming UV and emitted light, are not absorbed by Zn^{2+} ion due to the d^{10} electron configuration, this emission is considered as ligand-based.

The pure ligand exhibits a broad band emission in the UV/blue region upon UV excitation ($\lambda_{\text{em max}} = 360 \text{ nm}$, $\lambda_{\text{exc}} = 324 \text{ nm}$, Fig. S22, and S24†), while the emission band of CP 6 is located at $\lambda_{\text{em max}} = 337 \text{ nm}$ for excitation at 306 and 311 nm. At higher excitation wavelengths ($\lambda_{\text{exc}} = 324 \text{ nm}$; 346 nm) $\lambda_{\text{em max}} = 360 \text{ nm}$ is located at 395 nm (Fig. S23 and S25†).

Comparable photoluminescence behaviour was reported for other d^{10} transition metal compounds, e.g. for

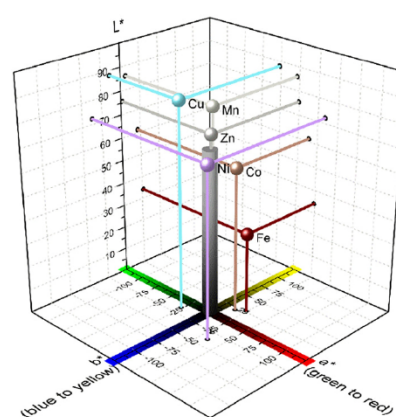


Fig. 7 $L^*a^*b^*$ scatter diagram with inserted $L^*a^*b^*$ chromaticity coordinates of the coordination polymers $1/\infty[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Mn}$ (1), Fe (2), Co (3), Ni (4), Cu (5), Zn (6)). Corresponding reflectance spectra are given in Fig. S20.† Calculated chromaticity coordinates are listed in Table S16.†

$[\text{Zn}_6(\text{H}_2\text{O})_3(\text{dmf})_6(\text{ur})_2(\text{tdc})_6] \cdot 4\text{H}_2\text{O}$ ($\text{ur} = 2,5$ -thiophenedicarboxylate), which exhibits a broad emission at 470 nm ($\lambda_{\text{exc}} = 380 \text{ nm}$) assigned to intra-ligand $\pi^* \rightarrow \pi$ or LMCT transitions,⁶³ or $[\text{Zn}_3(\text{btc})_2(\text{tpt})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ ($\text{btc} = 3,5$ -benzenetricarboxylate, $\text{tpt} = \text{tris}(4\text{-pyridyl})\text{triazine}$) featuring a broad emission around 380 nm ($\lambda_{\text{exc}} = 280 \text{ nm}$) assigned to the $\pi^* \rightarrow \pi$ transition of the N-donor ligand tpt .⁶⁴ Likewise, $[\text{Cu}(\text{bptzH})(\text{PPh}_3)_2](\text{ClO}_4)$, exhibits blue luminescence ($\lambda_{\text{em}} = 456 \text{ nm}$) upon UV excitation.⁵³ The observed luminescence of the coordination polymer (see lifetime determination following) is therefore considered ligand based and may be explained with $\pi^* \rightarrow \pi$ of higher energy levels (compared to pure ligand Hpt) of the deprotonated ligand pt^- and/or LMCT.^{63,65}



The photoluminescence properties render ${}^1_{\infty}[\text{Zn}(\text{pt})_2]$ a suitable candidate to function as the blue component of an RGB-type white light emitter. To generate a suchlike luminescent compound, an impregnation of the square-shaped pore channels of CP **6** with Eu^{3+} ions as red emitter, and Tb^{3+} ions as green emitter, was performed. For this purpose, an activated sample of CP **6** was dispersed and stirred in a solution containing equal amounts of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ for eight days followed by centrifugation, decantation and vacuum drying of the solid product.

Three different solvents, namely *N,N*-dimethylformamide (DMF), acetonitrile (MeCN), and methanol (MeOH), were evaluated (For detailed information, see Experimental section.). Exemplarily, emission and excitation spectra, besides the chromaticity diagram of the product of impregnation in DMF – which is hereafter to be referred to as $\text{EuTb@}{}^1_{\infty}[\text{Zn}(\text{pt})_2]$ – are shown in Fig. 8, and Fig. 9, respectively.

For excitation at $\lambda_{\text{exc}} = 306$ nm, 311 nm, and 324 nm, the emission spectra feature broad bands in the UV/blue region at wavelengths of 337 nm and 424 nm. Besides these, characteristic 4f–4f-transitions of the two lanthanide ions, Eu^{3+} and Tb^{3+} , are detected. As shown by the excitation spectra, the emission at 337 nm is initiated by excitation at 311 nm. The excitation spectrum for the emission band at $\lambda_{\text{em}} = 424$ nm features a maximum at $\lambda_{\text{exc}} = 306$ nm with a shoulder at 324 nm. The excitation spectra of most intense transitions of Tb^{3+} (544 nm) and Eu^{3+} (616 nm) exhibit a maximum at $\lambda_{\text{exc}} = 324$ nm with a shoulder at 346 nm. A comparison between the emission spectra of pure Hpt , ${}^1_{\infty}[\text{Zn}(\text{pt})_2]$ (**6**), and $\text{EuTb@}{}^1_{\infty}[\text{Zn}(\text{pt})_2]$ (Fig. S26†) shows, that the blue luminescence of $\text{EuTb@}{}^1_{\infty}[\text{Zn}(\text{pt})_2]$ corresponds to the luminescence observed for CP **6**.

However, the observed band at 424 nm for $\lambda_{\text{exc}} = 306$, 311, and 324 nm is not present within emission spectra of non-impregnated, pure ${}^1_{\infty}[\text{Zn}(\text{pt})_2]$. This indicates a different source of this band. One possible explanation is, that this band arises due to formation of exciplexes between the lanthanide species inside the pore system and the coordination polymer. Interestingly, the emission band at 424 nm vanishes at $\lambda_{\text{exc}} = 346$ nm and a new emission band is observed at $\lambda_{\text{em, max}} =$

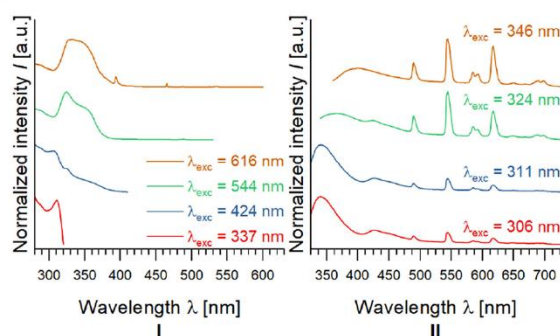


Fig. 8 Excitation (left) and emission spectra (right) of ${}^1_{\infty}[\text{Zn}(\text{pt})_2]$ impregnated with Eu^{3+} and Tb^{3+} ions for eight days using DMF as solvent.

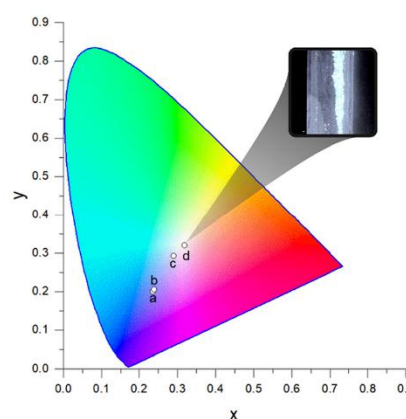


Fig. 9 CIE chromaticity diagram of ${}^1_{\infty}[\text{Zn}(\text{pt})_2]$ (CP **6**) impregnated with Eu and Tb in DMF as solvent with inserted chromaticity coordinates xy at different excitation wavelengths. a: $\lambda_{\text{exc}} = 306$ nm, b: $\lambda_{\text{exc}} = 311$ nm, c: $\lambda_{\text{exc}} = 324$ nm, d: $\lambda_{\text{exc}} = 346$ nm. Accordingly, the lanthanide luminescence results from a sensitisation effect of the direct surrounding of the respective lanthanide ions, also known as *antenna effect*.^{66–68}

395 nm, which coincides with the spectrum for non-impregnated CP **6** at the same excitation wavelength. For short excitation wavelengths, the blue CP-based emission exceeds the lanthanide-based luminescence, wherefore the resulting overall emission colour is neon blue.

With rising excitation wavelength, the lanthanide transitions become more dominant in the emission spectrum (Fig. 8) resulting in a shift of the chromaticity. Hence, a variation in intensity ratios of the observed bands in dependence of the excitation wavelength, was determined for $\text{EuTb@}{}^1_{\infty}[\text{Zn}(\text{pt})_2]$ synthesised in DMF. This results in variable chromaticity (Fig. 8 and 9). In fact, the emitted light of $\text{EuTb@}{}^1_{\infty}[\text{Zn}(\text{pt})_2]$ impregnated in DMF, when excited at $\lambda_{\text{exc}} = 346$ nm, exhibits chromaticity coordinates according to CIE of $xy = (0.32|0.32)$. It therefore reaches practically perfect white chromaticity ($xy = (0.333...|0.333...)$, Fig. 9). Thus, the concept of an excitation dependent red-shift of emission was utilised for an emission tuning towards RGB white light emission.

For the products of impregnations in methanol (Fig. S27†) and acetonitrile (Fig. S28†), qualitatively the same emission and excitation bands are observed, resulting in an analogous dependency of emission colour on excitation wavelength (Fig. S29, and S30†) Therefore, involved radiative processes are considered as independent from the chosen solvent.

As a result, the overall luminescence occurs due to excitation of the ligand followed by light emission of the CP (blue), as well as energy transfer to the lanthanides and subsequent characteristic Tb^{3+} (green) and Eu^{3+} (red) emissions. The respective solvent utilised for impregnation does not participate in the radiative luminescence processes. Corresponding chromaticities of the products from impregnation in acetonitrile and methanol at $\lambda_{\text{exc}} = 346$ nm are less ideal and given in Fig. S29 and S30.†



A comparison of scanning electron microscopy images before and after impregnation of **6** with Eu^{3+} and Tb^{3+} shows, that the habitus of CP **6** crystallites does not change upon impregnation (see Fig. S38†). Lanthanide contents between 1.7 and 2.3 wt% were determined by inductively coupled mass spectrometry (ICP-MS, for details, see Table S28†).

In summary, the coordination polymer $[\text{Zn}(\text{pt})_2]$ (**6**) being a blue light emitter, is capable of forming an RGB emitter by impregnation with Eu and Tb ions. Thereby, due to dependency of band intensities on excitation wavelength, the emission colour is tuneable from neon blue to white light (Fig. 9).

In addition to the qualitative photoluminescence characterisations, the luminescence lifetimes of the white light emitter $\text{EuTb}@\text{Zn}(\text{pt})_2$ were determined. For the emission band at $\lambda_{\text{em}} = 395$ nm excited at $\lambda_{\text{exc}} = 340$ nm of pure $[\text{Zn}(\text{pt})_2]$ (without lanthanide impregnation), the luminescence intensity decay can be described by a multi-exponential fit function leading to determination of the lifetimes $\tau_1 = 1.00(2)$ ns, and $\tau_2 = 3.10(3)$ ns. An average luminescence lifetime^{69,70} of $\tau_{\text{av}} = 1.95$ (3) ns was calculated. For the pure ligand, the lifetimes $t_1 = 1.16$ (1) ns, and $t_2 = 2.89(3)$ resulting in $\tau_{\text{av}} = 1.58(2)$ ns were determined, which are of the same magnitude as lifetimes of pure CP **6** (For detailed description of the calculation, see ESI†).

For $\text{EuTb}@\text{Zn}(\text{pt})_2$, τ_{av} for $\lambda_{\text{em}} = 395$ nm ($\lambda_{\text{exc}} = 340$ nm) was determined as 2.11(3) ns. Hence, the luminescence lifetime is slightly elongated for $[\text{Zn}(\text{pt})_2]$ (**6**) impregnated with lanthanides in comparison to non-impregnated CP **6**. This can be explained by rigidification due to coordination of pt to Zn^{2+} , which results in reduced vibrational freedom of the ligand and, hence, reduced rate of non-radiative depopulation of excited states⁷¹. The recorded luminescence intensity decays of lanthanides within $\text{EuTb}@\text{Zn}(\text{pt})_2$ had to be fitted with a multi-exponential function, as well, in order to obtain a good quality of fit. Thereby, for Eu^{3+} emission ($\lambda_{\text{em}} = 698$ nm, $\lambda_{\text{exc}} = 346$ nm), two luminescence lifetimes were found ($\tau_1 = 0.48(3)$ ms, $\tau_2 = 1.30(3)$ ms), resulting in $\tau_{\text{av}} = 1.04(2)$ ms. In case of Tb^{3+} emission ($\lambda_{\text{em}} = 544$ nm, $\lambda_{\text{exc}} = 346$ nm), lifetimes of $\tau_1 = 0.40(2)$ ms and $\tau_2 = 1.160(6)$ ms were determined resulting in $\tau_{\text{av}} = 1.028(6)$ ms. These values in the μs –ms region all coincide with the range, in which lifetimes of the respective lanthanide ions are expected.^{67,68,72} The discovery of two luminescence lifetimes for luminescent constituents indicates e.g. occupation of different positions within the pores resulting in varied chemical surroundings and, therefore, different non-radiative depopulation rates. In principle, the formation of lanthanide-containing side phases could also lead to detection of multiple luminescence lifetimes. However, PXRD patterns of $\text{EuTb}@\text{Zn}(\text{pt})_2$ impregnated in different solvents show reflections of the coordination polymer, only (Fig. S19†). Variations in reflection intensities further substantiate the assumption of lanthanide species intercalated in the pores of **6**.

An influence of the solvents utilised for impregnation on luminescence lifetimes by non-radiative processes can be assumed, as variations in τ_{av} are observed when using e.g. MeOH instead of DMF. For $\text{EuTb}@\text{Zn}(\text{pt})_2$ prepared in methanol, an average lifetime of the CP emission is deter-

mined to $\tau_{\text{av}} = 1.27(2)$ ns, which is 59% of the value for the composite prepared in DMF (2.14(2) ns). This can be explained by non-radiative depopulation processes involving the O–H group of methanol.⁷³ For Eu^{3+} ($\tau_{\text{av}} = 0.86(2)$ ms) and Tb^{3+} based emission ($\tau_{\text{av}} = 0.927(5)$ ms), the influence on lifetimes is less pronounced, resulting in the described overall changes of the chromaticity. All determined fitting parameters and calculated average luminescence lifetimes are summarised in Table S20.† Furthermore, the quantum yield was determined for the white light-emission of $\text{EuTb}@\text{Zn}(\text{pt})_2$ prepared in DMF. With an excitation wavelength of $\lambda_{\text{exc}} = 346$ nm, a quantum yield of 24(3) % was reached.

Absorption properties of $[\text{M}(\text{pt})_2]$. As described above, distinct colour of some coordination polymers $[\text{M}(\text{pt})_2]$ (depending on contained metal atom) was observed (Fig. 10, Fig. S20 and Table S16†). Accordingly, the absorption properties were investigated in the solid state. For $[\text{Fe}(\text{pt})_2]$ (**2**), high absorbance at 250–300 nm, most likely occurring from $\pi^* \leftarrow \pi$ transitions of the ligand, was observed.

Furthermore, high absorbance in the blue/green region (overlapping bands at approx. 400 and 500 nm) caused most likely by MLCT was detected, leading to the blood-red colour of CP **2**. Analogously, d–d transitions at $\lambda > 800$ nm are observed (Fig. S20†). This indicates the presence of both, high-spin and low-spin configuration of Fe^{II} .^{73–78} Upon increasing temperature, the absorbance at 350–600 nm decreases.

On the contrary, the intensity of the d–d transition band increases, indicating a continuous spin crossover (SCO) from low-spin to high-spin. Since the intensity decrease is more pro-

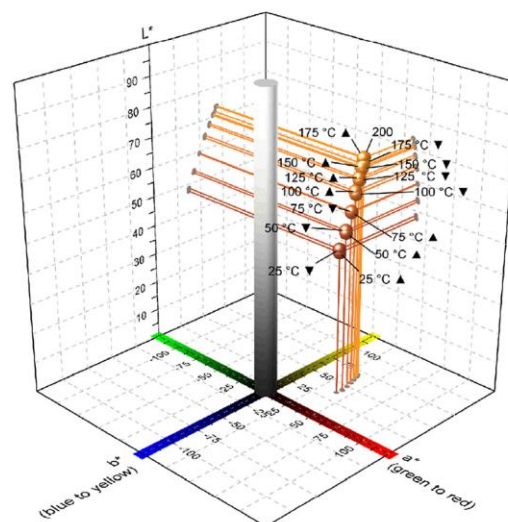


Fig. 10 $L^*a^*b^*$ scatter diagram with inserted $L^*a^*b^*$ chromaticity coordinates of $[\text{Fe}(\text{pt})_2]$ (CP **2**) at different measurement temperatures. Recorded points during heating up are marked with ▲. Accordingly, corresponding points recorded with decreasing temperature are marked with ▼. Corresponding $L^*a^*b^*$ chromaticity values are listed in Table S17.†



nounced for absorbance in the green region, the colour of the compound is shifted from blood red to orange/yellow (Fig. 10, Fig. S21, and Table S17†). Such thermochromic behaviour is known for Fe(II) complexes with octahedral FeN₆ coordination.^{73–78}

Investigations on the formation and crystal structures of complexes [MX₂(Hpt)₂]

In addition to the homoleptic coordination polymers, several heteroleptic complex compounds were obtained and characterised.

Single crystals of the heteroleptic complexes [MX₂(Hpt)₂] (MX₂ = MnCl₂ (9), FeCl₂ (10), CoCl₂ (11), CoBr₂ (12)) were obtained by solvothermal reaction of divalent transition metal halides and an excess of Hpt in pyridine without addition of a base, wherefore the ligand remains neutral within the compounds, different from the deprotonated form in 1–8. Single crystals of [ZnCl₂(Hpt)₂] (13) were found within the product of the single crystal preparation of ¹[Zn(pt)₂] (6).

The isotypic complexes [MX₂(Hpt)₂] (MX₂ = MnCl₂ (9), FeCl₂ (10), CoCl₂ (11), CoBr₂ (12), ZnCl₂ (13)) crystallise in the triclinic crystal system in the space group *P* $\bar{1}$. The respective metal ions are coordinated *trans* in a distorted octahedral geometry by two halido ligands and two η^2 -Hpt molecules binding via N1 of the pyridine ring and N4 of the triazole ring.

The complexes are interconnected by N3–H3...Cl1 hydrogen bonds.

A depiction of the crystal structure is exemplarily shown for [MnCl₂(Hpt)₂] (9) in Fig. 11. Crystallographic data for 9–13 is given in Tables S5, S7, S9, S11, and S13.† Interatomic distances and angles are listed in Tables S6, S8, S10, S12, and S14.† Mn–N distances for 9 were determined to 223.7(2) pm, and 225.2(2) pm, which are comparable to distances reported for e.g. [Mn₄(H₃bpa)₂(mpt)₄(N₃)₂·2H₂O (219–238 pm, H₃bpa =

N,N'-bis(picolinamide)azine). This compound contains the Hpt derivative mpt = 3-methyl-5-(2-pyridyl)-1*H*-1,2,4-triazolate and exhibits three crystallographically independent octahedrally coordinated Mn²⁺ ions.⁴⁶ Analogously, for the two-dimensional coordination polymer [Mn(N₃)(pytr)(H₂O)]_n (pytr = pt), which contains octahedrally coordinated Mn interconnected by N₃[−], interatomic Mn–N distances to the η^2 -pt ligand of 213–223 pm are reported.⁷⁹

In case of [FeCl₂(Hpt)₂] (10), the Fe–N distances of 218.48(8) pm and 220.20(8) pm coincide with the 213–223 pm in [Fe(Hpt)₃](BF₄)₂·H₂O,⁴³ which contains Fe²⁺ octahedrally coordinated by three η^2 -Hpt ligands.⁴³ For the complexes [CoCl₂(Hpt)₂] (11), and [CoBr₂(Hpt)₂] (12), respectively, the distances 213.6(6) pm and 214.6(2) pm for 11, and 213.4(2) pm and 218.8(2) pm for 12, are in good agreement to distances in [Co(Hpt)₂(H₂O)₂](NO₃)₂ (215 and 216 pm), which contains Co ions coordinated *trans* in an octahedral geometry by two aquo ligands and two η^2 -Hpt molecules.⁴⁵

The Zn–N distances in [ZnCl₂(Hpt)₂] (13), 214.0(2) pm and 215.7(1) pm, are in the range of Zn–pt distances observed for [ZnL(pt)]·0.5MeOH·1.5H₂O (200–225 pm; with L = tris(5-methyl-3-phenylpyrazolyl)borate), which features a fivefold coordinated Zn²⁺.⁴⁴ Alternatively, to the synthesis described above, the complexes 9–13 can be synthesised by choosing acetonitrile instead of pyridine as a non-basic solvent. Due to a lower solubility of the ligand, sublimation of excess Hpt is necessary after the reaction for the products' purification.

Additionally, synthesis utilising water-free chlorides or corresponding hydrates is also feasible (see Experimental section and Fig. 12).

Analogous reactions of FeBr₂ and Hpt in either pyridine, or acetonitrile result in phase mixtures containing ¹[Fe(pt)₂] (2) and [FeBr₂(Hpt)₂], which is isotypic to [FeCl₂(Hpt)₂] (10). Reactions of FeI₂ also result in phase mixtures containing ¹[Fe(pt)₂] (2) and [FeI₂(Hpt)₂], which again is isotypic to [FeCl₂(Hpt)₂] (10). Therefore, the existence of [FeBr₂(Hpt)₂], and [FeI₂(Hpt)₂], both being isotypic to 10, was proven by PXRD (see ESI†).

Accordingly, reactions of ZnCl₂ and Hpt in either pyridine, or acetonitrile result in phase mixtures containing ¹[Zn(pt)₂] (6). In case of the product synthesised in acetonitrile, [ZnCl₂(Hpt)₂] (13) is also contained within the product, as shown by PXRD.

Infrared spectroscopy

The synthesised coordination polymers ¹[M(pt)₂] (M = Mn (1), Fe (2), Co (3), Ni (4), Zn (6), Cd (7)), as well as the complexes [MX₂(Hpt)₂] (MX₂ = MnCl₂ (9), FeCl₂ (10), CoCl₂ (11), CoBr₂ (12)) were also characterised by infrared spectroscopy. For 1–7, respective spectra (Fig. S31†) feature bands being characteristic for functional groups of the ligand, as well as the solvents being present within the square-shaped pore channels. The broad band around 3400 nm can be assigned to both, ν (O–H) of intercalated water and ν (N–H) due to established C–H...N hydrogen bonds. For 9, 10, 11, and 12, bands of the neutral ligand are observable, as well (Fig. S32†). Wavenumbers of observed bands, as well as assignments of those are listed in Tables S22, and S23.†

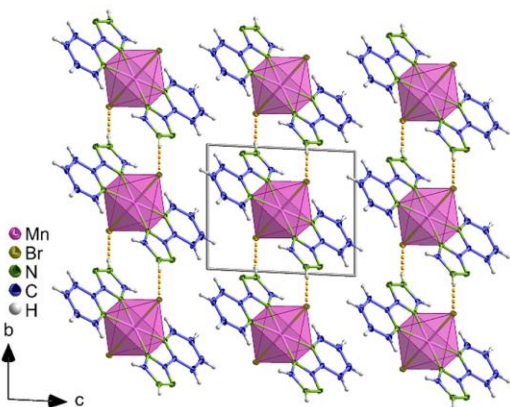


Fig. 11 Depiction of the crystal structure of [MnCl₂(Hpt)₂] (9) along the crystallographic *a* axis. The octahedral coordination of Mn²⁺ is highlighted in pink. Displayed thermal ellipsoids correspond to 50% probability level of the atoms. N–H...Cl hydrogen bonds are shown in dashed orange lines. Crystallographic data is summarised in Table S5.† Symmetry operations: *i* = 1 – *x*, 1 – *y*, 1 – *z*.



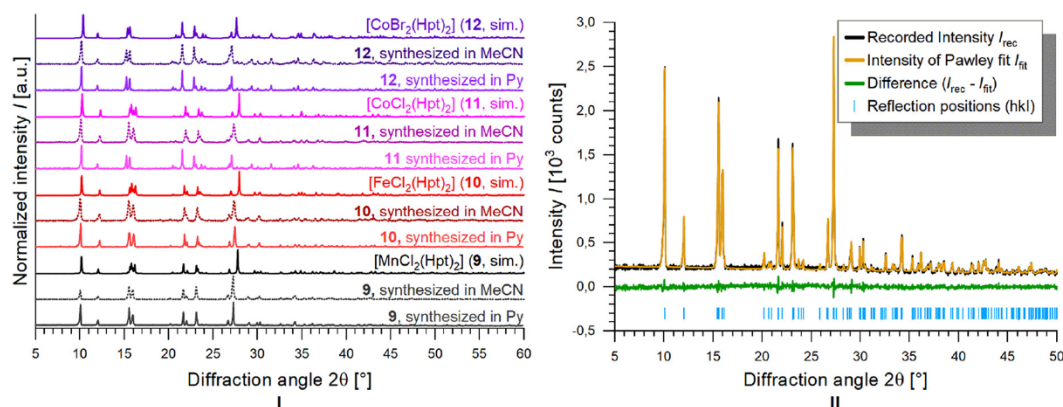


Fig. 12 I: Comparison of recorded and simulated PXRD patterns of the heteroleptic complexes $[MX_2(Hpt)_2]$ ($MX_2 = MnCl_2$ (9), $FeCl_2$ (10), $CoCl_2$ (11), $CoBr_2$ (12)), (sim., utilising SCXRD data). The complexes were obtained by synthesis in the stated solvents (Py = pyridine, solid lines; MeCN = acetonitrile, dotted lines) II: Difference plot of a Pawley refinement exemplarily performed for 9 with an R_{wp} of 6.3% and a goodness of fit of 1.03.

Composition and thermal analyses

Elemental analysis of the synthesised coordination polymers $^1_\infty[M(pt)_2]$ (1–7) confirm the assumption of intercalated solvent molecules (pyridine and water). For CPs 1–7, sum formulas considering amounts of solvents were calculated (Table S24†). Elemental analyses of the complexes $[MnCl_2(Hpt)_2]$ (9), $[FeCl_2(Hpt)_2]$ (10), $[CoCl_2(Hpt)_2]$ (11), and $[CoBr_2(Hpt)_2]$ (12) synthesised in pyridine confirm the phase purity already assumed from PXRD results, since calculated and determined elemental percentages are in good agreement (Table S25†). The same applies for complexes 9, 10, 11, and 12 synthesised in acetonitrile (Table S25†).

By simultaneous thermal analysis, $^1_\infty[Mn(pt)_2]$ (1), $^1_\infty[Co(pt)_2]$ (3), $^1_\infty[Ni(pt)_2]$ (4), and $^1_\infty[Zn(pt)_2]$ (6) were further investigated. In all cases, the relative mass decreases by 3–7% for temperatures up to approx. 130 °C followed by a plateau. This is considered to be an effect of solvent molecules escaping the solids. Upon further heating, subsequent to the plateau, a significant decrease in relative mass is detected for all investigated CPs, coinciding with a detection of water and carbon dioxide and/or nitrous oxide by mass spectrometry. This indicates an oxidation of the corresponding CP. Thereby, Hpt is combusted, leading to detection of H_2O , and CO_2/N_2O (Fig. S33–S36†). An overview of onsets and relative mass losses determined by STA is given within ESI (Table S26†). The obtained results are in good agreement with the high temperature behaviour of these CPs observed by temperature-dependent PXRD (Fig. 3, and Fig. S6–S18†).

Physiosorption experiments on $^1_\infty[M(pt)_2]$ ($M = Fe$ (2), Co (3), Zn (6))

To investigate the inner surface area of the CPs 2, 3, and 6, they were activated at 300 °C and 10^{-3} mbar for seven hours to remove solvent molecules from the pores. The samples were further degassed at 10^{-6} mbar. Subsequently, the inner surface area was determined by recording gas sorption isotherms of N_2 at 77 K (Fig. S37†).

The determined surface areas for BET and Langmuir are listed in Table 2. The determined, high C constants (>150) are considered to be an effect of filling narrow micropores,⁸⁰ which is consistent with the square-shaped pore channels observed by SCXRD.

Identification of additional compounds

Besides the coordination compounds described above, a series of additional compounds were identified. Since, in most of the cases, those are considered as intermediates or byproducts, the description of synthesis conditions and single crystal characterizations are discussed in the ESI.† This includes synthesis and SCXRD characterization of the homoleptic complex $[Zr(pt)_4]$ (14), the dinuclear complexes $[Fe_2Cl_2(pt)_2(Py)_4]$ (15) and $[Fe_2Br_2Cl_2(pt)_2(Py)_4]$ (16), the two-dimensional CP $^2_\infty[Cu_2Cl(pt)]$ (17), the one-dimensional CPs $^1_\infty[MnCl(bpt)]$ (bpt = 3,5-bis(2-pyridyl)-1,2,4-triazolate, 18) and $^1_\infty[Co_2Cl_3(pt)(H_2O)_2] \cdot 4CyOH$ (CyOH = cyclohexanol, 19), and finally the two-dimensional coordination polymer $^2_\infty[Co_2Br_2(pt)_2]$ (20).

Experimental

Synthesis procedure

Within this work, solvothermal syntheses were performed according to the following procedure: solid components were mortared and transferred into Duran® glass ampoules. Liquid

Table 2 Multipoint BET surface areas SA_{BET} , C constants for BET calculations, and Langmuir surface areas SA_L of $^1_\infty[M(pt)_2]$ ($M = Mn$ (1), Co (3), Zn (6))

CP	SA_{BET} [$m^2 g^{-1}$]	C constant	SA_L [$m^2 g^{-1}$]
$^1_\infty[Fe(pt)_2]$ (2)	217	181	286
$^1_\infty[Co(pt)_2]$ (3)	181	868	208
$^1_\infty[Zn(pt)_2]$ (6)	160	247	210



components and solvents were added, and the resulting mixture was frozen in liquid nitrogen. The ampoules were evacuated, and the mixtures were allowed to thaw again. This freeze–pump–thaw procedure was repeated, followed by freezing the mixture, evacuating the ampoule, and sealing it. The reaction mixtures within the sealed ampoules were homogenised by ultrasonication for three minutes. Afterwards, the ampoules were placed in resistance ovens with corundum tube and heated for several days. For single crystal X-ray diffraction (SCXRD) measurements, the ampoules were opened, and a small amount of the resulting products was isolated. In case of bulk syntheses, the ampoules were opened, the solids were transformed into centrifugation tubes and were washed by repeated centrifugation, decantation, and suspension in fresh solvent. The purified solids were dried for one hour under vacuum (10^{-3} mbar). In case of usage of air-sensitive compounds (e.g. anhydrous metal halides), mortaring and transferring the mixtures to ampoules were carried out under inert atmosphere.

Materials

2-(1,2,4-1*H*-Triazol-3-yl)pyridine (98%, BLD Pharmatech GmbH), europium(III) nitrate hexahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9% (REO), abcr GmbH), terbium(III) nitrate hexahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9% (REO), abcr GmbH), $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (99%, abcr GmbH), $\text{Fe}(\text{OAc})_2$ (anhydrous, 97%, abcr GmbH), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (98%, abcr GmbH), $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (98+%, Alfa Aesar), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (p.a., Riedel-de Haën AG), $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (p.a., Merck), $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (98%, abcr GmbH), MnCl_2 (99.99%, Alfa Aesar), FeCl_2 (anhydrous, 99.5%, Alfa Aesar), FeBr_2 (anhydrous, 98%, abcr GmbH), FeI_2 (ultra-dry, 99.99%, abcr GmbH), CoCl_2 (99+%, abcr GmbH), CoBr_2 (anhydrous, 97%, Alfa Aesar), CuCl_2 (anhydrous, 98%, abcr GmbH), ZnCl_2 (anhydrous, 98+%, Alfa Aesar), ZrCl_4 (anhydrous, 99.5+%, Alfa Aesar), benzylamine (99.5+%, dry, AcroSeal™, Acros Organics), benzene (99.0%, dry, AcroSeal™, Acros Organics), acetonitrile (99.9%, extra dry, AcroSeal™, Acros Organics) and pyridine (99%, VWR Chemicals) were used as purchased without further purification. When dry pyridine is specified, it was dried by stirring over 20 g L^{-1} KOH for several days and distilled under inert atmosphere.

Bulk synthesis of one-dimensional coordination polymers $^1[\text{M}(\text{pt})_2]$ (1–7)

Larger quantities of the coordination polymers $^1[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Mn}$ (1), Fe (2), Co (3), Cu (5), Zn (6), Cd (7)) were obtained by solvothermally combining 500 μmol (123 mg) $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, (87.0 mg) $\text{Fe}(\text{OAc})_2$, (125 mg) $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, (99.8) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, (114 mg) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, or (125 mg) $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ with 1.00 mmol (146 mg) 2-(1,2,4-1*H*-triazol-3-yl)pyridine in 4 mL pyridine following the general synthesis principle mentioned above. In case of $^1[\text{Ni}(\text{pt})_2]$ (4), 1.00 mmol (249 mg) $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and 2.00 mmol (292 mg) 2-(1,2,4-1*H*-triazol-3-yl)pyridine were used. The reaction mixtures were heated to 150 °C in 4 h, followed by heating to 180 °C with 2 °C h^{-1} . This temperature was held constant for 120 h.

Subsequently, the reaction mixtures were allowed to cool down to 150 °C with 2 °C h^{-1} , and to ambient temperature within 4 h. Obtained products were purified by centrifugation (12 000 rpm, 10 min), decantation of the liquid phase, addition of 4 mL fresh pyridine and ultrasonication for 10 min. Subsequent to a final centrifugation (12 000 rpm, 10 min) and solvent decantation, the products were vacuum-dried at 10^{-3} mbar. The yields were 49% for 1, 52% for 2, 77% for 3, 61% for 4, 65% for 5, 42% for 6, and 58% for 7, based on the corresponding metal acetate(s) and the sum formulae considering solvent molecules, as listed in Table S24.†

$^1[\text{Mn}(\text{pt})_2]$ (1): IR (KBr): $\tilde{\nu} = 3419$ (br), 3030 (multiple, m), 1604 (s), 1513 (m), 1472(s), 1449 (s), 1417 (s), 1384 (w), 1350 (m), 1271 (m), 1250 (m), 1203 (m), 1145 (m), 1112 (s), 1048 (m), 1029 (s), 1007 (m), 876 (m), 805 (m), 755 (m), 676 (m), 636 (m), 483 (m), 407 cm^{-1} (m). Anal. calcd for $^1[\text{Mn}(\text{pt})_2] \cdot 0.34\text{Py} \cdot 0.21\text{H}_2\text{O} = \text{C}_{15.70}\text{H}_{12.12}\text{MnN}_{8.34}\text{O}_{0.21}$: C 50.19, H 3.25, N 31.07; found: C 50.20, H 2.99, N 30.98.

$^1[\text{Fe}(\text{pt})_2]$ (2): $\tilde{\nu} = 3423$ (br), 3030 (multiple, m), 1605 (s), 1516 (m), 1471(s), 1448 (s), 1417 (s), 1384 (w), 1357 (m), 1274 (m), 1252 (m), 1201 (m), 1149 (m), 1115 (s), 1050 (m), 1031 (s), 1009 (m), 874 (m), 803 (m), 757 (m), 676 (m), 636 (m), 490 (m), 409 cm^{-1} (m). Anal. calcd for $^1[\text{Fe}(\text{pt})_2] \cdot 0.34\text{Py} \cdot 0.21\text{H}_2\text{O} = \text{C}_{15.7}\text{H}_{12.12}\text{FeN}_{8.34}\text{O}_{0.21}$: C 50.04, H 3.24, N 31.00; found: C 50.02, H 2.96, N 30.91.

$^1[\text{Co}(\text{pt})_2]$ (3): $\tilde{\nu} = 3445$ (br), 3034 (multiple, m), 1608 (s), 1516 (m), 1473(s), 1449 (s), 1419 (s), 1384 (w), 1360 (m), 1264 (m), 1252 (m), 1204 (m), 1149 (m), 1118 (s), 1050 (m), 1033 (s), 1009 (m), 874 (m), 805 (m), 757 (m), 674 (m), 638 (m), 496 (m), 411 cm^{-1} (m). Anal. calcd for $^1[\text{Co}(\text{pt})_2] \cdot 0.34\text{Py} \cdot 0.21\text{H}_2\text{O} = \text{C}_{15.7}\text{H}_{12.12}\text{CoN}_{8.34}\text{O}_{0.21}$: C 49.65, H 3.22, N 30.74; found: C 49.82, H 2.93, N 30.96.

$^1[\text{Ni}(\text{pt})_2]$ (4): $\tilde{\nu} = 3423$ (br), 3037 (multiple, w), 1608 (s), 1519 (m), 1473 (s), 1451 (s), 1418 (s), 1391 (w), 1367 (m), 1267 (m), 1254 (m), 1206 (m), 1150 (m), 1126 (s), 1051 (m), 1034 (s), 1012 (m), 871 (m), 803 (m), 757 (m), 676 (m), 639 (m), 502 (m), 415 cm^{-1} (m). Anal. calcd for $^1[\text{Ni}(\text{pt})_2] \cdot 0.11\text{Py} \cdot 0.63\text{H}_2\text{O} = \text{C}_{14.55}\text{H}_{11.81}\text{NiN}_{8.11}\text{O}_{0.63}$: C 47.38, H 3.23, N 30.78; found: C 47.37, H 3.20, N 30.88.

$^1[\text{Cu}(\text{pt})_2]$ (5): $\tilde{\nu} = 3441$ (br), 3031 (multiple, m), 1612 (s), 1598 (s), 1573 (m), 1517 (w), 1471 (s), 1452 (s), 1420 (s), 1369 (m), 1352 (m), 1286 (m), 1268 (m), 1252 (m), 1208 (w), 1137 (m), 1121 (s), 1095 (m), 1042 (m), 1022 (m), 998 (m), 870 (m), 801 (m), 752 (m), 676 (m), 723(s), 702 (m), 677 (m), 665 (m), 642 (m), 628 (m) 490 (w), 408 cm^{-1} (w). Anal. calcd for $^1[\text{Cu}(\text{pt})_2] \cdot 0.05\text{Py} \cdot 0.63\text{H}_2\text{O} = \text{C}_{14.25}\text{H}_{11.51}\text{CuN}_{8.05}\text{O}_{0.63}$: C 46.38, 3.14, N 30.55; found: C 46.07, H 2.78, N 29.64.

$^1[\text{Zn}(\text{pt})_2]$ (6): $\tilde{\nu} = 3421$ (br), 3035 (multiple, m), 1605 (s), 1517 (m), 1476 (s), 1451 (s), 1438 (s), 1421 (s), 1391 (w), 1363 (m), 1265 (m), 1252 (m), 1208 (m), 1149 (m), 1125 (s), 1050 (m), 1035 (s), 1007 (m), 876 (m), 806 (m), 755 (m), 674 (m), 635 (m), 493 (m), 408 cm^{-1} (m). Anal. calcd for $^1[\text{Zn}(\text{pt})_2] \cdot 0.39\text{Py} \cdot 0.63\text{H}_2\text{O} = \text{C}_{16.05}\text{H}_{13.31}\text{ZnN}_{8.41}\text{O}_{0.63}$: C 48.15, H 3.34, N 29.55; found: C 48.31, H 2.96, N 29.53.

$^1[\text{Cd}(\text{pt})_2]$ (7): $\tilde{\nu} = 3421$ (br), 3035 (multiple, m), 1605 (s), 1517 (m), 1476 (s), 1451 (s), 1438 (s), 1421 (s), 1391 (w), 1363



(m), 1265 (m), 1252 (m), 1208 (m), 1149 (m), 1125 (s), 1050 (m), 1035 (s), 1007 (m), 876 (m), 806 (m), 755 (m), 674 (m), 635 (m), 493 (m), 408 cm⁻¹ (m). Anal. calcd for $[\text{Cd}(\text{pt})_2] \cdot 0.24\text{Py} \cdot 0.63\text{H}_2\text{O} = \text{C}_{15.20}\text{H}_{12.46}\text{N}_{8.24}\text{CdO}_{0.63}$: C 42.15, H 2.90, N 26.66; found: C 41.97, H 2.53, N 26.26.

Synthesis of single crystals of $[\text{Zn}(\text{pt})_2]$ (6)

Single crystals suitable for single crystal X-ray diffraction (SCXRD) of CP 6 were obtained by reaction of 55 μmol (7.5 mg) of water-free ZnCl_2 , 0.15 mmol (22 mg) of 2-(1,2,4-1*H*-triazol-3-yl)pyridine (Hpt), and 2 droplets of benzylamine according to the procedure described above. A mixture of 0.9 mL water-free toluene and 0.1 mL water-free pyridine was used as solvent. The reaction mixture was heated to 180 °C with 2 °C h⁻¹ and held constant at this temperature for 480 h. Subsequently the mixture was allowed to cool down to ambient temperature with 2 °C h⁻¹.

Synthesis of single crystals of $[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (8)

Single crystals suitable for SCXRD of CP 8 were obtained by reaction of 0.46 mmol (91 mg) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and 1.00 mmol (146 mg) 2-(1,2,4-1*H*-triazol-3-yl)pyridine (Hpt) in 4 mL pyridine following the general synthesis principle mentioned above. The reaction mixture was heated to 150 °C in 4 h, followed by heating to 180 °C with 2 °C h⁻¹. This temperature was held constant for 120 h. Subsequently, the reaction mixture was allowed to cool down to 150 °C with 2 °C h⁻¹, and to ambient temperature within 4 h. It is noteworthy that this synthesis is analogous to the bulk synthesis of $[\text{M}(\text{pt})_2]$ (1–7) but *without* vacuum-drying of the obtained product. Consequently, CP 8 is only existent when still damp. Upon drying, the obtained product converts to 5.

Impregnation of $[\text{Zn}(\text{pt})_2]$ (6) with Eu and Tb

$[\text{Zn}(\text{pt})_2]$ (6) was activated at 300 °C for seven hours at 10⁻³ mbar. Subsequently, three samples of 15 mg (42 μmol) of the activated polymer were each dispersed in a solution of 18 mg (40 μmol) $\text{EuNO}_3 \cdot 6\text{H}_2\text{O}$ and 18 mg (40 μmol) $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 4 mL DMF, MeCN or MeOH. The resulting suspensions were homogenised by ultrasonication for ten minutes and were magnetically stirred for eight days. Afterwards, the solids were separated from the liquid phase by centrifugation (10 000 rpm, 10 min) and decantation of the solution. The obtained solids were dried in vacuum (10⁻³ mbar) for one hour.

Bulk syntheses of complexes $[\text{MX}_2(\text{Hpt})_2]$ ($\text{MX}_2 = \text{MnCl}_2$ (9) and FeCl_2 (10))

1.00 mmol (126 mg) MnCl_2 or (127 mg) FeCl_2 were reacted with 2.40 mmol (351 mg) 2-(1,2,4-1*H*-triazol-3-yl)pyridine (Hpt) in 0.5 mL pyridine following the general synthesis principle mentioned above under inert atmosphere. The reaction mixture was heated to 150 °C within four hours, followed by heating up to 200 °C with 2 °C h⁻¹. This temperature was held constant for 120 h. Subsequently, the mixture was allowed to cool down to 150 °C with 2 °C h⁻¹ and then to room temperature within four hours. The liquid phase was removed manu-

ally under inert atmosphere, and the obtained solid was dried in vacuum (10⁻³ mbar). The yield was 73% for 9 and 77% for 10, based on the corresponding metal halide.

$[\text{MnCl}_2(\text{Hpt})_2]$ (9): $\bar{\nu} = 3450$ (br), 3079 (s), 2994 (s), 2891 (s), 1816 (m), 1657 (m), 1603 (s), 1569 (m), 1537 (m), 1503 (s), 1477 (s), 1448 (s), 1422 (s), 1340 (s), 1289 (s), 1272 (s), 1188 (m), 1149 (m), 1133 (m), 1098 (m), 1085 (m), 1051 (s), 1016 (m), 993 (s), 974 (m), 912 (m), 846 (s), 797 (s), 749 (s), 724 (s), 714 (s), 639 (s), 479 (m), 412 cm⁻¹ (m). Anal. calcd for $[\text{MnCl}_2(\text{Hpt})_2] = \text{C}_{14}\text{H}_{12}\text{Cl}_2\text{MnN}_8$: C 40.32, H 2.30, N 26.80; found: C 40.06, H 2.70, N 26.19.

$[\text{FeCl}_2(\text{Hpt})_2]$ (10): $\bar{\nu} = 3442$ (br), 3085 (s), 3006 (s), 2901 (s), 1809 (w), 1639 (m), 1605 (s), 1569 (w), 1540 (m), 1503 (s), 1482 (m), 1448 (m), 1425 (s), 1341 (s), 1288 (s), 1271 (s), 1190 (m), 1150 (m), 1136 (m), 1098 (w), 1085 (m), 1051 (m), 1016 (m), 994 (s), 976 (m), 908 (m), 836 (s), 797 (m), 751 (s), 724 (s), 715 (m), 639 (s), 486 (m), 415 cm⁻¹ (m). Anal. calcd for $[\text{FeCl}_2(\text{Hpt})_2] = \text{C}_{14}\text{H}_{12}\text{Cl}_2\text{FeN}_8$: C 40.13, 2.89, N 26.74; found: C 40.87, H 2.80, N 26.43.

Synthesis of single crystals of $[\text{MnCl}_2(\text{Hpt})_2]$ (9) and $[\text{FeCl}_2(\text{Hpt})_2]$ (10)

Crystals suitable for SCXRD of the isotopic complexes 9 and 10 were obtained by solvothermal reaction of 0.20 mmol (25 mg) MnCl_2 or FeCl_2 and 0.48 mmol (70 mg) 2-(1,2,4-1*H*-triazol-3-yl)pyridine (Hpt) in 0.3 mL pyridine following the procedure described above. The reaction mixture was heated to 150 °C within 4 h, followed by heating to 200 °C with 2 °C h⁻¹. This temperature was held for 120 h. Subsequently the mixture was allowed to cool down to 150 °C with 2 °C h⁻¹, and to ambient temperature within 4 h.

Bulk syntheses of $[\text{MX}_2(\text{Hpt})_2]$ ($\text{MX}_2 = \text{CoCl}_2$ (11) and CoBr_2 (12))

0.40 mmol (52 mg) CoCl_2 , or (88 mg) CoBr_2 were reacted with 1.00 mmol (146 mg) 2-(1,2,4-1*H*-triazol-3-yl)pyridine (Hpt) in 1 mL acetonitrile following the general synthesis principle mentioned above under inert atmosphere. The reaction mixture was heated up to 115 °C within four hours. This temperature was held constant for 144 h followed by cooling down to room temperature within four hours. The liquid phase was manually removed under inert atmosphere and the obtained solid was vacuum-dried at 10⁻³ mbar. Excess ligand was separated from the product by sublimation at 150 °C for five days. The yield was 74% for 11 and 87% for 12, based on the corresponding metal halide.

$[\text{CoCl}_2(\text{Hpt})_2]$ (11): $\bar{\nu} = 3085$ (s), 2997 (s), 2892 (s), 1807 (w), 1657 (m), 1608 (s), 1569 (w), 1542 (w), 1504 (s), 1479 (m), 1449 (m), 1426 (m), 1344 (m), 1289 (m), 1271 (m), 1193 (w), 1152 (w), 1139 (m), 1099 (w), 1088 (w), 1051 (m), 1018 (m), 996 (m), 976 (m), 907 (w), 844 (s), 797 (m), 752 (m), 724 (s), 717 (m), 639 (m), 490 (w), 419 cm⁻¹ (w). Anal. calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{CoN}_8$: C 39.83, H 2.87, N 26.54; found: C 40.29, H 2.57, N 26.47.

$[\text{CoBr}_2(\text{Hpt})_2]$ (12): 3432 (br), 3085 (s), 3011 (s), 2898 (s), 1788 (w), 1635 (w), 1606 (s), 1569 (m), 1542 (w), 1501 (s), 1477 (s), 1448 (s), 1423 (s), 1341 (m), 1285 (s), 1265 (s), 1212 (m), 1190



(m), 1149 (m), 1137 (m), 1118 (m), 1098 (m), 1086 (m), 1067 (w), 1051 (m), 1031 (w), 1017 (m), 1006 (m), 996 (m), 974 (m), 923 (w), 899 (w), 894 (w), 874 (w), 817 (s), 797 (m), 752 (s), 724 (s), 717 (m), 676 (w), 635 (m), 490 (w), 419 cm⁻¹ (w) (Recorded for a product synthesised in pyridine). Anal. calcd for C₁₄H₁₂Br₂CoN₈: C 32.90, H 2.37, N 21.93; found: C 32.40, H 2.23, N 20.96.

Synthesis of single crystals of [CoCl₂(Hpt)₂] (11) and [CoBr₂(Hpt)₂] (12)

Crystals suitable for SCXRD of the isotopic complexes 13 and 14 were obtained by solvothermal reaction of 0.50 mmol (65 mg) CoCl₂ or (0.11 g) CoBr₂ and 1.20 mmol (176 mg) 2-(1,2,4-1*H*-triazol-3-yl)pyridine (Hpt) in 0.3 mL pyridine following the procedure described above. The reaction mixture was thermally treated in analogy to the synthesis of 9 and 10.

Synthesis of single crystals of [ZnCl₂(Hpt)₂] (13)

Single crystals of 13 were found within the solid product, in which crystals of ¹_∞[Zn(pt)₂] (6) were found, as well (see above).

Conclusions

Within this work, coordination compounds based on divalent 3d-transition metal ions and the ligand 2-(1,2,4-1*H*-triazol-3-yl)pyridine (Hpt) were synthesised. Altogether, 12 fully characterised compounds and the structures of eight more that were obtained as side products are reported. The deprotonated ligand is able to interconnect transition metal ions (here Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺) to form homoleptic one-dimensional coordination polymers (CPs) with a generalised sum formula of ¹_∞[M(pt)₂], which are stable to temperatures up to 300–400 °C, depending on the metal ion. Considering C–H...N interactions between the polymeric strands, the CPs can be described supermolecular three-dimensional structures exhibiting square-shaped channel pores, in which solvent molecules are intercalated from the syntheses, as shown by temperature-dependent PXRD, STA and elemental analyses.

Besides colourful products containing Fe, Co, Ni, and Cu, the polymers containing Mn and Zn are colourless solids. Especially for ¹_∞[Zn(pt)₂], this appearance – in combination with UV absorption and ligand-based blue light emission of the CP – allows creation of a white light-emitter according to the RGB concept by activation of the CP and subsequent impregnation with Eu³⁺ and Tb³⁺. The colour of the emitted light can be tuned from neon blue to practically perfect white light by choosing an appropriate excitation wavelength. Furthermore, the coordination polymer ¹_∞[Fe(pt)₂] shows thermochromic behaviour based on continuous spin crossover. In addition to the homoleptic coordination polymers, several mononuclear complexes [MX₂(Hpt)₂] and numerous crystalline by-products were found and their structures determined. They illuminate a product rich chemistry of the ligand Hpt with transition metal ions.

Data availability

Single crystal structures determined within the scope of this work were uploaded to the CCDC database. CCDC 2347927 (6), 2347920 (8), 2347949 (9), 2347948 (10), 2347938 (11), 2347937 (12), 2347952 (13), 2347953 (14), 2347947 (15), 2347946 (16), 2347951 (17), 2347925 (18), 2347917 (19), and 2347950 (20).

In addition, the ESI† (62 pages) contains detailed description of analytical methods used, tables with crystallographic data, selected interatomic distances and angles, UV-Vis spectra, photoluminescence spectra, IR spectra, powder X-ray diffraction plots, simultaneous thermal analysis graphs, sorption isotherms, and additional experiments and single crystal structures description. Besides references cited in the main paper, the authors have cited additional references within the ESI.†^{41,43,46,56–60,62,69,70,81}

Conflicts of interest

There are no conflicts to declare.

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5 Zusammenfassung und Ausblick

Im Rahmen dieser Arbeit wurden neuartige magneto-optische Komposite auf Basis von magnetischen Partikeln und lumineszierenden Koordinationsverbindungen entwickelt, präpariert und charakterisiert. Weiterhin wurden neue Übergangsmetall-basierte Koordinationsverbindungen synthetisiert, welche aufgrund ihrer optischen Eigenschaften zur Synthese magneto-optischer Komposite herangezogen werden könnten. Als magnetische Komponente dienten ferromagnetische und weichmagnetische α -Eisen- bzw. ferrimagnetische und hartmagnetische Eisenoxidpartikel sowie superparamagnetische Eisenoxid-Nanopartikel, welche entsprechend den gewünschten Eigenschaften und Interaktionen mit Koordinationsverbindungen mit zusätzlichen Funktionalisierungen versehen wurden. Photolumineszierende, Lanthanoid-basierte MOFs bzw. mit Lanthanoiden imprägnierte Koordinationsverbindungen dienten als Komponente mit optischen Eigenschaften.

In Kap. 294.1 wurde ein Komposit präsentiert, welches sowohl unter Tageslicht aufgrund diffuser Lichtstreuung weiß erscheint, als auch unter UV-Licht weiß luminesziert. Durch die lumineszierende Metall-organische Gerüstverbindung EuTb@IFP-1, welche mit Eu^{3+} und Tb^{3+} kodotiert ist, verfügt das generierte Komposit über Photolumineszenz als Eigenschaft. Die blaue Lumineszenz des IFP-1-Liganden in Kombination mit der charakteristischen roten (Eu^{3+}) und grünen (Tb^{3+}) Lumineszenz der Lanthanoide resultiert in Weißlichtemission. Diese Koordinationsverbindung wurde mit magnetischen Partikeln zu einem weißen Komposit, welcher weiß luminesziert, umgesetzt. Essenziell für das weiße Erscheinungsbild des Komposits ist eine bereits „weiße Farbe“ der Mikromagnete. Dies wurde über einen suprapartikulären Aufbau mit α -Eisen- bzw. Eisenoxid-Partikeln als Kernmaterial umgeben von einer TiO_2 -Partikelhülle erreicht. Durch den partikulären Charakter der Titandioxid-Schale wird einfallendes Licht diffus reflektiert und gebrochen wodurch die Mikromagnete weiß erscheinen. Ein zweiphasiger Sprühtrocknungsprozess ermöglichte diesen entscheidenden Aufbau der Mikromagnete. Über die Kontaktzeit der Kompositpartner kann die Strukturierung der Komposite variiert werden. So führten längere Kontaktzeiten zu größeren MOF-Kristalliten, welche teilweise mit den weißen Mikromagnet-Partikeln in einem Kern-Satellit-Aufbau beschichtet sind. Kürzere Reaktionszeiten haben einen Einbau von MOF-Partikeln in die TiO_2 -Partikelschicht der Mikromagnete zur Folge.

In Kap. 4.2 wurde der eben erwähnte Beschichtungsmodus von Satellitpartikeln auf lumineszierenden MOF-Kristalliten aufgegriffen und weiterentwickelt. Als lumineszierende Komponente wurde auf die Lanthanoid-haltigen MOFs ${}^3_{\infty}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ und ${}^3_{\infty}[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ zurückgegriffen. Kristallite dieser MOFs wurden mit Citrat-stabilisierten

superparamagnetischen Eisenoxid-Nanopartikeln (SPIONs) zu magneto-optischen Kompositen kombiniert. Erhaltene Komposite weisen einen *core-satellite* Aufbau auf, in welchem die Oberflächen der lumineszierenden MOF-Kristallite mit SPIONs beschichtet sind und welcher eine Feineinstellbarkeit der magneto-optischen Eigenschaften dieser Komposite ermöglicht. Über die Wahl des MOF:SPIONs-Verhältnisses konnte nicht nur die Magnetisierbarkeit präzise eingestellt werden, wie es sich an dem linearen Zusammenhang der Sättigungsmagnetisierung und des SPION-Gehaltes zeigte. Die massenbezogene Lumineszenzintensität lässt sich über einen exponentiellen Zusammenhang ebenso mit dem MOF:SPIONs-Verhältnis in Relation setzen. Hierüber sind die magneto-optischen Eigenschaften der Kern-Satellit-Partikel einstellbar und vorhersagbar. Die Bildung der Kern-Satellit-Komposite war sowohl vom Deprotonierungsgrad der Citrat-Funktionalitäten der SPIONs als auch von der Wahl des Lösungsmittels für die Synthese unabhängig. Weiterhin wiesen die untersuchten Kern-Satellit-Komposite eine bemerkenswerte Stabilität auf, da sie auch durch mehrmaliges, Ultraschall-assistiertes Dispergieren und magnetisches separieren nicht voneinander zu separieren waren. Aufgrund der guten Dispergierbarkeit war die Herstellung einer kolloidalen Suspension möglich. Die charakteristischen Zusammenhänge zwischen Lumineszenzfarbe, -intensität und Sättigungsmagnetisierung in Bezug auf den Superparamagnetismus verleihen entsprechenden Kompositen ein eindeutiges, schwer zu kopierendes Charakteristikumsprofil, worüber ein potenzieller Einsatz zur Fälschungssicherung denkbar wird.

Neben der Kombination von magnetischen Partikeln und lumineszierenden Koordinationsverbindungen wurden die in Kap. 4.3 dargestellten Untersuchungen zur Synthese und Charakterisierung neuartiger, Übergangsmetall-basierter Koordinationsverbindungen durchgeführt, welche aufgrund ihrer diversen optischen Eigenschaften auch für magneto-optische Komposite herangezogen werden können. Dies schließt auch einen Weißlichtemitter ein, welcher als potenzielle Alternative zu IFP-1 im *All White Magnet* verwendbar ist. Als Ligand für die erhaltenen Koordinationsverbindungen diente 2-(1,2,4-1*H*-Triazol-3-yl)pyridin (Hpt) bzw. dessen deprotonierte Spezies 3-(Pyridin-2-yl)-1,2,4-triazolat (pt). Je nach verwendeter Übergangsmetall-Quelle – Acetate oder Halogenide – und zugegebenen Reaktionspartnern variierte die Dimensionalität erhaltener Verbindungen von mono- und dinuklearen Komplexen bis hin zu eindimensional polymeren Strängen bzw. zweidimensional polymeren Schichten. Dies beinhaltete auch das eindimensionale Koordinationspolymer $1[\text{Zn}(\text{pt})_2]$, welches eine supermolekulare, dreidimensionale Struktur aufweist. Anhand von Trocknungszeit-abhängigen pulverdiffraktometrischen Untersuchungen der strukturell mit $1[\text{Zn}(\text{pt})_2]$ verwandten Verbindung $1[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ konnte die partielle Abgabe der in den Poren eingelagerten, kristallographisch geordnet vorliegenden Pyridinmoleküle und eine daraus resultierende Umwandlung zu einer zu $1[\text{Zn}(\text{pt})_2]$ isotypen

Form beobachtet werden, was eine mögliche Aktivierung von ${}^1[\text{Zn}(\text{pt})_2]$ bereits andeutete. Das Polymer ${}^1[\text{Zn}(\text{pt})_2]$ wurde nach erfolgreicher Bulk-Synthese und Aktivierung mit den Lanthanoidionen Eu^{3+} und Tb^{3+} imprägniert. Durch die Kombination der charakteristischen roten (Eu^{3+}) bzw. grünen (Tb^{3+}) Lumineszenz dieser Ionen, welche mittels des Antenneneffektes über den im CP enthaltenen Liganden erfolgt, mit der blauen Ligand-basierten Lumineszenz von ${}^1[\text{Zn}(\text{pt})_2]$ ergibt sich ein Lichtemitter, dessen Chromatizität über die Anregungswellenlänge von Neonblau über Kaltweiß hin zu faktisch reinweiß (*CIE xy*-Koordinaten: (0.32 | 0.32), Weißpunkt (0.333...|0.333...)) eingestellt werden kann. Neben dem Polymer ${}^1[\text{Zn}(\text{pt})_2]$ wurden die dazu isotypen Koordinationsverbindungen ${}^1[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Cd}$) erfolgreich synthetisiert, was sich anhand pulverdiffraktometrischer Untersuchungen zeigt. Einige Vertreter ${}^1[\text{Fe}(\text{pt})_2]$, ${}^1[\text{Co}(\text{pt})_2]$, ${}^1[\text{Ni}(\text{pt})_2]$, ${}^1[\text{Cu}(\text{pt})_2]$ weisen eine intensive Farbe auf. Durch temperaturabhängige, spektroskopische Charakterisierungen konnte ein thermochromes Verhalten des Eisen-haltigen Koordinationspolymers ${}^1[\text{Fe}(\text{pt})_2]$ nachgewiesen werden. Zusätzlich zu den als Reinsubstanz erhaltenen Verbindungen wurde eine Reihe an weiteren Substanzen einkristalldiffraktometrisch identifiziert. Dies umfasste zweidimensional (${}^2[\text{Cu}_2\text{Cl}(\text{pt})]$ und ${}^2[\text{Co}_2\text{Br}_2(\text{pt})_2]$) bzw. bpt = 3,5-bis(2-Pyridyl)-1,2,4-triazolat, CyOH = Cyclohexanol), sowie dinukleare ($[\text{Fe}_2\text{X}_2(\text{pt})_2(\text{Py})_4]$ ($\text{X} = \text{Cl}, \text{Br}$)) und mononukleare Komplexe ($[\text{Zr}(\text{pt})_4]$ und $[\text{ZnCl}_2(\text{Hpt})_2]$), welche anschaulich die strukturelle Vielfalt Hpt-basierter Koordinationsverbindungen zeigen. Aufgrund der vielseitigen optischen Eigenschaften von Übergangsmetall-basierten Koordinationsverbindungen mit dem Liganden 2-(1,2,4-1*H*-Triazol-3-yl)pyridin bzw. 3-(Pyridin-2-yl)-1,2,4-triazolat stellen die auf diesen Liganden basierenden und in dieser Arbeit vorgestellten Koordinationsverbindungen ideale Kandidaten für die Synthese neuer magneto-optischer Komposite dar. Dies beinhaltet auch den einfach und schnell zu synthetisierenden Weißlichtemitter, der als Alternative für EuTb@IFP-1 im *All White Magnet* Verwendung finden kann. Weiterhin ist eine Anwendung der thermochromen Verbindung ${}^1[\text{Fe}(\text{pt})_2]$ in Kombination mit magnetischen Partikeln als magnetisch separierbarer Temperatursensor denkbar.

Zusammenfassend ist festzuhalten, dass magneto-optische Komposite auf Basis von Koordinationsverbindungen und Eisen- bzw. Eisenoxidpartikeln ein vielversprechendes Gebiet für die Entdeckung neuartiger Systeme mit vielseitigen Eigenschaften ist. Sowohl Übergangsmetall-haltige MOFs wie IFP-1 oder ${}^1[\text{Zn}(\text{pt})_2]$, welche mit Lanthanoiden imprägniert wurden, als auch Lanthanoid-basierte Koordinationsverbindungen wie ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ und ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ können als Komponente mit optischen Eigenschaften genutzt werden. Je nach Material und Partikelgröße eignen sich Eisen- bzw. Eisenoxidpartikel aufgrund der ferro-, ferri- bzw. superparamagnetischen Eigenschaften als magnetische Komponente. Für die Strukturierung der magneto-optischen Komposite dieser Arbeit ist die Größe der

magnetischen Partikel in Relation zu den Partikeln der MOF-Komponenten ein entscheidendes Kriterium. Kleine MOF-Partikel sind in der Lage magnetische Mikropartikel zu funktionalisieren. Sind die Kristallite der Koordinationsverbindungen deutlich größer als die magnetischen Partikel, erfolgt eine Umkehr der Rollen und die MOF-Kristallite werden mit magnetischen Satellitpartikeln funktionalisiert. Im Einklang hiermit kann ein entsprechender Kern-Satellit-Aufbau bei der Funktionalisierung von MOF-Kristalliten mit superparamagnetischen Nanopartikeln erreicht werden. Je nach vorgesehenem Einsatzgebiet kann so über den Beschichtungsmodus das entsprechende magneto-optische Verhalten von Kompositen gewählt werden. Durch die Beschichtung magnetischer Partikel mit lumineszierenden Komponenten würde die Lumineszenzintensität in den Fokus gerückt werden, was für ästhetische Zwecke wie magnetische Tinten oder (im Falle des *All White Magnet*) weiß lumineszierendes magnetisches Papier oder schwer zu entdeckende Fälschungssicherungsmerkmale von Vorteil sein kann. Mithilfe eines Kern-Satellit-Aufbaus bestehend aus superparamagnetischen Eisenoxidnanopartikeln als magnetischen Satellit-Partikeln sind die luminomagnetischen Eigenschaften der Komposite exakt einstellbar. Weiterhin weisen Kern-Satellit-Partikel eine bemerkenswerte Stabilität und gute Dispergierbarkeit auf, was eine potenzielle Weiterverarbeitung und Verwendung erleichtert. Auch die optischen Eigenschaften von Übergangsmetall-basierten Koordinationsverbindungen auf Basis von Hpt bzw. pt machen diese Materialien zu vielversprechende Kandidaten in Bezug auf die potenzielle Verwendung in magneto-optischen Kompositen. Insgesamt zeigen die hergestellten Komposite, dass die Eigenschaften Lumineszenz und Magnetismus gut und definiert über einen Kompositaufbau kombinierbar sind. Es ergeben sich viele potenzielle Anwendungen. Nicht zu vernachlässigen ist auch die ästhetisch ansprechende Komponente, welche den wohl wichtigsten Sinn des Menschen anspricht – den Sehsinn.

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7 Anhang

7.1 Ergänzende Informationen zur ersten Publikation

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supporting Information

An all white magnet by combination of electronic properties of a white light emitting MOF with strong magnetic particle systems

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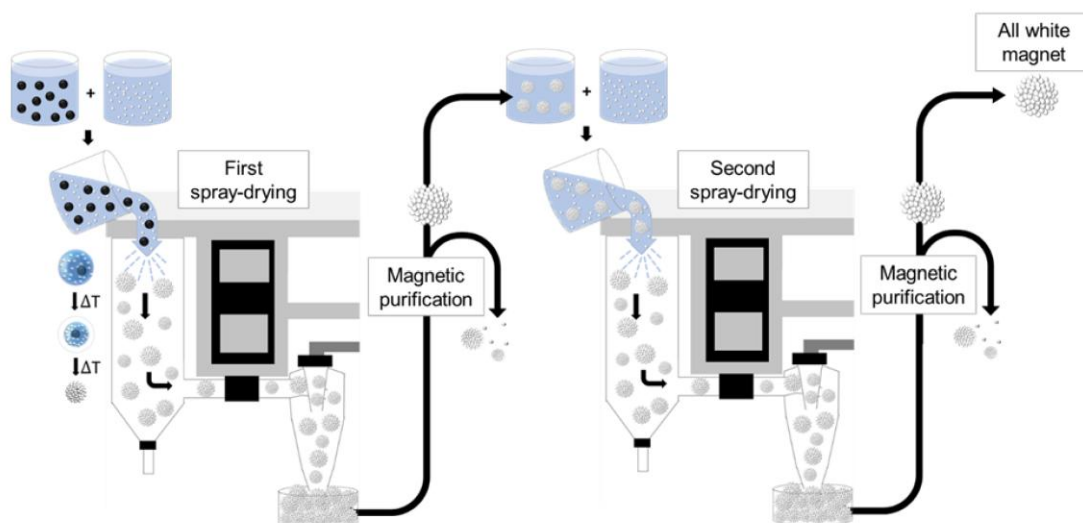


Figure S1. Principle scheme of the synthesis setup for the white micro magnet (WI and WO). The core material is covered by titania pigments by two spray-drying cycles followed by magnetic purification in order to remove non-magnetic side-products.

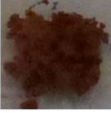
Scheme	Core particle / coating of core + shell consisting of nanoparticles	Appearance	Scheme	Core particle / coating of core + shell consisting of nanoparticles	Appearance
	Carbonyl iron /- + -			Iron oxide /- + -	
	Carbonyl iron / TiO ₂ + -			Iron oxide /- + TiO ₂	
	Carbonyl iron / TiO ₂ / Ag + -			Iron oxide & TiO ₂ /- + -	
	Carbonyl iron / TiO ₂ / Ag + TiO ₂			Iron oxide & TiO ₂ /- + TiO ₂	
	Carbonyl iron /- + TiO ₂			Iron oxide / SiO ₂ + -	
	Carbonyl iron /- + TiO ₂ , SiO ₂			Iron oxide / SiO ₂ + TiO ₂	
	Carbonyl iron /- + SiO ₂				

Figure S2. The creation of magnetic more or less whitish core-shell supraparticles via spray-drying. The choice of building blocks including the magnetic core material, titania and silica nanoparticles, addition of optional pre-treatment steps such as a coating with Ag or silica and a variation of the many spray-drying parameters lead to an enormous variety in terms of color appearance of obtained complex microparticles as shown in this figure exemplarily for several combinations and procedures.

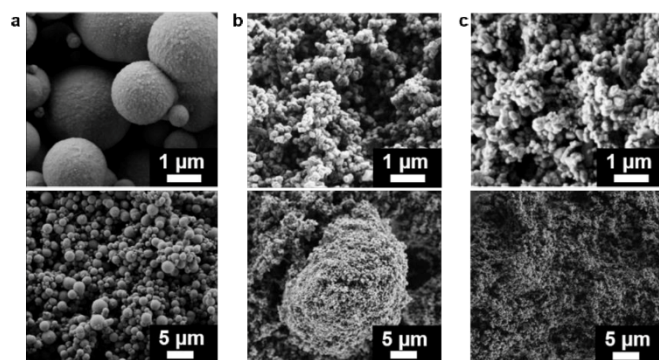


Figure S3. Scanning electron microscopy of precursor particles. Scanning electron micrographs of α -iron (a) and iron oxide particles (b), as well as TiO_2 nanoparticles (c).

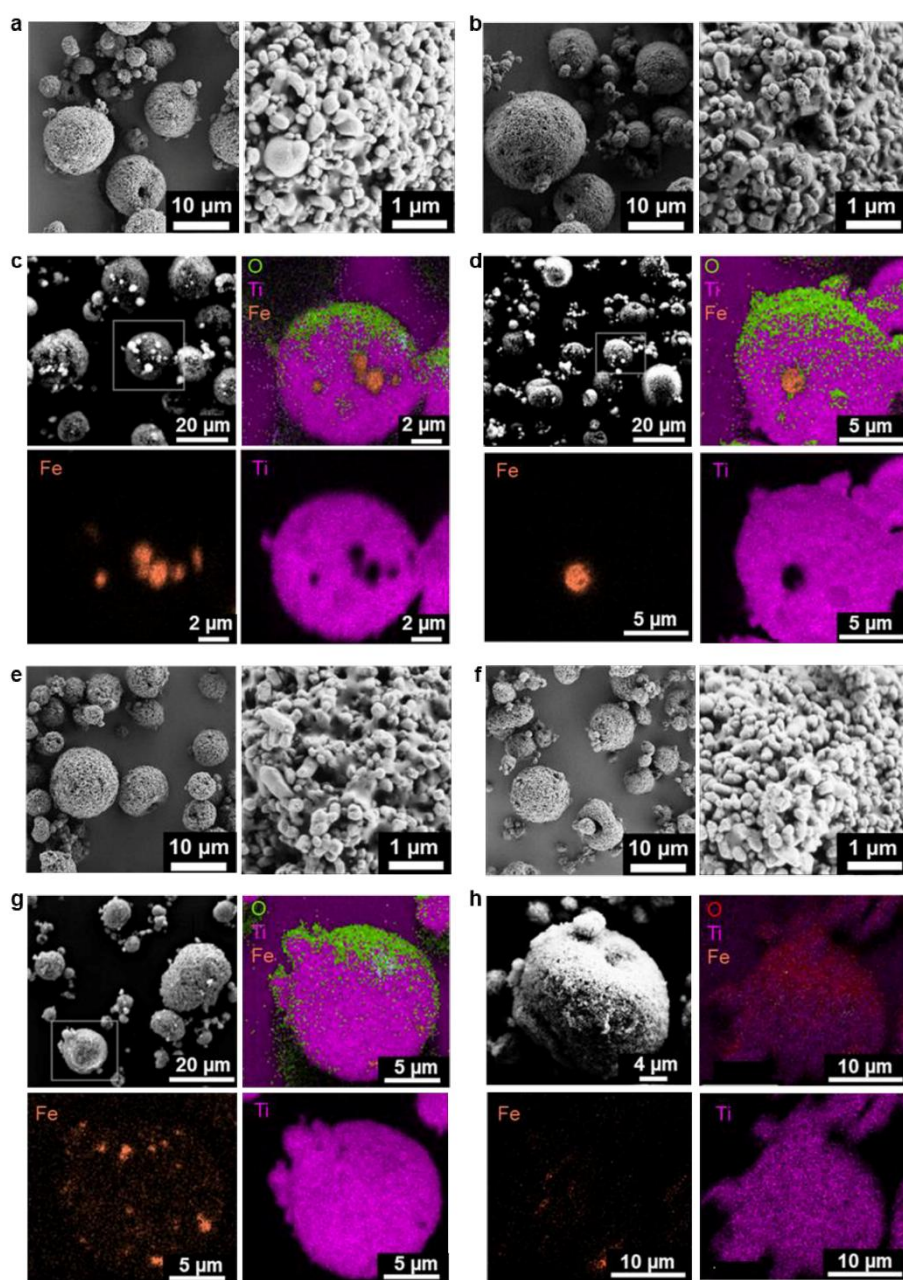


Figure S4. Scanning electron microscopy of white micro magnets. Scanning electron micrographs (a, b, e, f) and scanning electron micrographs in combination with energy dispersive X-ray spectroscopy (EDX, b, c, g, h) of α -iron containing (a-d) and iron oxide (e-h) containing white micro magnet after the 1st (a, c, e, g) and 2nd spray-drying cycle (b, d, f, h) with TiO_2 .

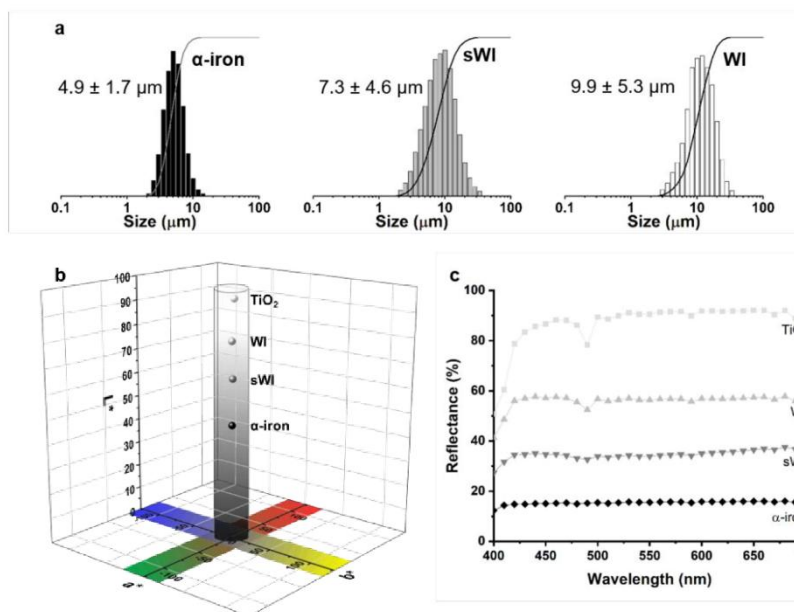


Figure S5. Particle size and color appearance of α -iron containing white micro magnet. (a) The mean particle size and standard deviation obtained from laser diffraction measurements of pure α -iron core material, α -iron containing white micro magnet after first (sWI) and second (WI) spray-drying cycle with TiO_2 . (b) CIE $L^*a^*b^*$ values and (c) reflectivity of α -iron containing white micro magnet after first (sWI) and second (WI) spray-drying cycle compared to pure α -iron core material and titania pigment (TiO_2).

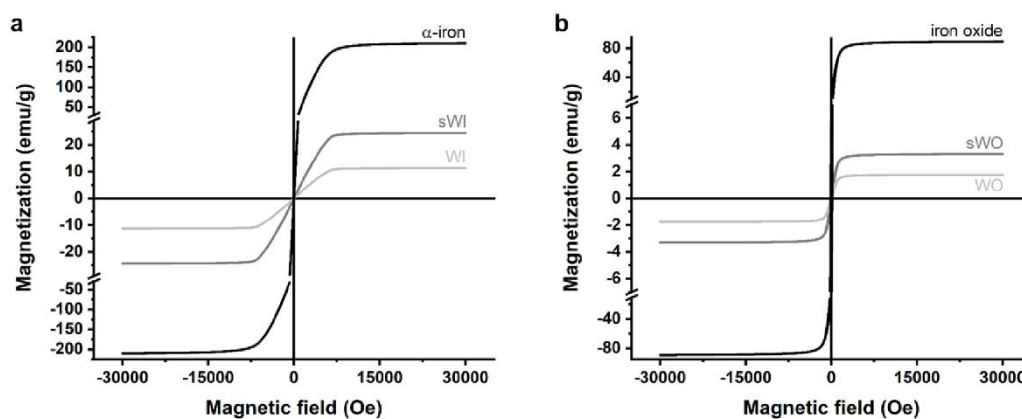


Figure S6. Magnetic properties of white micro magnets. Magnetization measurements of (a) α -iron containing and (b) iron oxide containing white micro magnet after the 1st (sWI and sWO) and 2nd spray-drying cycle with TiO_2 (WI and WO) compared to pure core materials.

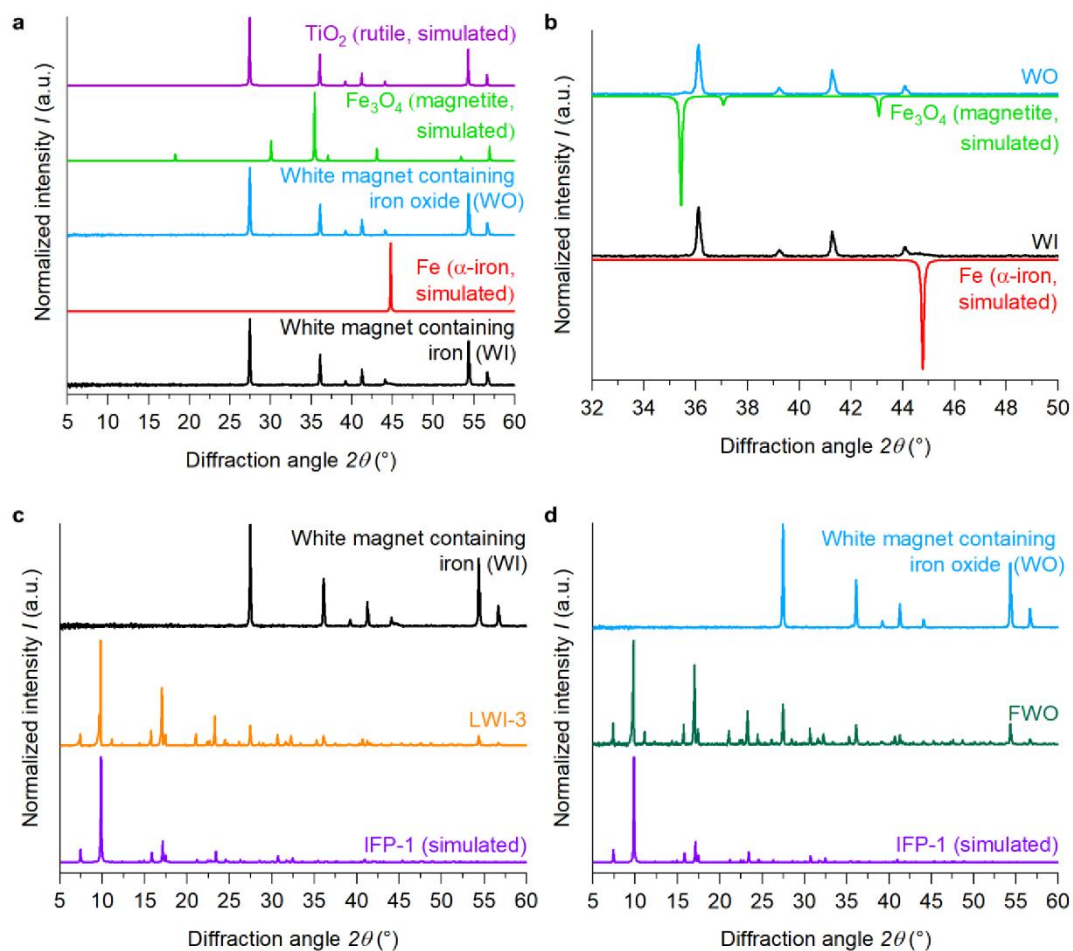


Figure S7. Powder X-ray diffraction patterns (a) and a detailed comparison (b) of α -iron containing white micro magnet (WI) and iron oxide containing white micro magnet (WO) in comparison to simulated powder X-ray diffraction patterns of rutile¹, α -iron² and magnetite³, as well as powder X-ray diffraction patterns of LWI-3 (c) and LWO (d) in comparison to the pattern of WI and WO, respectively, and the simulated diffraction pattern of IFP-1.⁴

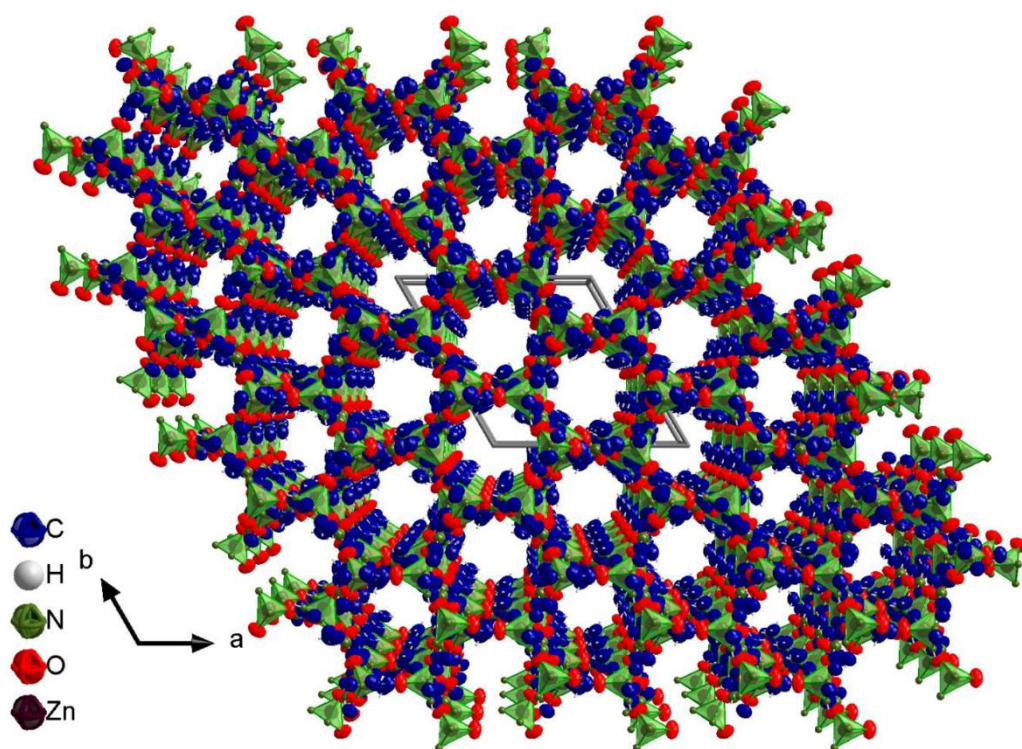


Figure S8. Perspective excerpt of the crystal structure of IFP-1⁴ along the crystallographic c-axis.

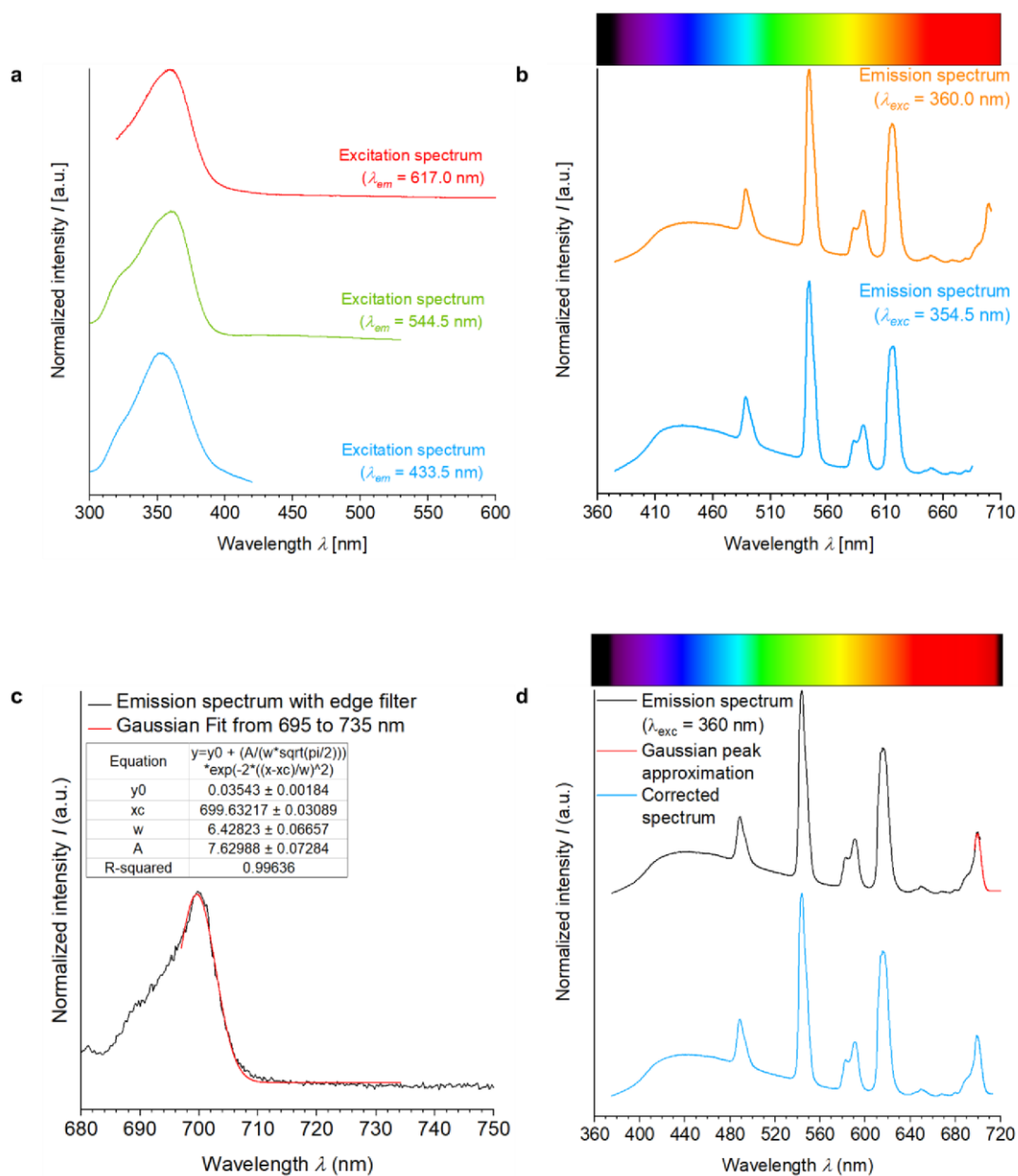


Figure S9. Excitation spectra (a) and emission spectra (b) of LWI-3. λ_{em} : emission wavelength, λ_{exc} : excitation wavelength. (c) Fitted emission spectra ($\lambda_{exc} = 360$ nm) of LWI-3. Black: spectrum as measured; red: Gaussian approximation for the rearmost europium emission band based on the Gaussian fit (d) of an emission spectrum ($\lambda_{exc} = 363$ nm) measured with an edgefilter (Newport).

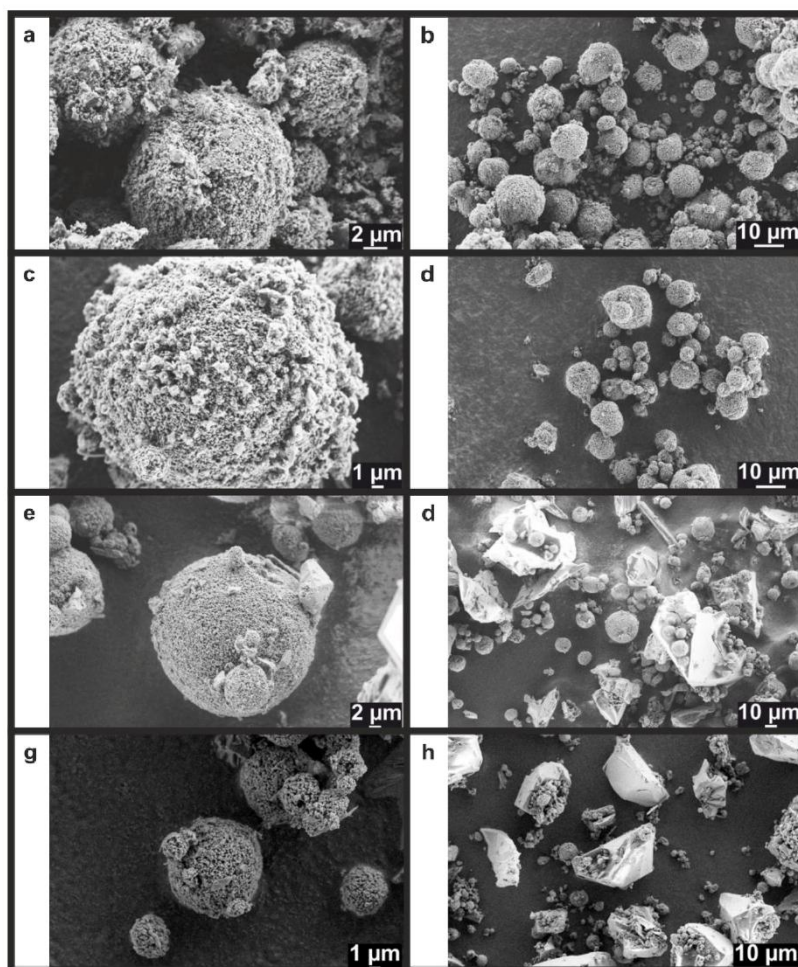


Figure S10. Electron micrographs of functionalized WI after (a, b) 1 h (LWI-1), (c, d) 3 h (LWI-2), and (e, f) 72 h (LWI-3) reaction time at 90 °C as well as electron micrographs of functionalized WO after (g, h) 72 h reaction time at 90 °C (LWO). The set-up of the composite goes from MOF crystallites of an approximate size of 1 – 3 μm in diameter as coating on magnetic particles (a – d) to magnetic particles on top of MOF crystallites of an approximate size of 50 – 70 μm in diameter (e – h) depending on the reaction time.

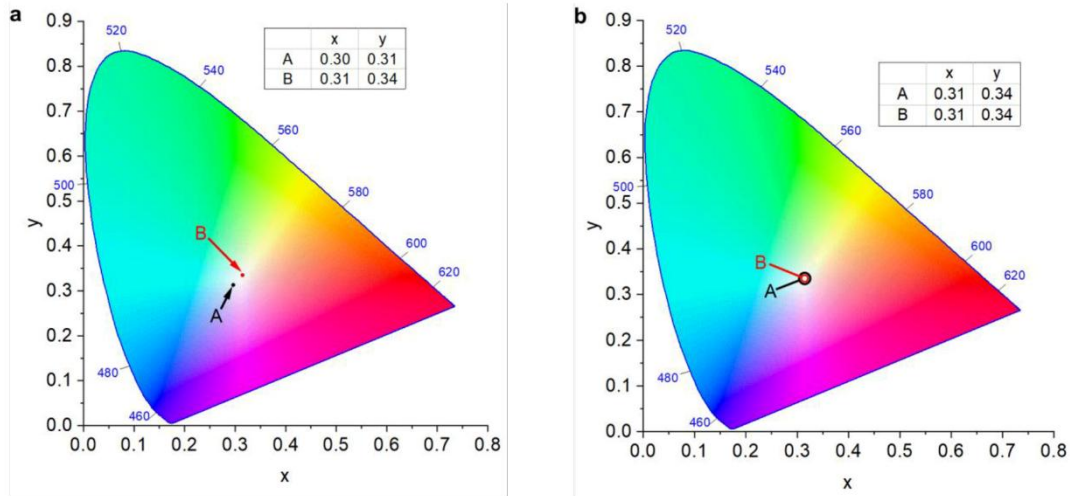


Figure S11. (a) Comparison of the chromaticity coordinates of LWI-3 in dependence of the excitation wavelength for $\lambda_{exc} = 354$ nm (A, black) and $\lambda_{exc} = 360$ nm (B, red) giving cold (A, black) as well as warm white light (B, red). (b) Comparison of the chromaticity coordinates of LWI-3 for the emission spectrum ($\lambda_{exc} = 360$ nm) as measured (A, black) as well as the emission spectrum with approximated rearmost europium emission band using a Gaussian fit (B, red) (for corresponding spectra, see Figure S9 a, b).

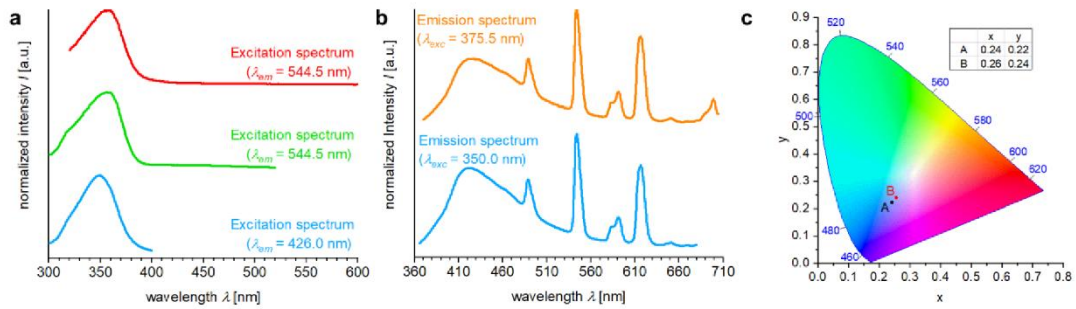


Figure S12. Excitation (a) and emission spectra (b) of LWO. λ_{em} : emission wavelength, λ_{exc} : excitation wavelength, as well as the comparison of the chromaticity coordinates of LWO (c) in dependence of the excitation wavelength for (A, black) $\lambda_{exc} = 350$ nm and (B, red) $\lambda_{exc} = 375$ nm.

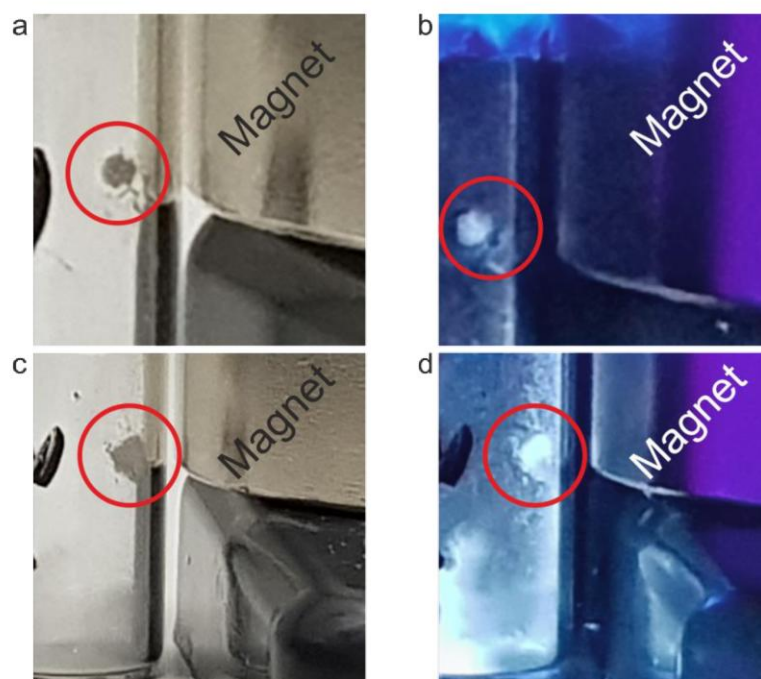


Figure S13. Visualization of white magnet particles containing α -iron (WI), functionalized with white luminescent EuTb@IFP-1 (LWI) after a reaction time of (a, b) 1 h (LWI-1) and (c, d) 3 h (LWI-2), attracted by a magnet under visible light (a, c) and under UV light excitation ($\lambda = 365$ nm; c, d).

Additional Experimental Section

Functionalization of white micro magnets with metal-organic frameworks.

For the preparation of luminescent white magnetic composite materials containing iron as magnetic component (LWI) the influence of various solvothermal reaction times was investigated. The resulting products are assigned with numbers depending on the solvothermal reaction time to illustrate these differences in reaction times and other parameters according to the designations listed in Table 1.

Table S1. Product designations of luminescent white magnets.

white magnet particle	EuTb @IFP-1	mass ratio (emitter:particle)	solvent volume	reaction time at 90 °C [h]	product designation
10.0 mg WI	5.0 mg	1:2	0.1 mL	1	LWI-1
10.0 mg WI	5.0 mg	1:2	0.1 mL	3	LWI-2
11.6 mg WI	25.1 mg	2.16:1	0.7 mL	72	LWI-3
14.3 mg WO	25.5 mg	1.79:1	0.7 mL	72	LWO

The following synthesis was performed for the product designated as LWI-3. The preparation of all other products (LWI-1, -2, and LWO) were performed analogous to this procedure with the reagent mass ratios and reaction times stated in Tab. S1. 0.5 eq. of terbium and europium ions were intercalated in-situ into the pores of IFP-1 from DMF solution. The components (WI and EuTb@IFP-1) were mixed in an agate mortar under inert atmosphere in a mass ratio of 2.16:1 (25.1 mg EuTb@IFP-1, 11.6 mg WI). After transferring the mixture into a Duran® glass ampoule and adding dry hexane (0.7 mL), the solvent was degassed by freezing the mixture, evacuating the ampoule and allowing the mixture to thaw again. This procedure was repeated one more time followed by freezing the reaction mixture, evacuating the ampoule and closing it by melting. The reaction mixture was allowed to warm up to room temperature and was homogenized in an ultrasonic bath for three minutes. Subsequently, the ampoule was placed in a corundum oven, which was heated up to 90 °C in four hours. This temperature was held constant for 72 hours before cooling to room temperature in four hours again. The solvent was removed manually under inert atmosphere and the product was dried in vacuo. After the synthesis the white luminescent, magnetic composites were magnetically separated from excess non-magnetic reactants.

For the synthesis of LWI-1 and LWI-2 the ampoules were placed in a preheated Büchi glass oven (Type GKR 50) for 1 h (LWI-1) or, respectively, 3 h (LWI-2). The synthesis of LWO was performed analogous to the synthesis of LWI. The resulting products are, depending on the reaction time, referred to the designations as listed in Tab. S1. MOF contact of WI and EuTb@IFP-1 at 90 °C for one hour (LWI-1) leads to a functionalization of the magnetic particles with MOF crystallites of an approximate size of 1 – 2 µm (Figure S10 a, b). A reaction time of three hours (LWI-2) increases the amount of MOF crystallites on top of the magnetic particles (Figure S10 c, d). Keeping the temperature at 90 °C for three days (LWI-3) results in MOF crystallites of an approximate size of 2 – 3 µm on top of the magnetic particles. In addition, larger MOF crystallites (50 – 70 µm) are functionalized by the particles, too (Figure S10 e, f). This functionalization mode is also observable for LWO (Figure S10 g, h).

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Supporting Information

Tuning Magnetic and Photophysical Properties of Luminomagnetic Metal-Organic Framework Composites in an Inverse Core-Satellite Structure

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1. Experimental

1.1 Powder X-ray Diffraction (PXRD)

Powder X-ray diffractograms were recorded using a PANalytical X'Pert Pro with an Empyrean Cu LFF X-ray tube at 40 kV and 40 mA, and an X'Celerator detector. The detection limits of the detector were adjusted to a window of 0.2025 – 11.2709 keV to minimize the detection of X-ray fluorescence caused by the iron containing samples. Within the incident beam path, a 0.04 rad Soller slit, a 10 mm beam mask, an anti-scatter slit of 1°, and a divergence slit of 1° were placed. An anti-scatter slit of 0.5°, a 0.04 rad Soller slit, and a Nickel Beta-filter (0.02 mm) were positioned within the diffracted beam path in front of the detector. For the measurements, the samples were placed on a silicon waver and flattened with a spatula. The specimens were placed in the beam path of the instrument and X-ray diffraction was recorded from 5 – 60° in 2 θ using Cu-K α radiation (λ = 150.46 pm).

1.2 Transmission Electron Microscopy (TEM) of SPIONs

SPIONs dispersed in water was dropped onto the carbon-coated side of copper grids (Plano GmbH, 300 mesh, S159). Excess liquid was removed with lint-free cloth and the samples were allowed to dry on air. Micrograph was taken with a JEM-2010 TEM from JEOL at 200 kV acceleration voltage.

1.3 Transmission Electron Microscopy (TEM) of Synthesized Composites

For measurement sample preparation, 2 mg of composites were dispersed in 1.5 mL of dichloromethane (DCM) with ultrasonication for 10 min. Subsequently, 0.25 mL of the obtained dispersion were diluted with 1.5 mL of DCM and were treated with ultrasonication for 10 min. This dilution process was repeated two more times. Afterwards, the obtained colloidal dispersions were dropped on 3.05 mm copper grids (Plano GmbH, S160) and micrographs were taken with a Philips CM30/STEM at 300 keV with a LaB₆ cathode and GATAN digital camera.

1.4 Magnetization Investigations

For the determination of magnetic properties, a vibrating-sample magnetometer VersaLabTM 3T from Quantum Design was used. Measurements were performed at 300 K by cycling the applied field from –30 kOe to +30 kOe with a step rate of 50 Oe · s⁻¹. Detailed analyses were carried out by cycling the applied field from –3 to +3 kOe with 5 Oe · s⁻¹. Temperature was set to 300 K. Magnetization values within this work are given in emu · g⁻¹ (cgs units) which can be set equal to A · m² · kg⁻¹ (SI units).

1.5 Determination of Photoluminescence Properties

Photoluminescence excitation and emission spectra were recorded using a Jobin Yvon Fluorolog 3 (Horiba) equipped with a photomultiplier tube (R928P) and double-grated excitation and emission monochromators. As a light source a Xe short-arc lamp (USHIO) was used. Recorded spectra were corrected using monochromator and detector corrections provided by the manufacturer. Additionally, recorded excitation spectra were corrected by the lamp's spectral distribution using a photodiode reference detector. The samples were filled in round quartz glass cuvettes and brought into the beam path. An edge filter (longpass filter, Newport, 345) was used.

For photoluminescence quantification (determination of mass-related emission intensity IM) and quantum yield determinations, the Jobin Yvon Fluorolog 3 (Horiba) was equipped with a HORIBA Quanta- ϕ Integrating Sphere (F-3029), and the samples were filled into Micro Cell Cuvettes (18-F/ST/C/Q/10) from Starna. Emission spectra of the quantification measurements were corrected for the spectral response of the monochromators and detectors using spectral corrections provided by the manufacturer as well as for the spectral response of the lamp by use of

a photodiode reference detector. Furthermore, an edge filter (longpass filter, Newport, 395 nm) was used. The sample amount required for luminescence quantification was determined by measuring one sample with different amounts (steps of 5 mg) until the ratio between intensity and mass did not fluctuate more than 10 %. Within this mass range, five points with different masses were recorded for each sample. Single data points of these measurements are shown in Figure S23. Quantum yields were determined with magnesium oxide as an additional reference material. Every sample was measured several times, and the quantum yield with standard deviation was calculated subsequently. Calibration of Quanta-φ Integrating sphere was checked by an additional standard (sodium salicylate powder, $\lambda_{\text{ex}} = 340 \text{ nm}$, $\lambda_{\text{em}} = 365\text{--}600 \text{ nm}$; determined quantum yield $\Phi = 53.4 \%$, literature value: 53 %).^[1]

The overall luminescence decay time was determined using a second Fluorolog 3 equipped with a dual lamp housing, a 450 W Xe short-arc lamp (USHIO), a UV xenon flashlamp (Exelitas FX-1102), double-grated excitation and emission monochromators, a photomultiplier tube (R928P) and a TCSPC (time-correlated single-photon counting) upgrade. For the measurements, the samples were filled in round quartz glass cuvettes. The overall emission intensity decays were recorded using the DataStation software and were subsequently fitted with a mono-exponential decay using the Decay Analysis Software 6.

1.6 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX)

Sticky carbon pads were affixed onto the specimen holders. The samples were trickled on the carbon pads. Excess of substance was removed by careful tapping and blowing pressurized air over the specimen holders. Scanning electron micrographs were taken with a Merlin Gemini (Zeiss) with an acceleration voltage of 3 kV, a current of 100 pA and a working distance of 3 mm. Energy dispersive X-ray spectral mappings were recorded with an XMAX-50 detector (Oxford Instruments) using a working distance of 5.5 mm, a current of 1 nA and an acceleration voltage of 8 kV.

1.7 Particle Size Determinations by Dynamic Light Scattering (DLS) of ${}^3[\text{Ln}_3(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Ln = Eu, Tb) and SPIONs@LnMOF-4 Composites

2 mg of the MOF ${}^3[\text{Eu}_3(\text{BDC})_3(\text{H}_2\text{O})_4]$, ${}^3[\text{Tb}_3(\text{BDC})_3(\text{H}_2\text{O})_4]$, or SPIONs@LnMOF-4 composites respectively, were gently mortared to break down larger chunks arising from the drying process. The mortared solids were dispersed in 4 mL of deionized water followed by ultrasonication for 10 minutes. 2 mL of the resulting dispersion were separated and diluted with 2 mL of deionized water followed by ultrasonication for 10 minutes. This dilution process was repeated two more times. The hydrodynamic particle size distribution within the final suspension was determined utilizing a StabiSizer® (Particle Metrix GmbH) with Microtrac FLEX Application Software 10.5.4. Particle size distributions of synthesized composites SPIONs@EuMOF-4 and SPIONs@TbMOF-4 were recorded analogously. The values given in the manuscript and the supporting information correspond to the average of three runs with $90 \text{ s} \pm 2\sigma$.

1.8 Particle Size Determinations by Dynamic Light Scattering (DLS) SPIONs

2 mg of SPIONs were gently mortared to break down larger chunks arising from the drying process. The mortared solids were dispersed in 4 mL of deionized water followed by ultrasonication for 10 minutes. The resulting dispersions were allowed to settle for the weekend for sedimentation of remaining larger chunks. The hydrodynamic particle size distribution within the remaining suspension was determined utilizing a StabiSizer®

(Particle Metrix GmbH) with Microtrac FLEX Application Software 10.5.4. The values given in the manuscript and the supporting information correspond to the average of three runs with $90 \text{ s} \pm 2\sigma$.

2. Additional tables and figures

Table S1. Composite designations of synthesized composites constituted by ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Eu-BDC) or ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Tb-BDC), or a mixture of both and superparamagnetic iron oxide nanoparticles (SPIONs, citrate-stabilized at pH = 2.1) in defined MOF(s):SPIONs weight ratios, as well as CIE chromaticity coordinates xy of the synthesized composites besides the chromaticity coordinates of pure Eu-BDC and Tb-BDC treated analogously to the synthesis procedure of the composites and resulting emission color.

Composite designation	Luminescent compound	Weight ratio MOF(s):SPIONs	CIE chromaticity coordinates		Chromaticity
			x	y	
${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Eu-BDC)	Eu-BDC	1:0	0.652	0.336	
SPIONs@EuMOF-0.5	Eu-BDC	0.5:1	0.657	0.332	
SPIONs@EuMOF-1	Eu-BDC	1:1	0.662	0.334	
SPIONs@EuMOF-2	Eu-BDC	2:1	0.663	0.335	
SPIONs@EuMOF-4	Eu-BDC	4:1	0.665	0.334	
SPIONs@EuMOF-8	Eu-BDC	8:1	0.663	0.336	
SPIONs@EuMOF-10	Eu-BDC	10:1	0.659	0.336	
SPIONs@EuTbMOF-4	Eu-BDC/Tb-BDC	2:2:1	0.469	0.493	
SPIONs@TbMOF-4	Tb-BDC	4:1	0.366	0.577	
${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Tb-BDC)	Tb-BDC	1:0	0.332	0.589	

Table S2. Designations of composite systems SPIONs@EuMOF- x comprising ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Eu-BDC) and SPIONs citrate-stabilized at a pH of 2.1 with listed MOF:SPIONs weight ratios used for their synthesis, as well as their saturation magnetization (M_s), mass-related emission intensity (I_M), and quantum yield (Φ).

Composite designation	MOF:SPIONs weight ratio	M_s	I_M	Φ
		[emu · g ⁻¹]	[10 ⁶ cps · mg ⁻¹]	[%]
SPIONs (citrate-stabilized at pH = 2.1)	0:1	60	-	-
SPIONs@EuMOF-0.5	0.5:1	42	0.085(6)	0.29(1)
SPIONs@EuMOF-1	1:1	30	0.15(1)	1.01(2)
SPIONs@EuMOF-2	2:1	21	0.47(3)	1.77(5)
SPIONs@EuMOF-4	4:1	13	0.72(3)	3.4(1)
SPIONs@EuMOF-8	8:1	7	1.05(5)	5.7(2)
SPIONs@EuMOF-10	10:1	6	1.22(8)	5.8(2)
${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$	1:0	-	3.6(2)	12.6(2)

Table S3. Composite designation and fit parameters for luminescence intensity decay measurements (time correlated single photon counting (TCSPC)) of SPIONs@EuMOF- x composites synthesized with different MOF:SPIONs weight ratios. The intensity of the emission band at $\lambda_{\text{em}} = 616$ nm ($\lambda_{\text{exc}} = 317$ nm) was determined in dependence of time after excitation pulse t . The intensity decay was fitted monoexponentially using $y = A + B_1 \cdot \exp(-t/\tau)$ with τ as luminescence lifetime. The goodness of fit was evaluated with χ^2 .

Designation	A	B ₁	τ [ms]	χ^2
SPIONs@EuMOF-0.5	1.36(9)	9866(6)	0.4235(3)	1.116
SPIONs@EuMOF-1	2.84(10)	9917(6)	0.4207(3)	1.242
SPIONs@EuMOF-2	1.80(8)	9863(6)	0.4061(3)	1.293
SPIONs@EuMOF-4	4.48(11)	9480(6)	0.4108(4)	1.446
SPIONs@EuMOF-8	5.26(01)	9646(6)	0.4064(3)	1.276
SPIONs@EuMOF-10	4.03(11)	9660(6)	0.4054(4)	1.295
${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$	3.2(2)	9990(5)	0.4380(3)	1.051

Table S4. Designations of the synthesized composites comprising ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Eu-BDC), or ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Tb-BDC), or a mixture of both and SPIONs (citrate-stabilized at pH = 2.1) in defined MOF(s):SPIONs weight ratios besides their CIE chromaticity coordinates *xy* and emission color before and after applying the correction regarding absorbance of SPIONs according to Equation 4, as well as the chromaticity coordinates and emission color of pure Eu-BDC and Tb-BDC treated analogously to the synthesis of the composites.

Composite designation	CIE chromaticity coordinates before absorption correction		Chromaticity	CIE chromaticity coordinates after absorption correction		Chromaticity
	x	y		x	y	
Eu-BDC	0.652	0.336		-	-	
SPIONs@EuMOF-0.5	0.657	0.332		0.646	0.330	
SPIONs@EuMOF-1	0.662	0.334		0.656	0.336	
SPIONs@EuMOF-2	0.663	0.335		0.660	0.338	
SPIONs@EuMOF-4	0.665	0.334		0.662	0.336	
SPIONs@EuMOF-8	0.663	0.336		0.660	0.338	
SPIONs@EuMOF-10	0.659	0.336		0.652	0.337	
SPIONs@EuTbMOF-4	0.469	0.493		0.420	0.520	
SPIONs@TbMOF-4	0.366	0.577		0.330	0.590	
Tb-BDC	0.332	0.589		-	-	

Table S5. Composite designations, luminescent compounds, amounts of luminescent MOF, amounts and stabilization pH values of SPIONs, as well as used solvents and their amounts for typical syntheses of SPIONs@LnMOF-*x* composites.

Composite designation	Luminescent MOF	Amount of MOF [mg]	Amount of SPIONs [mg]	Stabilization pH of SPIONs	Solvent
SPIONs@EuMOF-0.5	Eu-BDC	24	48	2.1	1.2 mL water
SPIONs@EuMOF-1	Eu-BDC	36	36	2.1	1.2 mL water
SPIONs@EuMOF-2	Eu-BDC	48	24	2.1	1.2 mL water
SPIONs@EuMOF-4	Eu-BDC	40	10	2.1	0.8 mL water
SPIONs@EuMOF-8	Eu-BDC	62	8	2.1	1.2 mL water
SPIONs@EuMOF-10	Eu-BDC	64	6	2.1	1.2 mL water
SPIONs@EuTbMOF-4	Eu-BDC / Tb-BDC	29 / 29	14	2.1	1.2 mL water
SPIONs@TbMOF-4	Tb-BDC	58	14	2.1	1.2 mL water
SPIONs@EuMOF-0.5		24	48	4.0	1.2 mL water
SPIONs@EuMOF-0.5	Eu-BDC	24	48	5.6	1.2 mL water
SPIONs@EuMOF-0.5		24	48	7.5	1.2 mL water
SPIONs@EuMOF-4		40	10	4.0	0.8 mL water
SPIONs@EuMOF-4	Eu-BDC	40	10	5.6	0.8 mL water
SPIONs@EuMOF-4		40	10	7.5	0.8 mL water
SPIONs@EuMOF-4	Eu-BDC	40	10	2.1	0.8 mL ethanol
SPIONs@EuMOF-4		57	14	2.1	1.2 mL cyclohexane

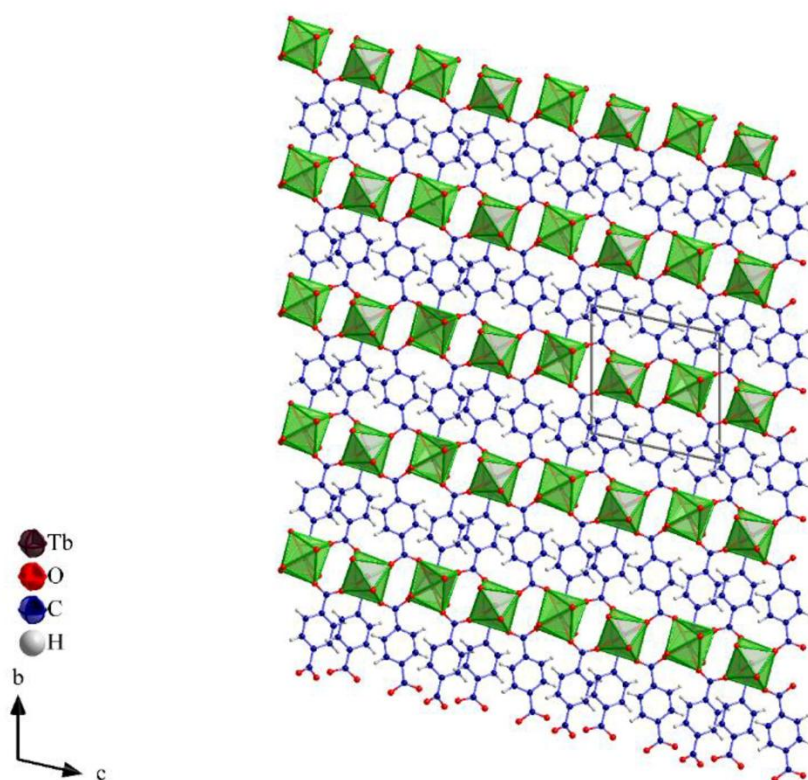


Figure S1. Graphical excerpt of the crystal structure of ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})]$ along the crystallographic *a* axis. The figure was created with Diamond 4.6.5 (Crystal Impact GbR) using published single crystal X-ray diffraction data.^[2]

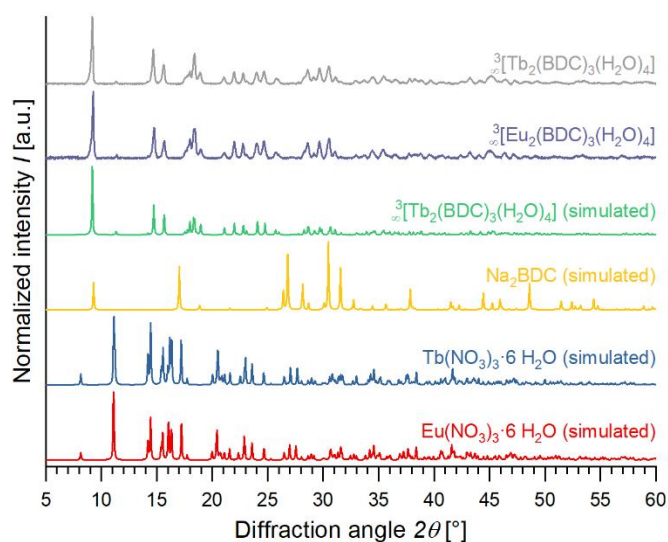


Figure S2. Powder X-ray diffractograms of the synthesized luminescent MOFs ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ and ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ in comparison to the diffractograms of $\text{Eu}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$,^[3] $\text{Tb}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$,^[4] and ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})]$,^[2] each simulated from single crystal X-ray diffraction data, as well as a diffraction pattern of Na_2BDC simulated from calculated single crystal structure obtained by synchrotron powder X-ray diffraction data.^[5]

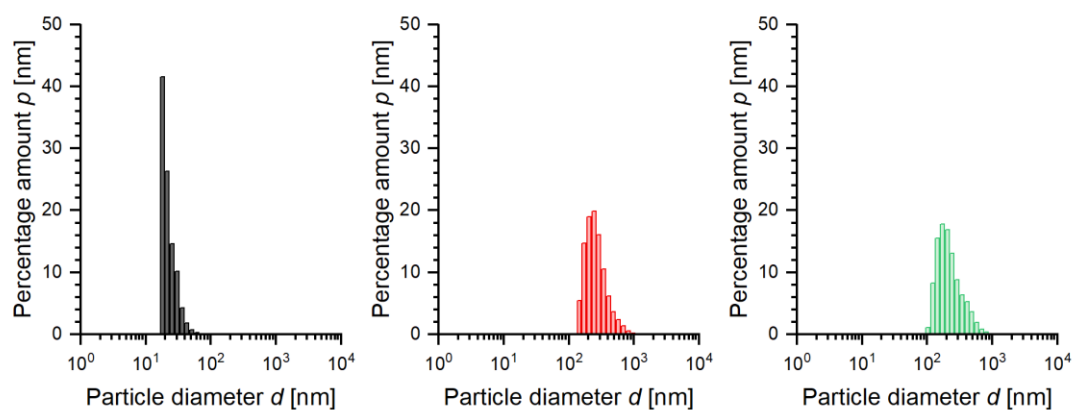


Figure S3. Distribution of hydrodynamic particle sizes of SPIONs citrate-stabilized at pH = 2.1 (left, black), ${}^3\text{[Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4\text{]}$ (center, red), and ${}^3\text{[Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4\text{]}$ (right, green).

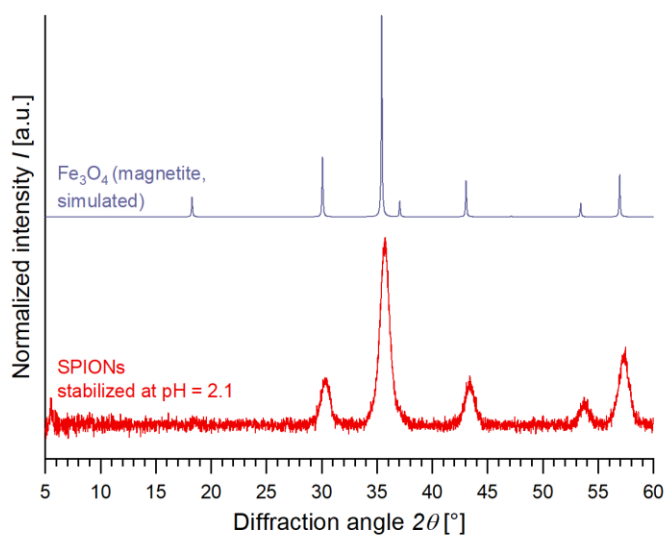


Figure S4. Powder X-ray diffractograms of iron oxide nanoparticles (SPIONs) stabilized with citric acid at a pH of 2.1, 4.0, 5.6 and 7.5 in comparison to the powder diffraction pattern of iron oxide in the magnetite structure simulated from single crystal X-ray diffraction data.^[6]

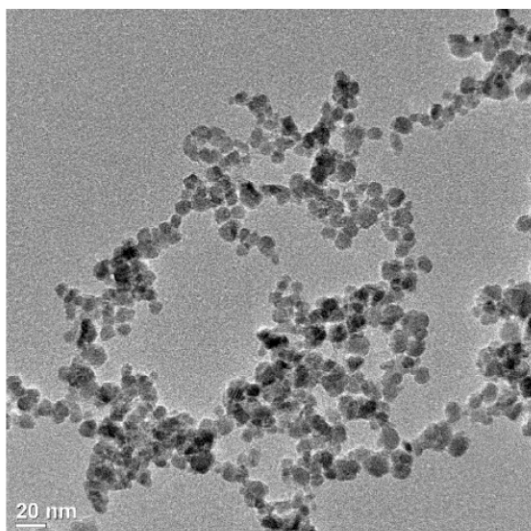


Figure S5. Transmission electron micrograph of superparamagnetic iron oxide nanoparticles (SPIONs) stabilized with citric acid at a pH of 4.0.

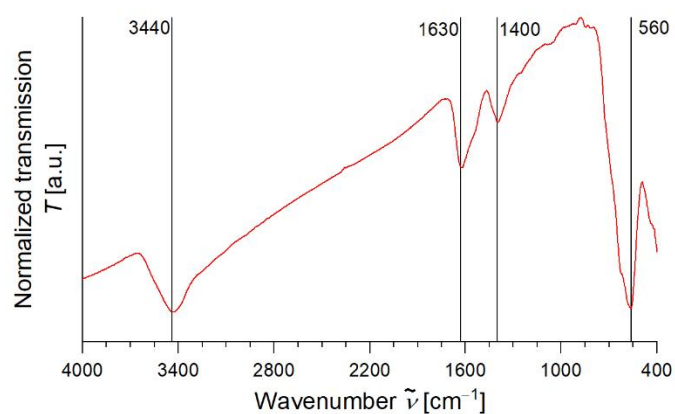


Figure S6. Infrared spectra of SPIONs stabilized with citric acid at a pH of 2.1. The observed bands can be assigned as follows:^[7] $\nu(\text{O-H}) = 3440 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{C=O}) = 1630 \text{ cm}^{-1}$, $\nu_{\text{s}}(\text{C=O}) = 1400 \text{ cm}^{-1}$, $\nu(\text{Fe-O}) = 560 \text{ cm}^{-1}$.

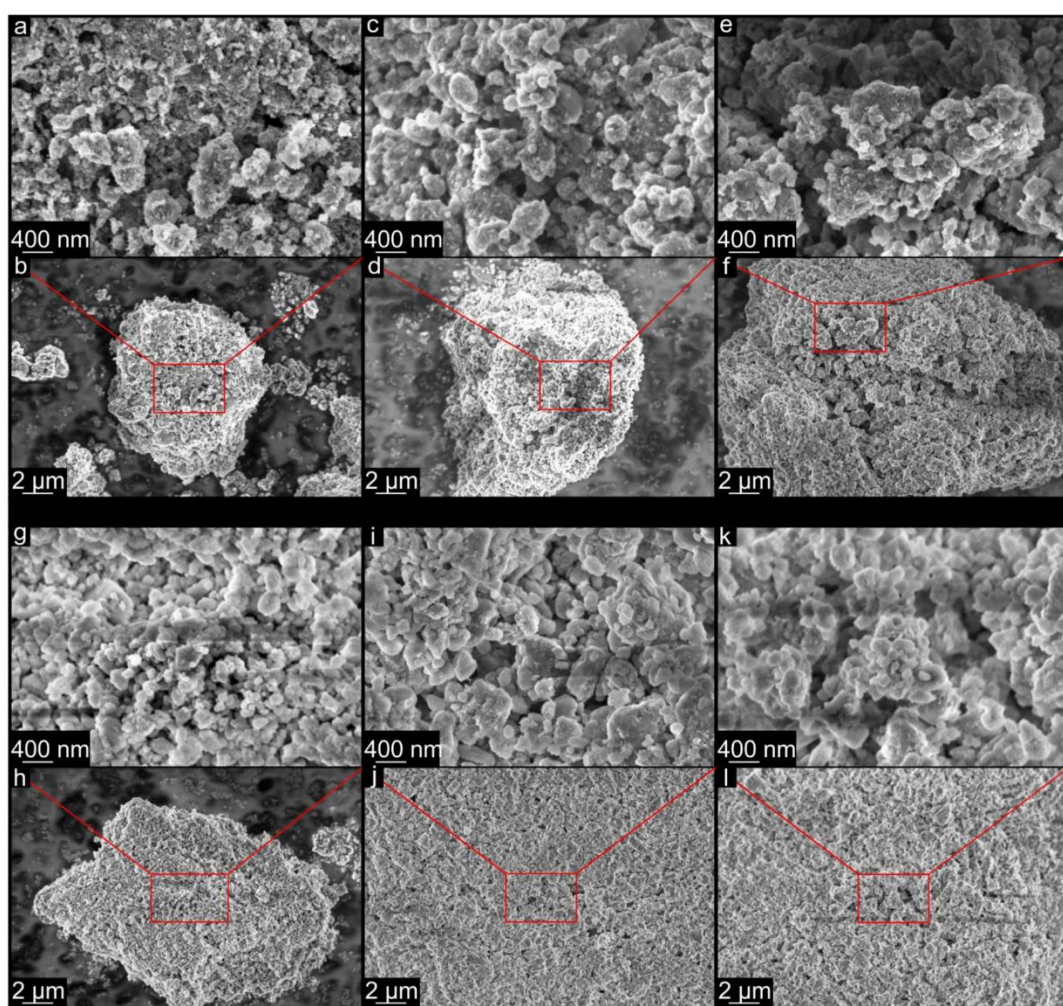


Figure S7. Scanning electron micrographs of synthesized SPIONs@EuMOF-*x* composites with different MOF:SPIONs weight ratios. a, b: SPIONs@EuMOF-0.5 (MOF:SPIONs = 0.5:1); c, d: SPIONs@EuMOF-1 (MOF:SPIONs = 1:1); e, f: SPIONs@EuMOF-2 (MOF:SPIONs = 2:1); g, h: SPIONs@EuMOF-4 (MOF:SPIONs = 4:1); i, j: SPIONs@EuMOF-8 (MOF:SPIONs = 8:1); k, l: SPIONs@EuMOF-10 (MOF:SPIONs = 10:1).

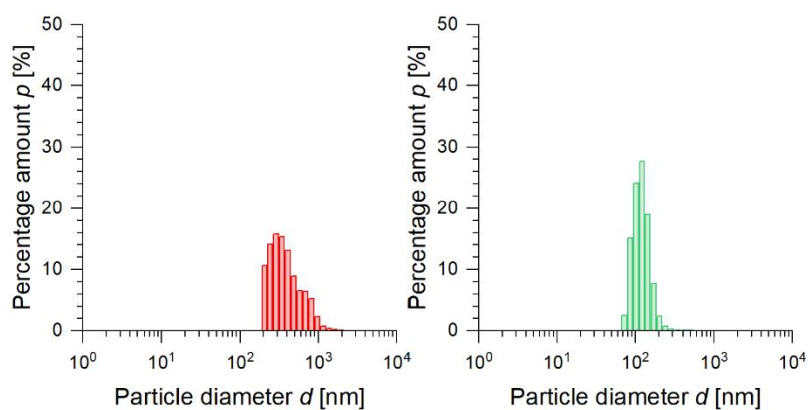


Figure S8. Hydrodynamic particle size distributions of SPIONs@EuMOF-4 (left, red) and SPIONs@TbMOF-4 composites (right, green).

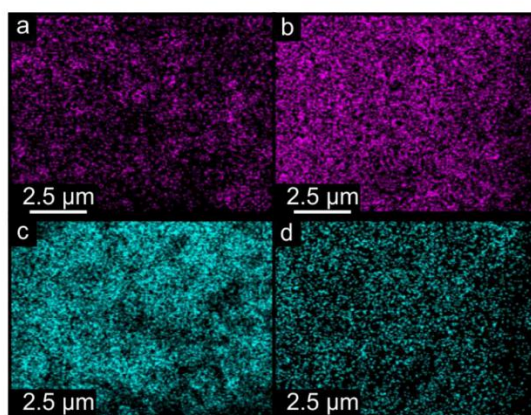


Figure S9: Energy dispersive X-ray (EDX) mappings of Eu M_{α} (a, b) and Fe $L_{\alpha1,2}$ (c, d) radiation of the composites SPIONs@EuMOF-0.5 (a, c) and SPIONs@EuMOF-10 (b, d).

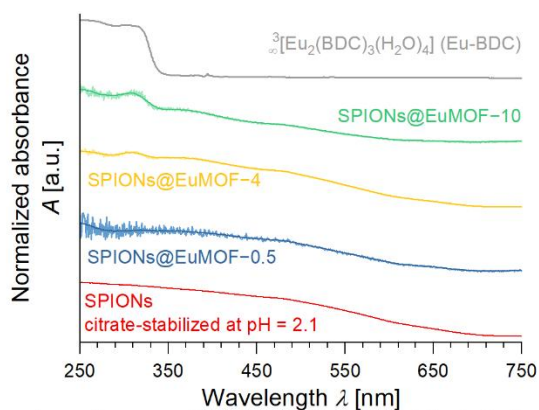


Figure S10. Absorbance spectra of pure iron oxide nanoparticles (SPIONs), citrate-stabilized at pH = 2.1, in comparison to the absorbance spectra of the composites SPIONs@EuMOF-0.5, SPIONs@EuMOF-4, and SPIONs@EuMOF-10, as well as the absorbance spectrum of $3[Eu_2(BDC)_3(H_2O)_4]$ (Eu-BDC). The absorbance spectra of the composites have been smoothed.

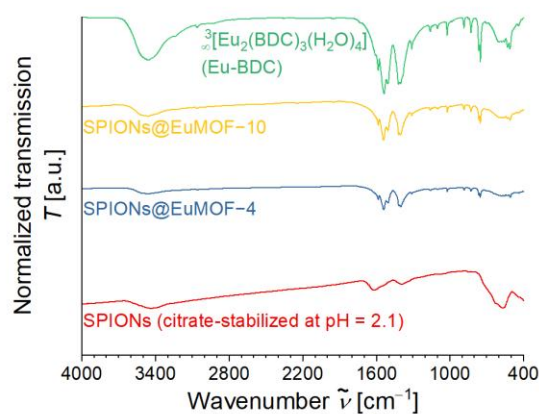


Figure S13. IR spectra of SPIONs@EuMOF-4 and SPIONs@EuMOF-10 composites in comparison to spectra of iron oxide nanoparticles (SPIONs) citrate-stabilized at pH = 2.1 and pure Eu-BDC.

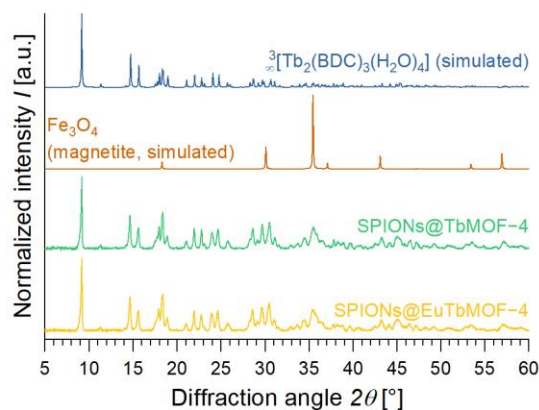


Figure S14. Powder X-ray diffraction pattern of a composite comprising a mixture of ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Tb-BDC) and ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (1:1) and SPIONs citrate-stabilized at pH = 2.1 in a MOFs:SPIONs weight ratio of 4:1 (SPIONs@EuTbMOF-4), as well as a composite comprising Tb-BDC and SPIONs in a MOF:SPIONs ratio of 4:1 (SPIONs@TbMOF-4) in comparison to diffraction patterns of iron oxide^[6] and ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$,^[2] both simulated from SCXRD data.

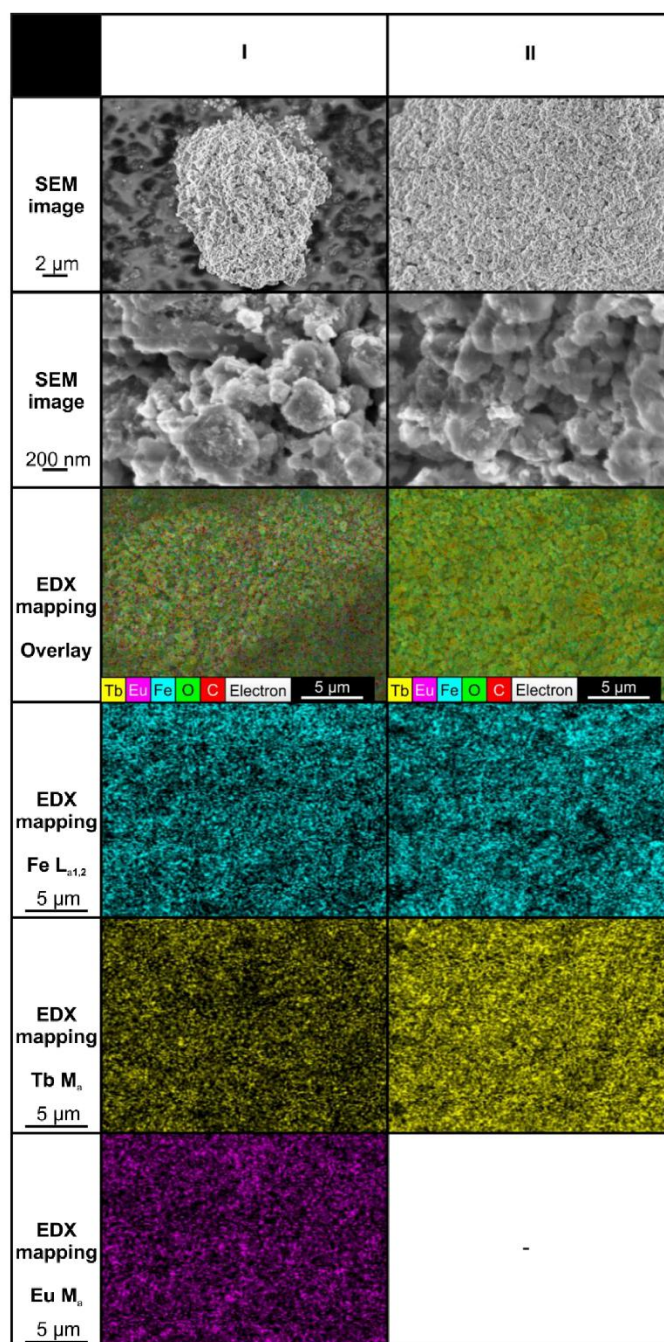


Figure S15. Scanning electron micrographs and energy dispersive X-ray spectroscopy mappings of a composite comprising ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ and ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (1:1 weight ratio) as well as SPIONs citrate-stabilized at pH = 2.1 (I), besides SEM images and EDX mappings of a composite comprising ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ and SPIONs (II). Both composites were synthesized with a MOF:SPIONs weight ratio of 4:1.

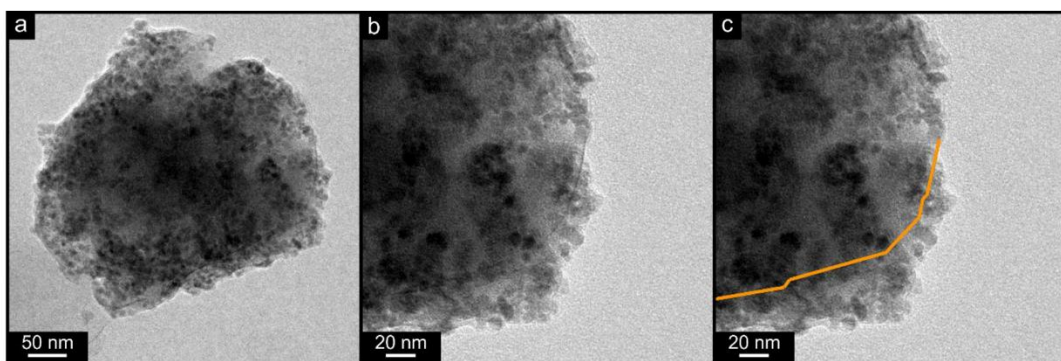


Figure S16. Transmission electron micrographs of isolated SPIONs@TbMOF-4 composites (a, b); a micrograph with surfaces of ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ highlighted, the surface coverage with SPION particles is imminent (c).

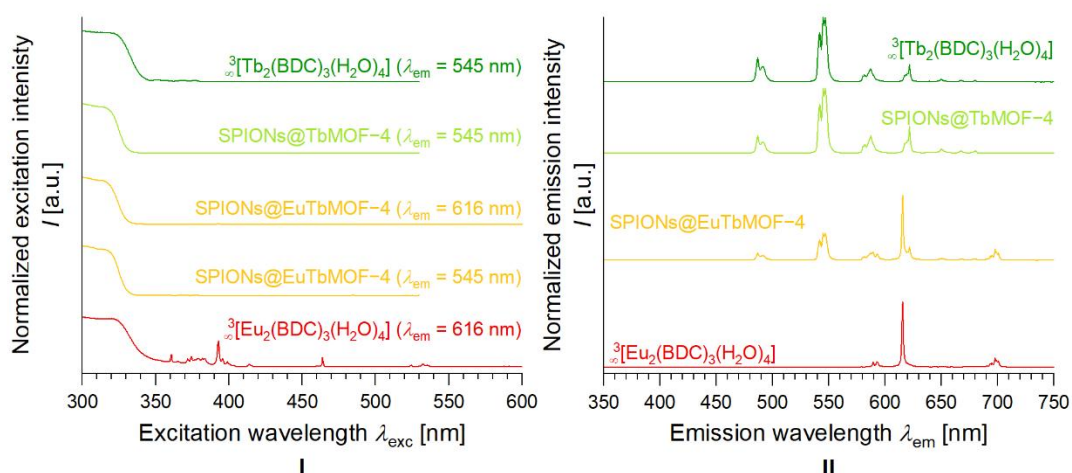


Figure S17. Excitation (I) and emission (II) spectra of synthesized composites SPIONs@EuMOF-4, SPIONs@EuTbMOF-4, SPIONs@TbMOF-4 besides the spectra of pure ${}^3[\text{Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (Ln = Tb, Eu).

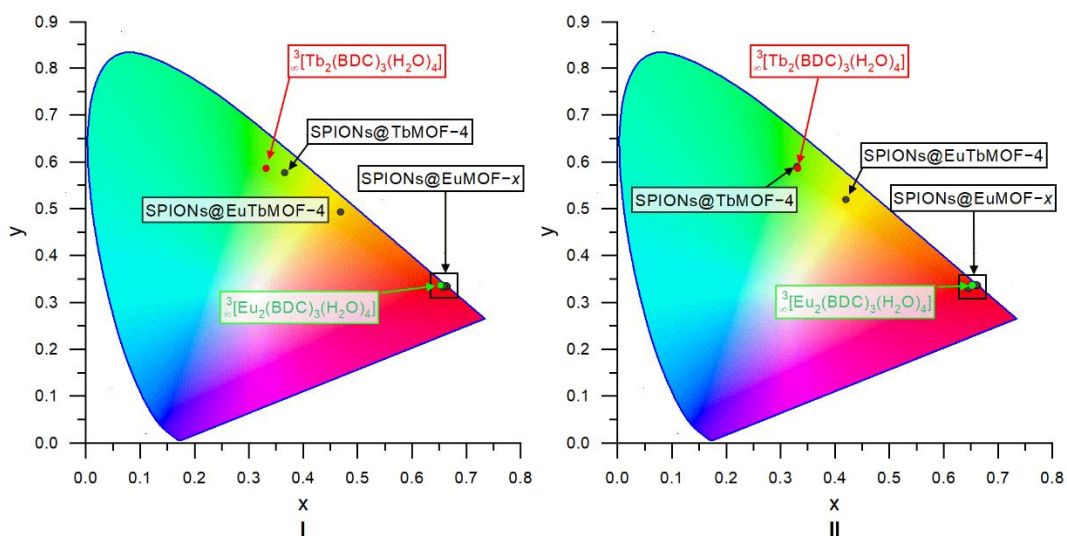


Figure S18. CIE chromaticity diagrams with inserted chromaticity coordinates xy of ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$, ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$, SPIONs@EuMOF- x composites, SPIONs@EuTbMOF-4, and SPIONs@TbMOF-4 before (I) and after (II) applying an absorption correction (see Equation 4 in the manuscript) corresponding to the absorbance A (see Figure S8) of iron oxide nanoparticles citrate-stabilized at pH = 2.1.

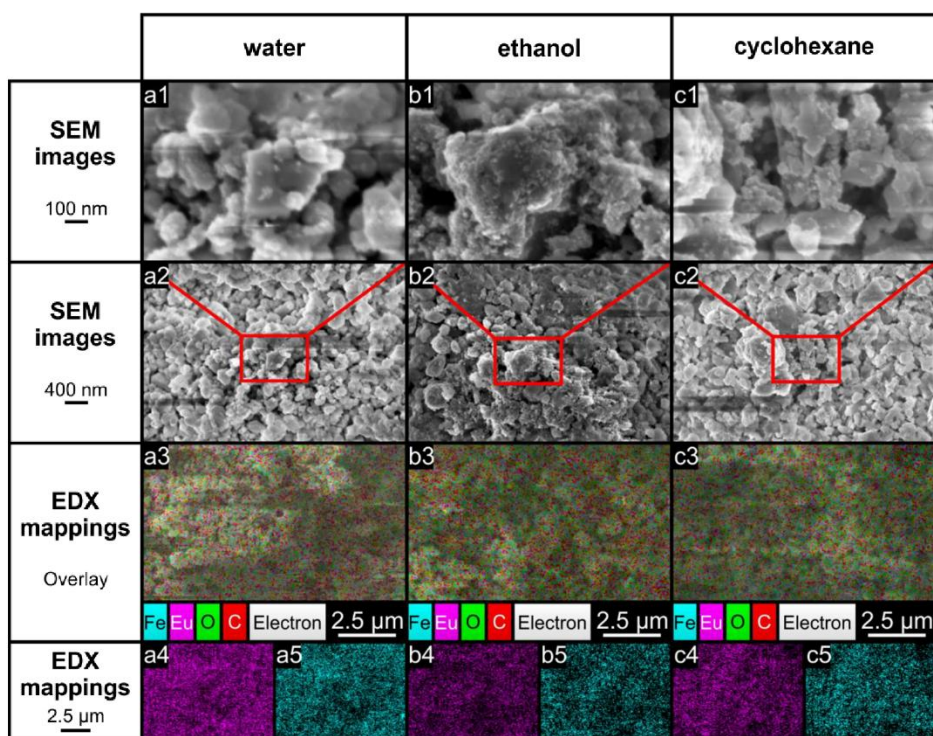


Figure S19. Scanning electron micrographs (indices 1 and 2), as well as EDX mappings (indices 3 and 4) of the composite systems SPIONs@EuMOF-4 containing iron oxide nanoparticles (SPIONs) stabilized at a pH of 2.1 synthesized in water (a), ethanol (b), and cyclohexane (c). An overlay of the detected characteristic X-ray radiations (indices 3) of Eu (M_a , magenta), Fe ($L_{\alpha 1,2}$, cyan), O ($K_{\alpha 1}$, green) and C ($K_{\alpha 1,2}$, red), and mappings of characteristic X-ray radiations of Eu (M_a , magenta, indices 4) and Fe ($L_{\alpha 1,2}$, magenta, indices 5) are depicted.

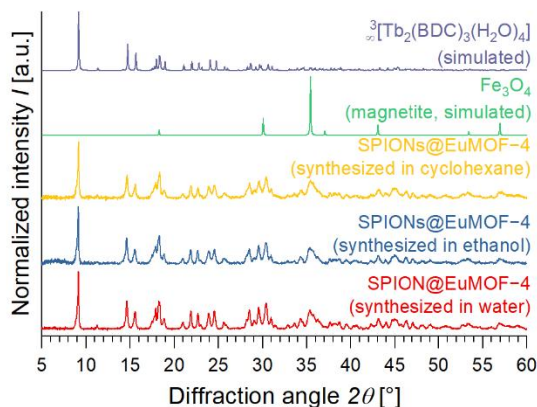


Figure S20. Powder X-ray diffraction pattern of composites comprising $3[Eu_2(BDC)_3(H_2O)_4]$ (Eu-BDC) and iron oxide nanoparticles (SPIONs) citrate-stabilized at pH = 2.1 in a MOF:SPIONs weight ratio of 4:1 synthesized in different solvents in comparison to diffraction patterns of iron oxide^[6] and $3[Tb_2(BDC)_3(H_2O)_4]$ ^[2] both simulated from SCXRD data.

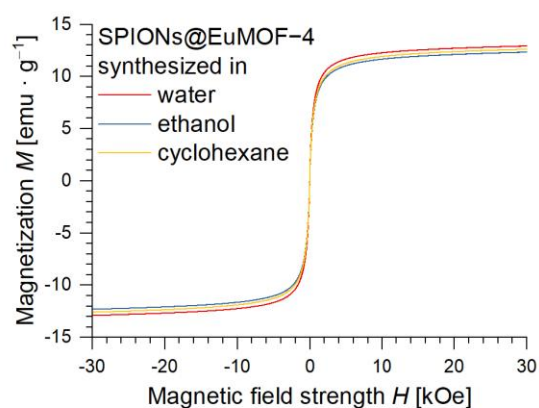


Figure S21. Magnetization curves of SPIONs@EuMOF-4 composites synthesized in different solvents.

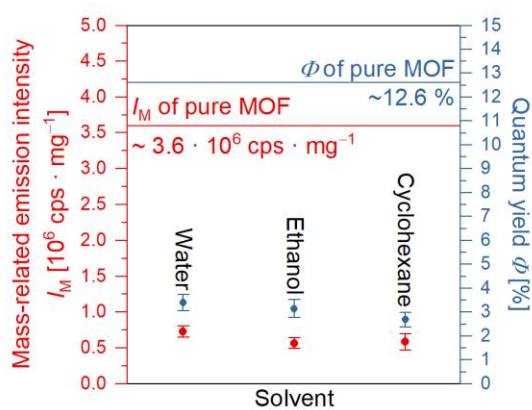


Figure S22. Mass-related emission intensity I_M ($\lambda_{em} = 616$ nm, $\lambda_{exc} = 317$ nm, red) and quantum yields ϕ ($\lambda_{em} = 550$ -725 nm, $\lambda_{exc} = 317$ nm, blue) of SPIONs@EuMOF-4 composites synthesized in different solvents in comparison to I_M and ϕ of pure Eu-BDC MOF.

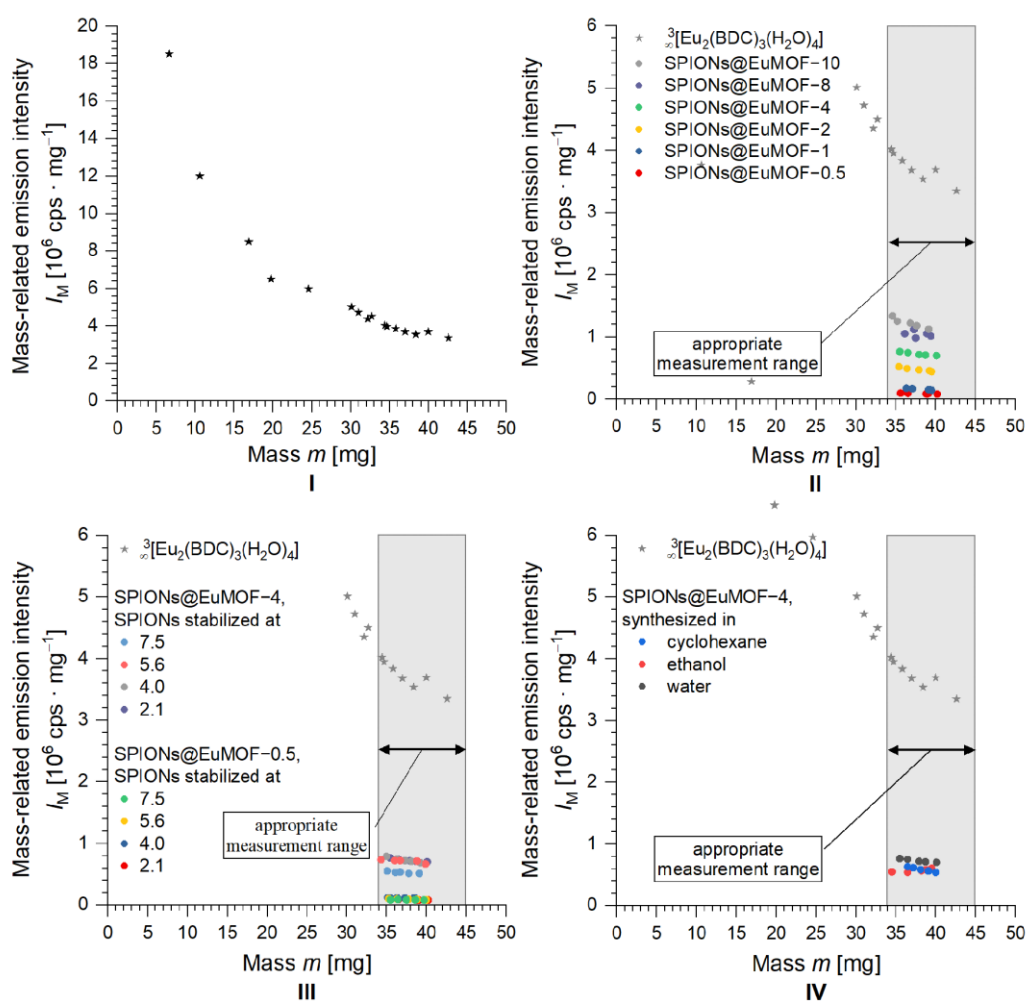


Figure S23. Mass-related emission intensity I_M in dependence of used masses for the emission measurements of synthesized, pure MOF ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ (I), SPIONs@EuMOF- x composites with different MOF:SPIONs weight ratios (II), SPIONs@EuMOF-4 and SPIONs@EuMOF-0.5 composites synthesized with SPIONs stabilized at different pH values (III), and SPIONs@EuMOF-4 composites synthesized in different solvents (IV).

3. Further Investigations on Property Dependencies

3.1 Influence of the pH-Value During Stabilization of Iron Oxide Nanoparticles on the Properties of Inverse Core-Satellite Composites

Citric acid, as a multiple proton carboxylic acid, in principle offers another option to adjust the composite system's properties. The three carboxyl functionalities allow binding to the iron oxide particle or – in case of the described functionalization of nanoparticles – to the luminescent MOF. Thereby, the protonation grade of the carboxyl functionalities can play a crucial role for the bonding to the iron oxide nanoparticles or the MOF. Citric acid exists in four possible species containing differently protonated carboxyl groups, whereby these functionalities are fully protonated (H_3Cit), deprotonated at one (H_2Cit^-) or two functionalities ($HCit^{2-}$), or fully deprotonated (Cit^{3-}) depending on the pH value. These species can be assigned to three pK_a values ($pK_{a1} = 3.128$, $pK_{a2} = 4.761$, $pK_{a3} = 6.396$).^[9] All these species in solution are in equilibrium, which depends on the pH value. The percentage α_m of each species i at a certain pH can be calculated by utilizing the following equations:

$$\alpha_m = \frac{[H_3O^+]^{3-m}}{D_n} \cdot \prod_{i=0}^3 K_{ai} \quad (S1)$$

$$D_n = [H_3O^+]^3 + K_{a1}[H_3O^+]^2 + K_{a1}K_{a2}[H_3O^+] + K_{a1}K_{a2}K_{a3} \quad (S2)$$

with m being the number of protons in the respective species, and K_{ai} the dissociation constant K_a of the species i . To investigate the influence of these different deprotonation grades, the pH value has been adjusted to 2.1, 4.0, 5.6, or 7.5 during the stabilization reaction. This results in one of the above-described deprotonation grades of citric acid being the majority species (see Figure S24).

It should be mentioned, that at high pH values, the OH group can play a role in coordination to the iron oxide surface as well.^[10] However, due to the chosen pH range from 2.1 to 7.5 in this work, this species is neglected here. Powder X-ray diffraction (Figure S25), infrared spectroscopy (Figure S26), UV-vis absorbance spectra (Figure S27) and magnetization measurements (Figure S28) reveal no significant difference between pure iron oxide nanoparticles citrate-stabilized at different pH values. Hydrodynamic particle diameters were determined to 21 nm (± 10 nm), 23 nm (± 11 nm), 23 nm (± 10 nm), and 24 nm (± 11 nm) for SPIONs citrate-stabilized at 2.1, 4.0, 5.6, and 7.5 (Figure S29). Considering a solvent shell around the magnetic particles, these sized correspond with the particle size of SPIONs citrate-stabilized at pH = 4.0 observed by transmission electron microscopy (see Figure S5).

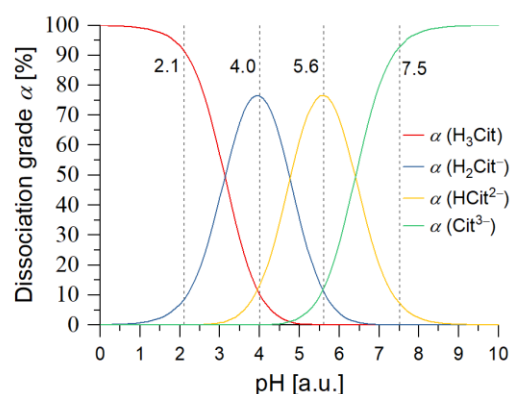


Figure S24. Graphical display of the calculated percentages α of the differently protonated species of citric acid (H_3Cit , H_2Cit^- , $HCit^{2-}$, Cit^{3-}) depending on the pH value according to Equation S1 and S2.

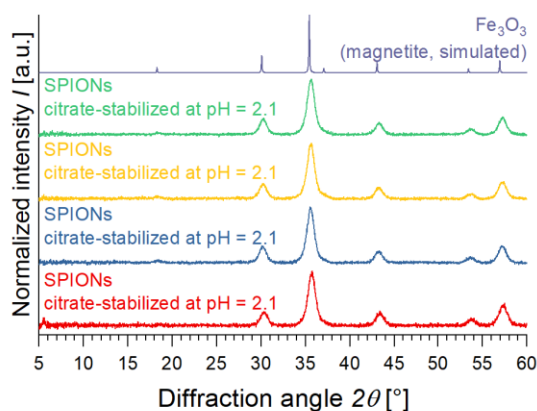


Figure S25. Powder X-Ray diffractogram of magnetite simulated from single crystal X-ray diffraction data^[6] in comparison to the diffractograms of SPIONs citrate-stabilized at pH values of 2.1, 4.0, 5.6 and 7.5.

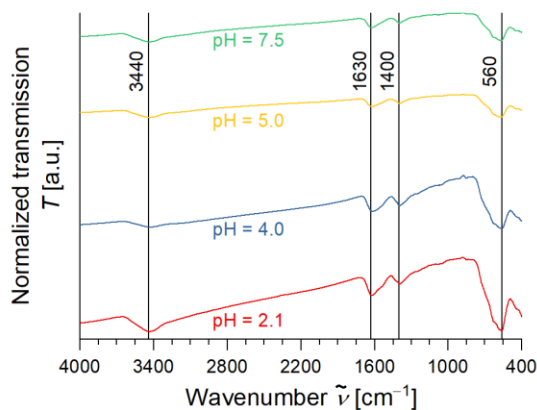


Figure S26. Infrared spectra of SPIONs stabilized with citric acid at a pH of 2.1 (red), 4.0 (blue), 5.0 (yellow), and 7.5 (green). The observed bands can be assigned as follows:^[7] $\nu(O-H) = 3440\text{ cm}^{-1}$, $\nu_{as}(C=O) = 1630\text{ cm}^{-1}$, $\nu_s(C=O) = 1400\text{ cm}^{-1}$, $\nu(Fe-O) = 560\text{ cm}^{-1}$.

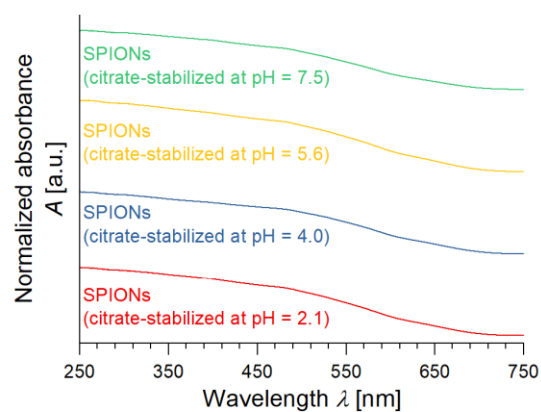


Figure S27. Absorbance spectra of pure iron oxide nanoparticles citrate-stabilized at pH values of 2.1, 4.0, 5.6, and 7.5.

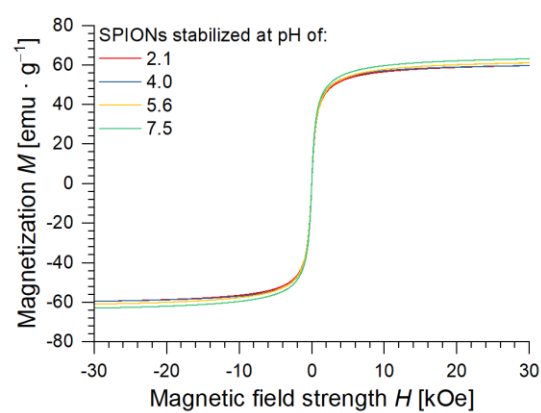


Figure S28. Magnetization curves of iron oxide nanoparticles (SPIONs) citrate-stabilized at different pH values.

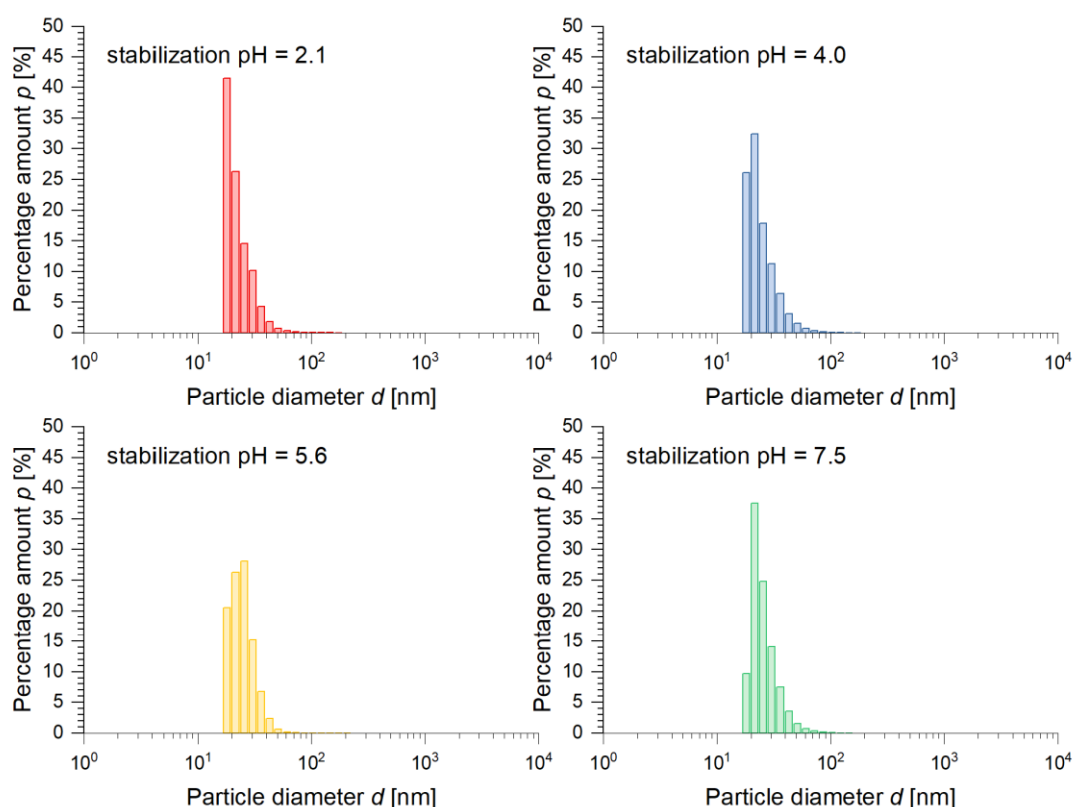


Figure S29. Hydrodynamic particle size distributions of SPIONs citrate-stabilized at a pH of 2.1 (top left, red), 4.0 (top right, blue), 5.6 (bottom left, orange), and 7.5 (bottom right, green).

A subsequent functionalization of Eu-BDC – analogously to the procedure for the previously discussed composites – with the differently stabilized nanoparticles in an exemplary MOF:SPIONs weight ratio of 4:1 again results in luminomagnetic composites (see Figure S30). Both, composition and inverse core-satellite structuring, as well as homogeneous element distribution of the resulting composites were confirmed by PXRD (see Figure S31) and SEM/EDX (see Figure S32) in analogy to the manuscript. Only minor differences in photophysical properties I_M and Φ of the composites can be observed (Figure S33). Thereby, the lower mass-related emission intensity of SPIONs@EuMOF-4 with SPIONs citrate-stabilized at a pH of 7.5 can be explained by a deviation of the weight ratio of the constituents to the desired 4:1 for MOF:SPIONs. The respective luminescence property determinations were repeated several times with freshly synthesized composites SPIONs@EuMOF-4 containing SPIONs stabilized at pH values of 2.1, 4.0 and 7.5 revealing no significant differences relative to one another. Additionally, the luminescence lifetime was again determined to approximately 0.4 ms (see Table S6) for each composite. This coincides with lifetimes reported in the literature^[11] and is therefore in good agreement with the results described within the manuscript.

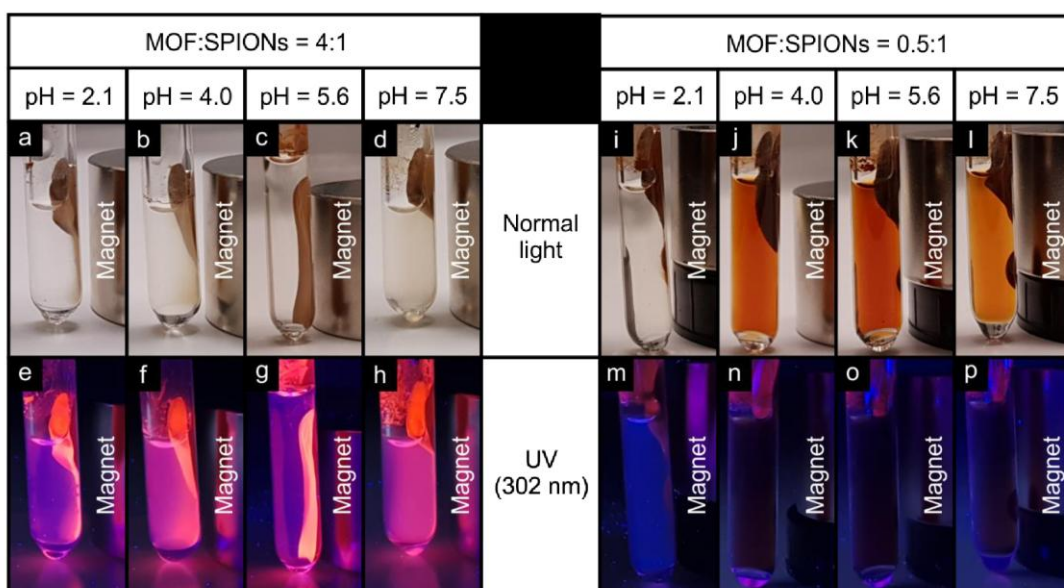


Figure S30. Composites synthesized with SPIONs stabilized at a pH of 2.1 (a, e, i, m), 4.0 (b, f, j, n), 5.6 (c, g, k, o), or 7.5 (d, h, l, p) under normal light (a – d, i – l) and UV excitation ($\lambda_{exc} = 302$ nm, e – h, m – p). The MOF:SPIONs ratio was held constant at 4:1 (a – h) and 0.5:1 (i – p), respectively.

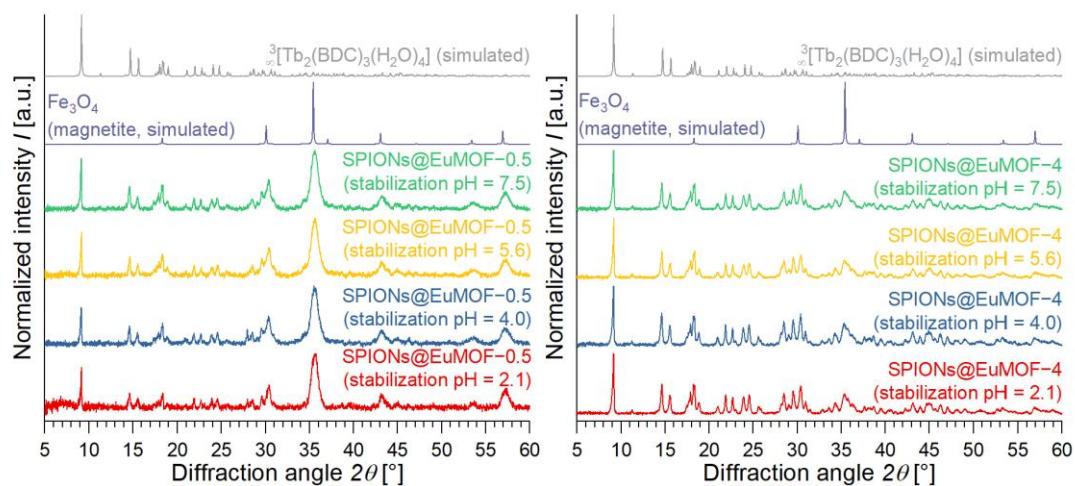


Figure S31. Powder X-ray diffractograms of the composite systems SPIONs@EuMOF-0.5 (I) and SPIONs@EuMOF-4 (II) comprising ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ and SPIONs citrate-stabilized at pH values of 2.1, 4.0, 5.6 and 7.5 in comparison to the diffractograms of ${}^3[\text{Tb}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ ^[2] and magnetite,^[6] both simulated from respective single crystal X-ray data.

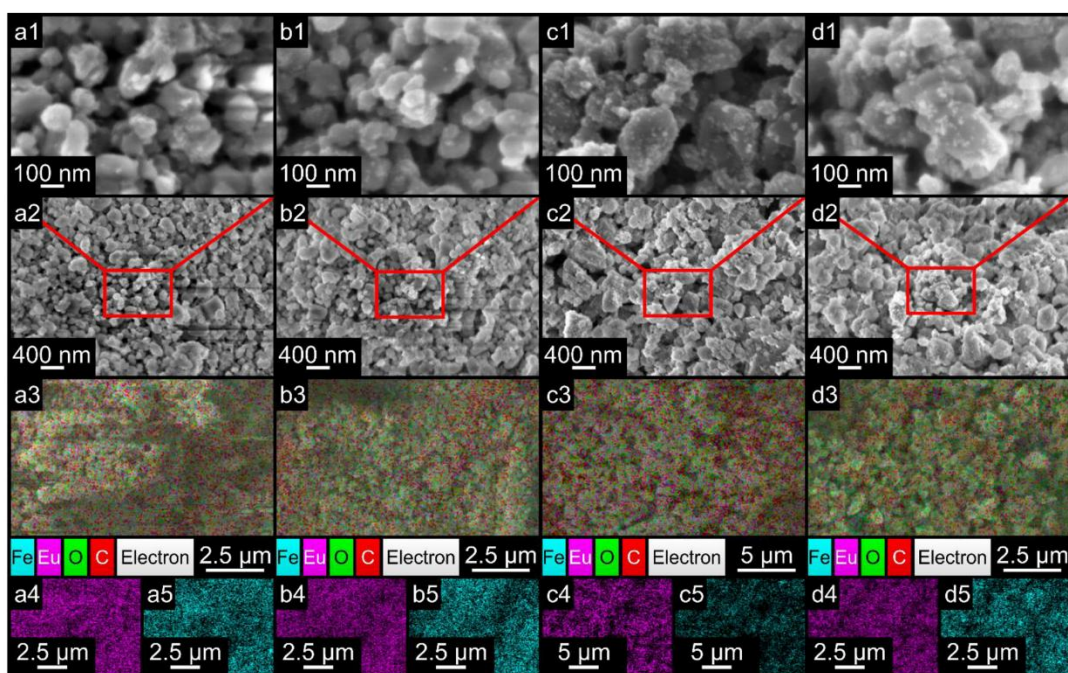


Figure S32. Scanning electron micrographs (indices 1 and 2) as well as EDX mappings (indices 3, 4, and 5) of the composite systems SPIONs@EuMOF-4 containing iron oxide nanoparticles (SPIONs) stabilized at a pH of 2.1 (a), 4.5 (b), 5.6 (c), and 7.5 (d). An overlay (a3, b3, c3, d3) of the detected characteristic X-ray radiations of Eu (M_a), Fe ($L_{a1,2}$), O (K_{a1}) and C ($K_{a1,2}$), and mappings of the Fe $L_{a1,2}$ (a4, b4, c4, d4) and Eu M_a (a5, b5, c5, d5) are depicted.

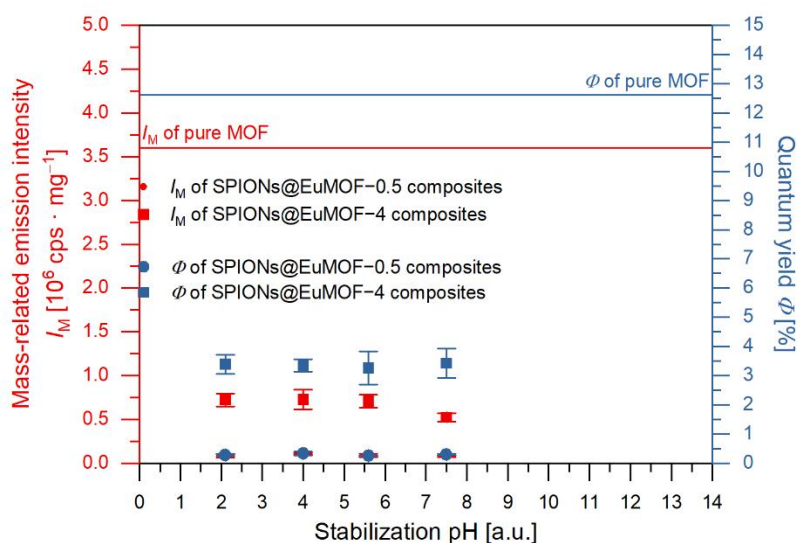


Figure 33. Mass-related emission intensity I_M ($\lambda_{em} = 616$ nm, $\lambda_{exc} = 317$ nm, red) and quantum yields ϕ ($\lambda_{em} = 550-725$ nm, $\lambda_{exc} = 317$ nm, blue) of composites comprising of $3[Eu_2(BDC)_3(H_2O)_4]$ and SPIONs citrate-stabilized at a pH value of 2.1, 4.0, 5.6, and 7.5 in a MOF:SPIONs ratio of 0.5:1 (SPIONs@EuMOF-0.5, dots) and 4:1 (SPIONs@EuMOF-4, squares). The error bars correspond to 3σ .

Table S6. Stabilization pH of SPIONs used for composites SPIONs@EuMOF-4, recorded mass-related emission intensities I_M , quantum yields Φ , and the fit parameters A , B_1 and τ for determination of luminescence intensity decay (time correlated single photon counting (TCSPC)). The intensity of the emission band at $\lambda_{em} = 616$ nm ($\lambda_{exc} = 317$ nm) was determined in dependence of time after the excitation pulse t . The intensity decay was fitted monoexponentially using $y = A + B_1 \cdot \exp(t/\tau)$ with τ as luminescence lifetime. The goodness of fit was evaluated with χ^2 . The deviation to values listed in Table S2 can be explained by instrumental fluctuations.

Stabilization pH	I_M [10^5 counts $\cdot$ s $^{-1}$ $\cdot$ mg $^{-1}$]	Φ [%]	A	B_1	τ [ms]	χ^2
2.1	4.3(5)	2.28(5)	0.52(7)	9809(6)	0.4265(3)	1.282
4.0	4.8(9)	2.31(3)	1.04(9)	9793(6)	0.4284(3)	1.160
7.5	4.9(4)	2.09(3)	0.17(9)	9629(6)	0.4277(3)	1.228

When the MOF:SPIONs weight ratio is adjusted to 0.5:1, again inverse core-satellite composites are obtained for all tested stabilization pH values (see Figure S34). However, a brown coloration of the solvent is observable for stabilization pH values above 2.1 (see Figure S30). The coloration of the solvent already indicates iron oxide nanoparticles, which are not contacted to the MOF. This can be explained by NH_4^+ ions and NH_3 being present due to the stabilization reaction conditions. In principle, during the particle synthesis and stabilization, an equilibrium between citric acid, water and ammonia at the iron oxide surface exists. At a pH of 2.1, water is replaced by citric acid, which binds to iron oxide by hydrogen bonds to the Fe-OH functionalities.^[12] The carboxylic functionalities can establish a bond to the metal-organic framework during the subsequent functionalization reaction. Increasing the pH with aqueous ammonia, citric acid is deprotonated leading to a coordination of one or two carboxylic functionalities to the iron ions of the magnetic particle. However, a certain amount of ammonia binds to the carboxyl groups as well^[12] preventing them from establishing a bond to the MOF, which explains a certain amount of SPIONs not being attached to the MOF crystallites and hence remaining in colloidal dispersion. This assumption is confirmed by observation of the Tyndall effect for the separated liquid phases of the syntheses of SPIONs@EuMOF-0.5 composites containing SPIONs stabilized at pH = 5.6 and 7.5 (see Figure S35). After applying a magnetic field for several days, the dispersions cleared up and a dark brown solid is collected at the bottom of the vessel. As this solid is non-luminescent, it contains no MOF and hence consists of SPIONs only (see Figure S35). Since at pH = 2.1 no NH_4^+ and NH_3 is present, the carboxylic functionalities are not blocked and can establish a bond to the MOF unhindered, leading to the lack of a brown solvent coloration in case of SPIONs@EuMOF-0.5 (see Figure S30). However, the amount of SPIONs remaining in colloidal dispersion is too low to affect the magnetization of corresponding SPIONs@EuMOF-0.5 composites substantially (see Figure S36). These effects diminish when adjusting the MOF:SPIONs ratio to 4:1. Due to a lower amount of SPIONs in general, the amount remaining in dispersion diminishes as well leading to no observable solvent coloration.

In summary, neither the composite composition, inverse core-shell structure (see Figure S32 and Figure S34), photophysical properties (see Figure S33), nor magnetization (see Figure S36) are influenced significantly by different stabilization pH values of the SPIONs.

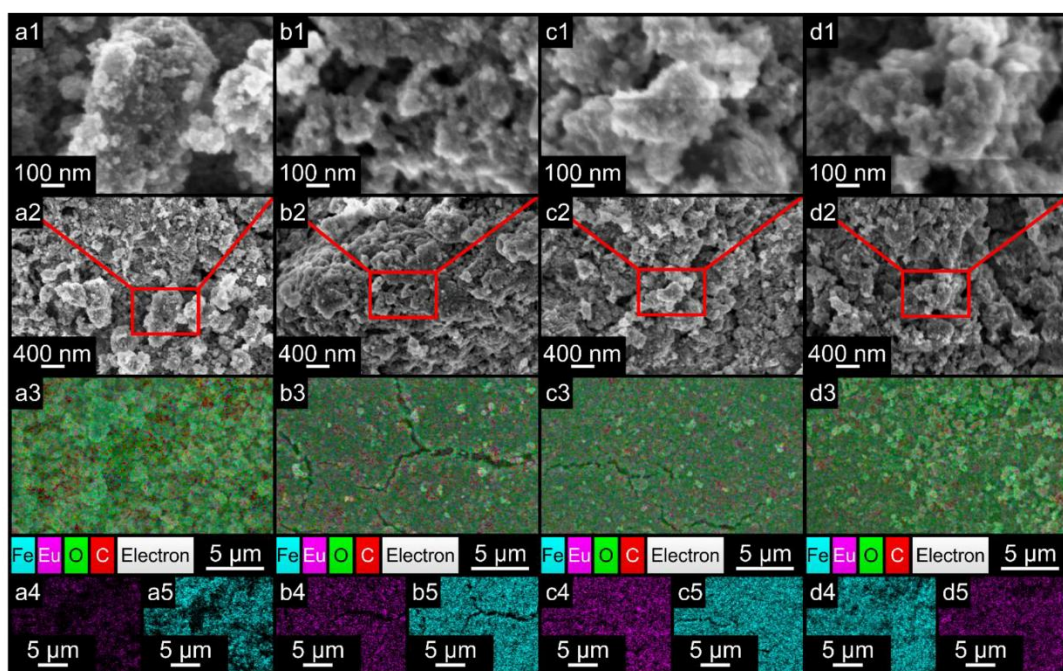


Figure S34. Scanning electron micrographs (indices 1 and 2) as well as EDX mappings (indices 3, 4, and 5) of the composite systems SPIONs@EuMOF-0.5 containing SPIONs citrate-stabilized at a pH of 2.1 (a), 4.5 (b), 5.6 (c), and 7.5 (d) (a-c). An overlay (a3, b3, c3, d3) of the detected characteristic X-ray radiations of Eu (M_{α}), Fe ($L_{\alpha 1,2}$), O ($K_{\alpha 1}$) and C ($K_{\alpha 1,2}$), and mappings of the Fe $L_{\alpha 1,2}$ (a4, b4, c4, d4) and Eu M_{α} (a5, b5, c5, d5) are depicted.

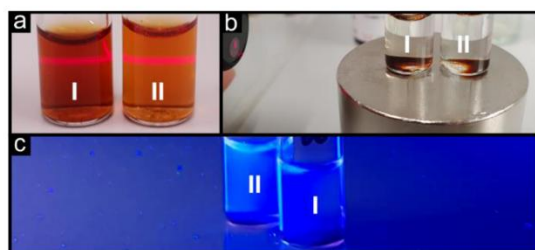


Figure S35. Photographs of the solvents after synthesis and magnetic separation of composites comprising ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ and SPIONs in a ratio of 0.5:1 (SPIONs@EuMOF-0.5) before (a) and after (b) applying an external magnetic field overnight, as well as the solvents after applying an magnetic field overnight under UV light (c, $\lambda_{\text{exc.}} = 302 \text{ nm}$). The iron oxide nanoparticles were citrate-stabilized before functionalization at pH values of 5.6 (I) and 7.5 (II).

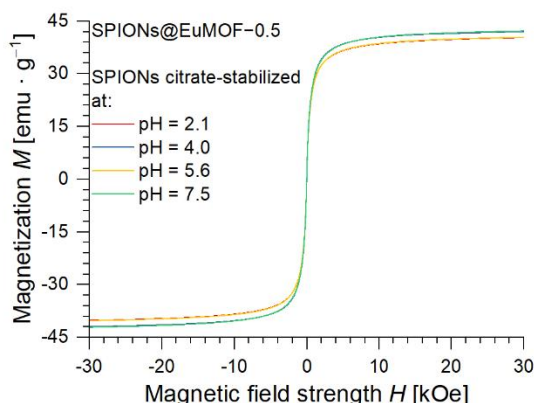


Figure S36. Magnetization curves for SPIONs@EuMOF-0.5 composites comprising ${}^3[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ and SPIONs citrate-stabilized at the listed pH values prior to functionalization.

3.2 Differences Between Formation of a Closed Shell or a Partly Coverage With Satellite Particles

In order to evaluate the differences between and the influence on the formation of a closed shell or a partly coverage with particles, the ratio of the composite components is an important parameter. In order to understand the molar ratio established in the composites, first, the composition of the pure, stabilized nanoparticles was determined. In case of SPIONs citrate-stabilized at pH = 2.1, an amount of 7.0 wt-% citric acid and 3.2 wt-% water was reported.^[12] Taking the molar masses of iron oxide (Fe_3O_4), citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and water to account, a sum formula of $(\text{Fe}_3\text{O}_4)_{10.6}(\text{H}_2\text{O})_{4.9}(\text{C}_6\text{H}_7\text{O}_7)_1$ can be assumed, corresponding to $\text{C}_6\text{H}_{17.8}\text{Fe}_{31.8}\text{O}_{54.3}$. Considering a measurement uncertainty of approximately 1 wt-%, this sum formula is confirmed by comparison of calculated and determined elemental wt-% of SPIONs citrate-stabilized at pH = 2.1 (see Table S7).

Table S7. Composite designations, calculated sum formulas (utilizing the assumed molar mass of SPIONs), and calculated (calcd.) elemental weight percentages of carbon, hydrogen and nitrogen in comparison to determined (found) elemental weight percentages of both, composites and pure citrate-stabilized SPIONs.

Substance	Calculated sum formula according to Equation 2 ^{a)}	C (calcd.) [wt-%]	C (found) [wt-%]	H (calcd.) [wt-%]	H (found) [wt-%]	N (calcd.) [wt-%]	N (found) [wt-%]
SPIONs@EuMOF-1	$(\text{Eu-BDC})_{3.1}(\text{SPIONs})_1$	17.80	17.67(8)	1.48	1.51(13)	0	0.06(8)
SPIONs@EuMOF-2	$(\text{Eu-BDC})_{6.3}(\text{SPIONs})_1$	23.01	22.93(2)	1.77	1.75(3)	0	0.17(3)
SPIONs@EuMOF-4	$(\text{Eu-BDC})_{12.6}(\text{SPIONs})_1$	27.09	26.83(4)	1.99	1.92(2)	0	0.00(0)
SPIONs@EuMOF-10	$(\text{Eu-BDC})_{31.5}(\text{SPIONs})_1$	30.42	29.8(2)	2.17	2.08(4)	0	0.18(4)
SPIONs (stabilized at pH = 2.1) $(\text{Fe}_3\text{O}_4)_{10.6}(\text{H}_2\text{O})_{4.9}(\text{C}_6\text{H}_7\text{O}_7)_1$		2.64	3.32(15)	0.66	0.69(3)	0.00	0.36(17)

^{a)} $\text{Eu-BDC} = \frac{1}{3}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4] = \text{C}_{24}\text{H}_{20}\text{Eu}_2\text{O}_{16}$, $\text{SPIONs} = (\text{Fe}_3\text{O}_4)_{10.6}(\text{H}_2\text{O})_{4.9}(\text{C}_6\text{H}_7\text{O}_7)_1 = \text{C}_6\text{H}_{17.8}\text{Fe}_{31.8}\text{O}_{54.3}$.

Taking this assumed sum formula and the resulting molar mass of SPIONs $M(\text{SPIONs}) = 2734.63 \text{ g} \cdot \text{mol}^{-1}$ to account, the molar ratio of Eu-BDC and SPIONs in the composites can be calculated in dependence of the component weight ratio x (see Table 1 within the manuscript) and the ratio of molar masses of the components according to

$$\frac{n(\text{Eu-BDC})}{n(\text{SPIONs})} = x \cdot \frac{M(\text{SPIONs})}{M(\text{Eu-BDC})} \quad (\text{S3})$$

with $n(\text{SPIONs})$ being the amount of SPIONs $(\text{Fe}_3\text{O}_4)_{10.6}(\text{H}_2\text{O})_{4.9}(\text{C}_6\text{H}_7\text{O}_7)_1$, $n(\text{Eu-BDC})$ the amount of Eu-BDC, and $M(\text{Eu-BDC})$ the molar mass of the MOF $\frac{1}{3}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$ ($868.33 \text{ g} \cdot \text{mol}^{-1}$). Utilizing Equation S3, sum formulas for the synthesized composites SPIONs@EuMOF-1, SPIONs@EuMOF-2, SPIONs@EuMOF-4, and SPIONs@EuMOF-10 can be assumed according to the formulas/ratios listed in Table 3. A comparison of the determined elemental weight percentages within the composites with calculated percentages shows good accordance, which substantiates the assumed sum formulas (see Table S7). Analogously, the molar ratios and sum formulas of all synthesized SPIONs@EuMOF- x composites can be calculated to the values listed in Table S8.

Altogether, the magnetization and luminescence intensity of inverse core-satellite composites comprising Eu-BDC and citrate-stabilized SPIONs can be varied by adjusting the ratio of the two components. Thereby, an inverse core-satellite structure is established independently from the chosen ratio of components. In contrast, the photophysical and magnet properties are directly influenced by different amounts of the constituents. By reducing

the amount of MOF, the luminescence intensity decreases according to Equation 1 (see main article) due to light absorption caused by the SPIONs part. Simultaneously, the saturation magnetization increases following a linear trend with regard to the component weight ratio. In combination with elemental analyses, this confirms, that the component ratio chosen for synthesis matches the ratio in the composites.

Table S8. Composite designation, MOF:SPIONs weight ratio (r_w), molar ratio r_m and resulting sum formula of synthesized SPIONs@EuMOF-x composites.

Composite	Applied weight ratio (MOF:SPIONs) r_w	Calculated molar ratio ^{a)} (MOF:SPIONs) r_m	Sum formula ^{b)}
SPIONs@EuMOF-0.5	0.5 : 1	1.6 : 1	(Eu-BDC) _{1.6} (SPIONs) ₁
SPIONs@EuMOF-1	1 : 1	3.1 : 1	(Eu-BDC) _{3.1} (SPIONs) ₁
SPIONs@EuMOF-2	2 : 1	6.3 : 1	(Eu-BDC) _{6.3} (SPIONs) ₁
SPIONs@EuMOF-4	4 : 1	12.6 : 1	(Eu-BDC) _{12.6} (SPIONs) ₁
SPIONs@EuMOF-8	8 : 1	25.2 : 1	(Eu-BDC) _{25.2} (SPIONs) ₁
SPIONs@EuMOF-10	10 : 1	31.5 : 1	(Eu-BDC) _{31.5} (SPIONs) ₁

^{a)} Molar ratios were calculated using the assumed molar mass of SPIONs $M(\text{SPIONs}) = 2734.63 \text{ g} \cdot \text{mol}^{-1}$

^{b)} Eu-BDC = $\frac{1}{3}[\text{Eu}_2(\text{BDC})_3(\text{H}_2\text{O})_4] = \text{C}_{24}\text{H}_{20}\text{Eu}_2\text{O}_{16}$; SPIONs = $(\text{Fe}_3\text{O}_4)_{10.6}(\text{H}_2\text{O})_{4.9}(\text{C}_6\text{H}_7\text{O}_7)_1$.

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7.3 Ergänzende Informationen zur dritten Publikation

Supplementary Information (SI) for Dalton Transactions.
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Homoleptic Coordination Polymers and Complexes of Transition Metals with 2-(1,2,4-1*H*-triazol-3-yl) pyridine and Tuning towards White-Light Emission

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1. Analytical Methods

1.1 Single Crystal X-ray diffractometry

All single crystal X-ray data were recorded at 100 K utilizing $\text{MoK}\alpha$ radiation ($\lambda = 71.073$ pm). Data for $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**), $[\text{FeCl}_2(\text{Hpt})_2]$ (**10**), $[\text{ZnCl}_2(\text{Hpt})_2]$ (**13**), $[\text{Zr}(\text{pt})_4]$ (**14**), $[\text{Fe}_2\text{Cl}_2(\text{pt})_2(\text{Py})_4]$ (**15**), $[\text{Fe}_2\text{Br}_2\text{Cl}_2(\text{pt})_2(\text{Py})_4]$ (**16**), $\frac{2}{3}[\text{Cu}_2\text{Cl}(\text{pt})]$ (**17**), $\frac{1}{2}[\text{MnCl}(\text{bpt})]$ (**18**), $\frac{1}{2}[\text{Co}_2\text{Cl}_3(\text{pt})(\text{H}_2\text{O})_2] \cdot 4\text{CyOH}$ (**19**), and $\frac{2}{3}[\text{Co}_2\text{Br}_2(\text{pt})_2]$ (**20**) were recorded using radiation on a BRUKER AXS D8 VENTURE with Incoatec μS micro-focus sealed tube as radiation source, Incoatec μS multilayer optics and a PHOTON III C14 detector and Oxford Cryosystems 800 low-temperature system. Data for $\frac{1}{2}[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (**8**) was acquired using $\text{MoK}\alpha 1$ radiation on a BRUKER AXS D8 VENTURE with Incoatec μS micro-focus sealed tube as radiation source, Incoatec μS multilayer optics and a PHOTON100 detector and an OXFORD CRYOSYSTEMS 700 low temperature system. Diffraction data for $[\text{MnCl}_2(\text{Hpt})]$ (**9**), $[\text{CoCl}_2(\text{Hpt})_2]$ (**11**), $[\text{CoBr}_2(\text{Hpt})_2]$ (**12**) were recorded using a BRUKER AXS Smart Apex 1 with graphite monochromator and Bruker Cryoflex cooling system. Measurements were performed utilizing the Bruker AXS Apex software package.¹ Data processing was carried out with XPREP.² Crystal structures were solved with SHELXT-2018.³ Obtained structures were refined with least square techniques utilizing SHELXL-2018⁴ with the graphical platform shelXle.⁵ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms (except those in H_2O within CP **21**) were assigned to idealized geometric positions and included in structure factor calculations. Graphical depictions of crystal structures were created with Diamond Version 4.6.8 (Crystal Impact GbR).⁶

Due to disordering, the solvent molecules (cyclohexanol) within $\frac{1}{2}[\text{Co}_2\text{Cl}_3(\text{pt})(\text{H}_2\text{O})_2] \cdot 4\text{CyOH}$ (**19**) were refined with help of restraints to achieve an appropriate structure model. Because of ligand disordering within $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**) and $\frac{1}{2}[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (**8**), the refinement of the ligand pt^- was performed with the aid of restraints. Since $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**) and $\frac{1}{2}[\text{MnCl}(\text{bpt})]$ (**18**) contain potential solvent-accessible voids, in which solvent molecules can be trapped without being ordered in a crystallographic manner, SQUEEZE algorithm⁷ of the Program PLATON⁸ was utilized to treat those molecules as diffuse contribution to overall scattering. Thereby, four voids with a total potential solvent accessible void volume of $842 \text{ \AA}^3$ and 215 electrons in each void were found within the unit cell. In case of **18**, three voids with a total volume of $2281 \text{ \AA}^3$ and 770, 775, and 776 electrons in total were found. The residual electron density of **20** was refined to $+2.0/-1.34 \text{ e} \cdot 10^{-6} \text{ pm}^{-3}$.

1.2 Powder X-ray diffractometry

For recording powder X-ray diffraction patterns, four different instruments were used: **1.:** BRUKER D8 DISCOVER with DaVinci design, a focusing Göbel mirror and a linear LynxEye detector utilizing DIFFRAC.SUITE (BRUKER AXS). **2.:** PANalytical X'Pert Pro equipped with a 0.04° Soller slit, a 10 mm beam mask, as well as an anti-scatter slit and divergence slit with 0.5° within the incident beam path, besides another 0.04° Soller slit, a Nickel Beta-filter, an anti-scatter slit of 0.5° and an X'Celerator detector within the diffracted beam path utilizing PANalytical Data Collector. **3.:** Stoe Stadi P equipped with a Ge(111) monochromator and a MYTHEN 1K strip detector (DECTRIS) utilizing software package WinXPOW. **4.:** Stoe Stadi P diffractometer equipped with Ge(111) monochromator, a Mythen 2K strip detector (DECTRIS) and a Stoe HT1 capillary furnace utilizing software package WinXPOW.

$\text{Cu-K}\alpha 1$ radiation was used in all three cases. Baseline corrections were performed using the DIFFRAC.EVA software (BRUKER AXS). All diffractograms were recorded from $5 - 60^\circ$ in 2θ . For temperature-dependent powder X-ray diffraction experiments, another Stoe Stadi diffractometer equipped with Ge(111) monochromator and a Stoe

HT1 capillary furnace was used. Samples were ground in an agate mortar and filled in quartz glass capillaries (Lindemann), which were placed within the HT1 furnace. In case of air-sensitive compounds, samples were ground with an agate mortar under inert atmosphere (glovebox filled with argon). Subsequently the powders were filled into glass capillaries (Lindemann), which were sealed with picein. The capillaries were positioned within the beam path of either the Bruker or the Stoe diffractometer.

Pawley refinements of recorded diffractograms were performed with BRUKER AXS Topas-Academic 7⁹ within the range of 5 – 50° in 2 θ .

1.3 Photoluminescence spectroscopy

Photoluminescence excitation and emission spectra were recorded with a Jobin Yvon Fluorolog 3 (Horiba), equipped with photomultiplier tube (R928P), and double-grated monochromators for both, excitation and emission. A Xe short-arc lamp (USHIO) was used as light source. Recorded spectra were corrected with monochromator and detector corrections, which were provided by the manufacturer. Additionally, recorded excitation spectra were corrected with regard to the spectral distribution of the lamp by using a photodiode reference detector. For spectra recording, samples were filled in round quartz glass cuvettes and brought into the beam path. To prevent the detection of high-order reflections of the excitation wavelengths whilst recording emission spectra, an edge filter (longpass, Newport, 395 nm) was added to the beam path. Since the addition of filters affects the intensity of detected light emission, the instrumental parameters were adjusted to obtain reasonable data. Therefore, the intensity of the spectral part, which was recorded with additional edge filter, was normalized to comply with the intensity of the spectral part recorded without edge filter at the marked wavelength. Afterwards, the two parts were combined, and the obtained overall spectra were normalized.

1.4 Photoluminescence lifetime determinations

After excitation, the intensity of emitted light of a luminescent compound decays according to Equation 1

$$I_t = A + \sum_i B_i e^{-\frac{t}{\tau_i}}, \quad (1)$$

with I_t being the luminescence intensity after a time interval t , A as background factor, B_i as the pre-exponential factor B of the i^{th} exponential term, and τ_i as corresponding luminescence lifetime. In case of a multi-exponential luminescence intensity decay and resulting determination of multiple lifetimes, an average luminescence lifetime τ_{av} can then be calculated according to Equation 3:¹⁰

$$\tau_{av} = \frac{\sum_i \alpha_i \tau_i}{\sum_i \alpha_i} \quad (2)$$

with α_i being the relative amplitude contribution of the luminescence process with a lifetime of τ_i to overall luminescence intensity, which can readily be transformed into

$$\tau_{av} = \frac{\sum_i \frac{B_i \tau_i}{\sum_j B_j \tau_j} \tau_i}{\sum_i \frac{B_i \tau_i}{\sum_j B_j \tau_j}} = \frac{\sum_i B_i \tau_i^2}{\sum_i B_i \tau_i}. \quad (3)$$

For determination of two lifetimes, as it is the case for the data presented this work Equation 3 can be transformed to

$$\tau_{av} = \frac{B_1 \tau_1^2 + B_2 \tau_2^2}{B_1 \tau_1 + B_2 \tau_2} . \quad (4)$$

According to the error propagation, the standard deviation of the average luminescence lifetime $\sigma(\tau_{av})$ is calculated by:

$$\sigma(\tau_{av}) = \sqrt{\sum_i \left(\frac{\delta}{\delta B_i} \tau_{av} \right)^2 \cdot \sigma(B_i)^2 + \left(\frac{\delta}{\delta \tau_i} \tau_{av} \right)^2 \cdot \sigma(\tau_i)^2} , \quad (6)$$

which is equivalent to

$$\sigma(\tau_{av}) = \left\{ \frac{B_2^2 \tau_1^2 \tau_2^2 (\tau_1 - \tau_2)^2 \sigma_{B_1}^2 + B_1^2 [B_1 \tau_1^2 + B_2 \tau_2 (2\tau_1 - \tau_2)]^2 \sigma_{\tau_1}^2}{(B_1 \tau_1 + B_2 \tau_2)^4} + \frac{B_1^2 \tau_1^2 \tau_2^2 (\tau_2 - \tau_1)^2 \sigma_{B_2}^2 + B_2^2 [B_2 \tau_2^2 + B_1 \tau_1 (2\tau_2 - \tau_1)]^2 \sigma_{\tau_2}^2}{(B_1 \tau_1 + B_2 \tau_2)^4} \right\}^{1/2} \quad (7)$$

for two determined luminescence lifetimes with σ_{B_1} , σ_{τ_1} , σ_{B_2} , and σ_{τ_2} being the determined standard deviations of B_1 , τ_1 , B_2 , and τ_2 , respectively.

The decay time of overall luminescence intensity was determined using a second Fluorolog 3 equipped with dual lamp housing, a UV xenon flashlamp (Exelitas FX-1102), a 450 W Xe short-arc lamp (USHIO), double-grated monochromators for excitation and emission, a photomultiplier tube (R928P) and a TCSPC (time-correlated single-photon counting) upgrade. The samples were investigated within round quartz glass cuvettes. The overall emission intensity decays were recorded with the DataStation software and subsequently fitted with a multi-exponential decay using Decay Analysis Software 6.

1.5 Luminescence quantum yield determination

Quantum yield (ϕ) determination was performed with a Jobin Yvon Fluorolog 3 (Horiba) equipped with a HORIBA Quanta- ϕ Integrating Sphere (F-3029). The sample was filled into a Micro Cell Cuvette (18-F/ST/C/Q/10) from Starna. The emission spectrum was corrected for the spectral response of monochromators and detectors using manufacturer-provided spectral corrections, as well as for the spectral response of the lamp by aid of a photodiode reference detector. Furthermore, an edge filter (longpass filter, Newport, 395 nm) was used. Calibration of Quanta- ϕ Integrating sphere was examined by additional standards (sodium salicylate powder, $\lambda_{exc} = 340$ nm, $\lambda_{em} = 365$ – 600 nm; determined $\phi = 55.7(4)$ %, published ϕ :¹¹ 53 – 57 %; γ -[Eu₄(OAc)₁₂(ptpy)₂], determined ϕ : 55(2) %, published ϕ :¹² 57.9 %; γ -[Eu₄(OAc)₁₂(ptpy)₂], determined ϕ : 43.6(9) %, published ϕ :¹² 45.8 %).

1.6 UV-VIS spectroscopy

UV-Vis reflectance spectra were recorded with a Cary 5000 Series UV-VIS-NIR spectrophotometer (Agilent Technologies) with Praying MantisTM (Harrick Scientific Products) as diffuse reflectance accessory with full slit height in double-beam mode. As reference material, powdered PTFE (Sigma-Aldrich, 1 μ m particle size) was used. A tungsten-halogen VIS-lamp was utilized as light source. Before recording, the reference and the compound to be investigated were ground, filled into specimen cups, and flattened. In the beginning, a background spectrum (of PTFE as reference of high reflectance in the visible spectrum) was acquired. Then, the sample spectrum was recorded and baseline corrected with the instrument software (Cary WinUV).

1.7 Thermal and composition analyses

Simultaneous thermogravimetry and differential thermal analysis (STA) were performed using a NETZSCH STA-409-PC in combination with a QMS 403 Aëolos Quadro. Synthetic air ($30 \text{ mL} \cdot \text{min}^{-1}$) was used as a working gas,. Argon ($20 \text{ mL} \cdot \text{min}^{-1}$) was used as a protective gas. Samples (10–20 mg) were heated to 1000°C with a heating rate of $5^\circ\text{C} \cdot \text{min}^{-1}$.

For elemental CHN analysis, compounds were placed in a tin crucible. Analyses were done with a Thermo FlashEA 1112 Series or Vario Unicube.

1.8 Physisorption experiments

For investigation of physisorption properties, a Quantachrome Autosorb-1 was used. The samples were pre-activated and filled into the measurement cell under inert atmosphere within a glovebox filled with argon. Prior to recording of isotherms, the samples were degassed at ultrahigh vacuum at 300°C for 24 h mounted on the Autosorb-1. Subsequently, N_2 sorption isotherms were recorded at 77 K. Obtained data was analysed with VersaWin™ Version 1.0 (Quantachrome Instruments).

1.9 Scanning electron microscopy (SEM)

Sticky carbon pads were affixed onto the specimen holders. The samples were placed onto the carbon pads and scanning electron micrographs were taken with a Merlin Gemini (Zeiss) with an acceleration voltage of 1 kV, a and a working distance of 2.1 mm.

2.0 Inductively coupled plasma mass spectrometry

For analysis, an Agilent 8900 triple quadrupole ICP-MS (ICP-QQQ) with ISIS autosampler was used. For calibration, dilutions were prepared, which contained ICPMS-71A multi-element standard solution and Tb standard solution manufactured by Inorganic Ventures, besides a solution of 1 vol-% concentrated HNO_3 (ultrapure) in MilliQ water. A six-point calibration was performed with dilutions of Eu and Tb with concentrations of 0, 0.2, 1, 10, and $500 \mu\text{g} \cdot \text{L}^{-1}$. Samples of $\text{EuTb@}\frac{1}{6}[\text{Zn}(\text{pt})_2]$ were dissolved in a solution containing 1 vol-% of concentrated HNO_3 (ultrapure) in MilliQ water. Concentration of analytes was adjusted to be within the calibration range.

2. Tables with crystallographic data

Table S1. Crystallographic data for $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**). Deviations are given in brackets.

Empirical formula	$\text{C}_{15.25}\text{H}_{10.88}\text{N}_{8.25}\text{O}_{0.31}\text{Zn}$
Formula weight [$\text{g} \cdot \text{mol}^{-1}$]	380.07
Crystal colour and shape	colourless needle
Crystal size	$0.778 \times 0.102 \times 0.061 \text{ mm}^3$
Crystal system	Tetragonal
Space group	$I4_1/acd$
a [pm]	2268.81(6)
b [pm]	2268.81(6)
c [pm]	1272.47(6)
V [10^6 pm^3]	6550.0(5)
α [°]	90
β [°]	90
γ [°]	90
Z	16
ρ_{calc} [$\text{g} \cdot \text{cm}^{-3}$]	1.542
$\mu(\text{MoK}\alpha)$ [mm^{-1}]	1.518
X-ray radiation	$\text{MoK}\alpha, \lambda = 71.073 \text{ pm}$
Measurement temperature [K]	100(2)
Absorption correction type	multi-scan
2θ range [°]	3.59 to 52.794
No. of measured reflections	41383
No. of independent reflections	1689
R_{int}	0.0942
No. of independent reflections ($I > 2\sigma(I)$)	1689
No. of parameters	205
R_1 ($I > 2\sigma(I)$)	0.0311
wR_2 (all data)	0.075
GOF	0.999
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ [$\text{e} \cdot 10^{-6} \text{ pm}^{-3}$]	0.431, -0.456

Table S2. Interatomic distances and angles for $\frac{1}{3}[\text{Zn}(\text{pt})_2]$ (**6**). Deviations are given in brackets. Symmetry operations: I = $1/4+y$, $1/4-x$, $-1/4+z$; II = x , $-y$, $1/2-z$; III = $1/4-y$, $1/4-x$, $1/4-z$. The suffixes A and B indicate the affiliation of respective atoms to one of two disorders of the ligand molecule.

Atoms	Distance [pm]	Atoms	Angle [°]	Atoms	Angle [°]
Zn1–N1A	232(3)	N1A–Zn1–N1A ^{III}	81(1)	N1B ^{III} –Zn1–N3A ^I	168(2)
Zn1–N1A ^{III}	232(3)	N1A–Zn1–N2A ^{III}	92(2)	N1B ^{III} –Zn1–N2A	94(2)
Zn1–N1B	228(4)	N1A–Zn1–N3A ^{II}	168(2)	N1B ^{III} –Zn1–N2B ^{III}	75(2)
Zn1–N1B ^{III}	228(4)	N1A–Zn1–N3A ^I	90(2)	N1B ^{III} –Zn1–N3B ^{II}	90(2)
Zn1–N2A	214(3)	N1A–Zn1–N2A	75(2)	N1B ^{III} –Zn1–N3B ^I	168(2)
Zn1–N2A ^{III}	214(3)	N1A–Zn1–N1B ^{III}	82(1)	N1B ^{III} –Zn1–N2B	93(2)
Zn1–N2B	208(3)	N1A–Zn1–N2B ^{III}	912(2)	N2A ^{III} –Zn1–N3A ^{II}	93(2)
Zn1–N2B ^{III}	208(3)	N1A–Zn1–N3B ^{II}	168(2)	N2A ^{III} –Zn1–N3A ^I	97(2)
Zn1–N3A ^I	212(4)	N1A–Zn1–N3B ^I	91(2)	N2A ^{III} –Zn1–N2A	164(2)
Zn1–N3A ^{II}	212(4)	N1A–Zn1–N2B	76(2)	N2A ^{III} –Zn1–N3B ^{II}	94(2)
Zn1–N3B ^I	206(5)	N1B–Zn1–N1A ^{III}	82(1)	N2A ^{III} –Zn1–N3B ^I	97(2)
Zn1–N3B ^{II}	206(5)	N1B–Zn1–N2A ^{III}	94(2)	N2A ^{III} –Zn1–N2B	164(1)
		N1B–Zn1–N3A ^{II}	168(2)	N2B ^{III} –Zn1–N3A ^{II}	94(2)
		N1B–Zn1–N3A ^I	90(2)	N2B ^{III} –Zn1–N3A ^I	96(2)
		N1B–Zn1–N2A	74(2)	N2B ^{III} –Zn1–N2A	164(2)
		N1B–Zn1–N1B ^{III}	83(2)	N2B ^{III} –Zn1–N3B ^{II}	95(2)
		N1B–Zn1–N2B ^{III}	93(2)	N2B ^{III} –Zn1–N3B ^I	95(2)
		N1B–Zn1–N3B ^{II}	168(2)	N2B ^{III} –Zn1–N2B	164(2)
		N1B–Zn1–N3B ^I	90(2)	N3A ^{II} –Zn1–N3A ^I	99(2)
		N1B–Zn1–N2B	75(2)	N3A ^{II} –Zn1–N2A	97(2)
		N1A ^{III} –Zn1–N2A ^{III}	75(2)	N3A ^{II} –Zn1–N3B ^I	99(2)
		N1A ^{III} –Zn1–N3A ^{II}	90(2)	N3A ^{II} –Zn1–N2B	96(2)
		N1A ^{III} –Zn1–N3A ^I	168(2)	N3B ^I –Zn1–N3A ^I	99(2)
		N1A ^{III} –Zn1–N2A	92(2)	N3B ^I –Zn1–N2A	96(2)
		N1A ^{III} –Zn1–N2B ^{III}	76(2)	N3B ^I –Zn1–N3B ^I	98(2)
		N1A ^{III} –Zn1–N3B ^{II}	91(2)	N3B ^I –Zn1–N2B	95(2)
		N1A ^{III} –Zn1–N3B ^I	168(2)	N3A ^I –O–N2A	93(2)
		N1A ^{III} –Zn1–N2B	91(2)	N3A ^I –O–N2B	94(2)
		N1B ^{III} –Zn1–N2A ^{III}	74(2)	N3B ^I –O–N2A	94(2)
		N1B ^{III} –Zn1–N3A ^{II}	90(2)	N3B ^I –O–N2B	95(2)

Table S3. Crystallographic data for $\frac{1}{2}[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (**8**). Deviations are given in brackets.

Empirical formula	$\text{C}_{33}\text{H}_{25}\text{Cu}_2\text{N}_{17}$
Formula weight [$\text{g} \cdot \text{mol}^{-1}$]	786.78
Crystal colour and shape	blue block
Crystal size	$0.285 \times 0.111 \times 0.060 \text{ mm}^3$
Crystal system	orthorhombic
Space group	<i>Ibca</i>
a [pm]	1245.19(4)
b [pm]	2224.20(8)
c [pm]	2354.63(8)
V [10^6 pm^3]	6521.3(4)
α [°]	90
β [°]	90
γ [°]	90
Z	8
ρ_{calc} [$\text{g} \cdot \text{cm}^{-3}$]	1.603
$\mu(\text{MoK}\alpha)$ [mm^{-1}]	1.36
X-ray radiation	$\text{MoK}\alpha, \lambda = 71.073 \text{ pm}$
Measurement temperature [K]	100(2)
Absorption correction type	multi-scan
2θ range [°]	5.038 to 69.948
No. Of measured reflections	125482
No. of independent reflections	7150
R_{int}	0.1018
No. of independent reflections ($I > 2\sigma(I)$)	7150
No. Of parameters	362
R_1 ($I > 2\sigma(I)$)	0.0589
wR_2 (all data)	0.1547
GOF	1.113
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ [$\text{e} \cdot 10^{-6} \text{ pm}^{-3}$]	0.753, -1.124

Table S4. Interatomic distances and angles for $\frac{1}{2}[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (**8**). Deviations are given in brackets. Symmetry operations: I = $1-x, 3/2-y, z$, II = $3/2-x, y, 1-z$. The suffixes A and B indicate the affiliation of respective atoms to one of the two disorders of the disordered ligand molecule.

Atoms	Distance [pm]	Atoms	Angle [°]
Cu1–N1	209.9(3)	N1–Cu1–N6B ^{II}	90(1)
Cu1–N2	201.1(3)	N1–Cu1–N6A ^{II}	91(1)
Cu1–N3 ^I	199.8(3)	N1–Cu1–N4B	86(1)
Cu1–N4A	260(2)	N1–Cu1–N4A	80(1)
Cu1–N4B	249(3)	N1–Cu1–N2	79(1)
Cu1–N5A	198(3)	N1–Cu1–N5A	91(1)
Cu1–N5B	200(4)	N1–Cu1–N5B	93(2)
Cu1–N6A ^{II}	233(2)	N1–Cu1–N3 ^I	171(1)
Cu1–N6B ^{II}	216(2)	N4A–Cu1–N2	92(1)
		N4A–Cu1–N5A	72(1)
		N4A–Cu1–N5B	75(2)
		N4A–Cu1–N3 ^I	93(1)
		N4A–Cu1–N6A ^{II}	167(1)
		N4A–Cu1–N6B ^{II}	165(1)
		N4B–Cu1–N2	94(1)
		N4B–Cu1–N5A	71(1)
		N4B–Cu1–N5B	74(2)
		N4B–Cu1–N3 ^I	88(1)
		N4B–Cu1–N6A ^{II}	169(1)
		N4B–Cu1–N6B ^{II}	168(1)
		N2–Cu1–N6A ^{II}	97(1)
		N2–Cu1–N6B ^{II}	97(1)
		N2–Cu1–N5A	162(1)
		N2–Cu1–N5B	166(2)
		N2–Cu1–N3 ^I	95(1)
		N5A–Cu1–N3 ^I	93(1)
		N5A–Cu1–N6A ^{II}	98(1)
		N5A–Cu1–N6B ^{II}	98(1)
		N5B–Cu1–N6A ^{II}	95(2)
		N5B–Cu1–N6B ^{II}	95(2)
		N5B–Cu1–N3 ^I	92(2)
		N3 ^I –Cu1–N6A ^{II}	96(1)
		N3 ^I –Cu1–N6B ^{II}	97(1)

Table S5. Crystallographic data for [MnCl₂(Hpt)₂] (**9**). Deviations are given in brackets.

Empirical formula	C ₁₄ H ₁₂ Cl ₂ MnN ₈
Formula weight [g · mol ⁻¹]	418.16
Crystal colour and shape	pink block
Crystal size	0.239 x 0.213 x 0.166 mm ³
Crystal system	Triclinic
Space group	$P\bar{1}$
a [pm]	643.3(3)
b [pm]	802.2(4)
c [pm]	916.0(4)
V [10 ⁶ pm ³]	410.3(3)
α [°]	85.08(2)
β [°]	71.51(2)
γ [°]	66.40(2)
Z	1
ρ _{calc} [g · cm ⁻³]	1.692
μ(MoKα) [mm ⁻¹]	1.146
X-ray radiation	MoKα, λ = 71.073 pm
Measurement temperature [K]	296(2)
Absorption correction type	multi-scan
2θ range [°]	5.548 to 61.014
No. Of measured reflections	31499
No. of independent reflections	2511
R _{int}	0.0664
No. of independent reflections (I > 2σ(I))	2511
No. Of parameters	116
R ₁ (I > 2σ(I))	0.0252
wR ₂ (all data)	0.064
GOF	1.052
Δρ _{max} , Δρ _{min} [e · 10 ⁻⁶ pm ⁻³]	0.457, -0.304

Table S6. Interatomic distances and angles for [MnCl₂(Hpt)₂] (**9**). Deviations are given in brackets. Symmetry operations: I = 1-x, 1-y, 1-z, II = x, 1+y, z.

Atoms	Distance [pm]	Atoms	Angle [°]
Mn1-N1	225.2(2)	N1-Mn1-N1 ^I	180
Mn1-N1 ^I	225.2(2)	N1-Mn1-N4	75(1)
Mn1-N4	223.7(2)	N1-Mn1-N4 ^I	105(1)
Mn1-N4 ^I	223.7(2)	N1-Mn1-Cl1	90(1)
Mn1-Cl1	255.66(9)	N1-Mn1-Cl1 ^I	90(1)
Mn1-Cl1 ^I	255.66(9)	N4-Mn1-N1 ^I	105(1)
Cl1-H3 ^{II}	225(2)	N4-Mn1-N4 ^I	180
		N4-Mn1-Cl1	90(1)
		N4-Mn1-Cl1 ^I	90(1)
		Cl1-Mn1-N1 ^I	90(1)
		Cl1-Mn1-N4 ^I	90(1)
		Cl1-Mn1-Cl1 ^I	180
		N1 ^I -Mn1-N4 ^I	75(1)
		N1 ^I -Mn1-Cl1 ^I	90(1)
		N4 ^I -Mn1-Cl1 ^I	90(1)
		Mn1-Cl1-H3 ^{II}	102(1)
		Cl1-H3 ^{II} -N3 ^{II}	169(2)

Table S7. Crystallographic data for [FeCl₂(Hpt)₂] (**10**). Deviations are given in brackets.

Empirical formula	C ₁₄ H ₁₂ Cl ₂ FeN ₈
Formula weight [g · mol ⁻¹]	419.07
Crystal colour and shape	yellow block
Crystal size	0.426 x 0.316 x 0.314 mm ³
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
a [pm]	645.09(2)
b [pm]	791.28(3)
c [pm]	913.97(3)
V [10 ⁶ pm ³]	405.34(2)
α [°]	80.775(2)
β [°]	71.580(2)
γ [°]	66.411(2)
Z	1
ρ_{calc} [g · cm ⁻³]	1.717
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	1.276
X-ray radiation	MoK α , λ = 71.073 pm
Measurement temperature [K]	100(2)
Absorption correction type	multi-scan
2 θ range [°]	4.7 to 65.146
No. Of measured reflections	46829
No. of independent reflections	2944
R _{int}	0.0727
No. of independent reflections (<i>I</i> > 2 σ (<i>I</i>))	2944
No. Of parameters	117
R ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0238
wR ₂ (all data)	0.0632
GOF	1.042
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ [e · 10 ⁻⁶ pm ⁻³]	0.521, -0.673

Table S8. Interatomic distances and angles for [FeCl₂(Hpt)₂] (**10**). Deviations are given in brackets. Symmetry operations: I = 1 $\bar{0}$ x, 1 $\bar{0}$ y, 1 $\bar{0}$ z, II = 01 $\bar{0}$ x, 1 $\bar{0}$ y, z.

Atoms	Distance [pm]	Atoms	Angle [°]
Fe1–N1	220.20(8)	N1–Fe1–N1 ^I	180
Fe1–N1 ^I	220.20(8)	N1–Fe1–N4	76(1)
Fe1–N4	218.48(8)	N1–Fe1–N4 ^I	104(1)
Fe1–N4 ^I	218.48(8)	N1–Fe1–Cl1	90(1)
Fe1–Cl1	248.55(2)	N1–Fe1–Cl1 ^I	90(1)
Fe1–Cl1 ^I	248.55(2)	N1 ^I –Fe1–N4	104(1)
Cl1–H3 ^{II}	230(2)	N4 ^I –Fe1–N4 ^I	76(1)
		N1 ^I –Fe1–Cl1	90(1)
		N1 ^I –Fe1–Cl1 ^I	90(1)
		N4–Fe1–N4 ^I	180
		N4–Fe1–Cl1	90(1)
		N4–Fe1–Cl1 ^I	90(1)
		N4 ^I –Fe1–Cl1	90(1)
		N4 ^I –Fe1–Cl1 ^I	90(1)
		Cl1 ^I –Fe1–Cl1	180
		Fe1–Cl1–H3 ^{II}	103(1)
		Cl1–H3 ^{II} –N3 ^{II}	168(2)

Table S9. Crystallographic data for [CoCl₂(Hpt)₂] (**11**). Deviations are given in brackets.

Empirical formula	C ₁₄ H ₁₂ Cl ₂ CoN ₈
Formula weight [g · mol ⁻¹]	422.15
Crystal colour and shape	pink block
Crystal size	0.178 x 0.077 x 0.063 mm ³
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
a [pm]	645.4(3)
b [pm]	786.9(3)
c [pm]	908.4(4)
V [10 ⁶ pm ³]	400.1(3)
α [°]	81.03(2)
β [°]	71.62(2)
γ [°]	66.10(2)
Z	1
ρ_{calc} [g · cm ⁻³]	1.752
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	1.423
X-ray radiation	MoK α , λ = 71.073 pm
Measurement temperature [K]	296(2)
Absorption correction type	multi-scan
2 θ range [°]	4.728 to 61.006
No. Of measured reflections	28943
No. of independent reflections	2447
R _{int}	0.0469
No. of independent reflections (<i>I</i> > 2 σ (<i>I</i>))	2447
No. Of parameters	116
R ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0233
wR ₂ (all data)	0.0576
GOF	1.061
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ [e · 10 ⁻⁶ pm ⁻³]	0.510, -0.349

Table S10. Interatomic distances and angles for [CoCl₂(Hpt)₂] (**11**). Deviations are given in brackets. Symmetry operations: I = 1-x, 1-y, 1-z, II = -1+x, 1+y, z.

Atoms	Distance [pm]	Atoms	Angle [°]
Co1–N1	214.6(2)	N1–Co1–N1 ^I	180
Co1–N1 ^I	214.6(2)	N1–Co1–N4	78(5)
Co1–N4	213.6(2)	N1–Co1–N4 ^I	102(5)
Co1–N4 ^I	213.6(2)	N1–Co1–Cl1	90(1)
Co1–Cl1	248.22(8)	N1–Co1–Cl1 ^I	90(1)
Co1–Cl1 ^I	248.22(8)	N4–Co1–N1 ^I	102(5)
Cl1–H3 ^{II}	228(2)	N4–Co1–N4 ^I	180
		N4–Co1–Cl1	90(1)
		N4–Co1–Cl1 ^I	90(1)
		Cl1–Co1–N1 ^I	90(1)
		Cl1–Co1–N4 ^I	90(1)
		Cl1–Co1–Cl1 ^I	180
		N1 ^I –Co1–N4 ^I	78(1)
		N1 ^I –Co1–Cl1 ^I	90(1)
		N4 ^I –Co1–Cl1 ^I	90(1)
		Co1–Cl1–H3 ^{II}	103(1)
		Cl1–H3 ^{II} –N3 ^{II}	167(2)

Table S11. Crystallographic data for [CoBr₂(Hpt)₂] (**12**). Deviations are given in brackets.

Empirical formula	C14H12Br2CoN8
Formula weight [g · mol ⁻¹]	511.07
Crystal colour and shape	pink block
Crystal size	0.132 x 0.120 x 0.090 mm ³
Crystal system	triclinic
Space group	P $\bar{1}$
a [pm]	663.2(4)
b [pm]	806.6(6)
c [pm]	910.4(6)
V [106 pm ³]	417.1(5)
α [°]	80.71(2)
β [°]	69.67(2)
γ [°]	66.02(2)
Z	1
ρ_{calc} [g · cm ⁻³]	2.034
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	5.834
X-ray radiation	MoK α , λ = 71.073 pm
Measurement temperature [K]	296(2)
Absorption correction type	multi-scan
2 θ range [°]	4.772 to 60.062
No. Of measured reflections	19899
No. of independent reflections	2446
Rint	0.0637
No. of independent reflections (I > 2 σ (I))	2446
No. Of parameters	116
R ₁ (I > 2 σ (I))	0.0292
wR2 (all data)	0.0589
GOF	1.017
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ [e · 10 ⁻⁶ pm ⁻³]	0.647, -0.599

Table S12. Interatomic distances and angles for [CoBr₂(Hpt)₂] (**12**). Deviations are given in brackets. Symmetry operations: I = 1-x, 1-y, 1-z, II = -1+x, 1+y, z.

Atoms	Distance [pm]	Atoms	Angle [°]
Co1-N1	214.8(2)	N1-Co1-N1 ^I	180
Co1-N1 ^I	214.8(2)	N1-Co1-N4	78(1)
Co1-N4	213.5(2)	N1-Co1-N4 ^I	102(1)
Co1-N4 ^I	213.4(2)	N1-Co1-Br1	90(1)
Co1-Br1	263.4(2)	N1-Co1-Br1 ^I	90(1)
Co1-Br1 ^I	263.4(2)	N4-Co1-N1 ^I	102(1)
Br1-H3 ^{II}	242(3)	N4-Co1-N4 ^I	180
		N4-Co1-Br1	90(1)
		N4-Co1-Br1 ^I	90(1)
		Br1-Co1-N1 ^I	90(1)
		Br1-Co1-N4 ^I	90(1)
		Br1-Co1-Br1 ^I	180
		N1 ^I -Co1-N4 ^I	78(1)
		N1 ^I -Co1-Br1 ^I	90(1)
		N4 ^I -Co1-Br1 ^I	90(1)
		Co1-Br1-H3 ^{II}	100(1)
		Br1-H3 ^{II} -N3 ^{II}	169(3)

Table S13. Crystallographic data for [ZnCl₂(Hpt)₂] (**13**). Deviations are given in brackets.

Empirical formula	C ₁₄ H ₁₂ Cl ₂ N ₈ Zn
Formula weight [g · mol ⁻¹]	428.59
Crystal colour and shape	colourless block
Crystal size	0.414 x 0.183 x 0.111 mm ³
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
a [pm]	646.59(7)
b [pm]	792.52(9)
c [pm]	906.7(1)
V [10 ⁶ pm ³]	402.08(8)
α [°]	80.982(4)
β [°]	71.419(4)
γ [°]	65.979(4)
Z	1
ρ_{calc} [g · cm ⁻³]	1.77
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	1.876
X-ray radiation	MoK α , λ = 71.073 pm
Measurement temperature [K]	100(2)
Absorption correction type	multi-scan
2 θ range [°]	4.742 to 63.002
No. Of measured reflections	24602
No. of independent reflections	2684
R _{int}	0.0499
No. of independent reflections (<i>I</i> > 2 σ (<i>I</i>))	2684
No. Of parameters	116
R ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0245
wR ₂ (all data)	0.0621
GOF	1.09
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ [e · 10 ⁻⁶ pm ⁻³]	0.384, -0.495

Table S14. Interatomic distances and angles for [ZnCl₂(Hpt)₂] (**13**). Deviations are given in brackets. Symmetry operations: I = 1-x, 1-y, 1-z, II = -1+x, 1+y, z.

Atoms	Distance [pm]	Atoms	Angle [°]
Zn1–N1	214.0(2)	N1–Zn1–N1 ^I	180
Zn1–N1 ^I	214.0(2)	N1–Zn1–N4	78(1)
Zn1–N4	215.7(1)	N1–Zn1–N4 ^I	102(1)
Zn1–N4 ^I	215.7(1)	N1–Zn1–Cl1	90(1)
Zn1–Cl1	253.71(4)	N1–Zn1–Cl1 ^I	90(1)
Zn1–Cl1 ^I	253.71(4)	N4–Zn1–N1 ^I	102(1)
Cl1–H3 ^{II}	227(2)	N4–Zn1–N4 ^I	180
		N4–Zn1–Cl1	90(1)
		N4–Zn1–Cl1 ^I	90(1)
		Cl1–Zn1–N1 ^I	90(1)
		Cl1–Zn1–N4 ^I	90(1)
		Cl1–Zn1–Cl1 ^I	180
		N1 ^I –Zn1–N4 ^I	79(1)
		N1 ^I –Zn1–Cl1 ^I	90(1)
		N4 ^I –Zn1–Cl1 ^I	90(1)
		Zn1–Cl1–H3 ^{II}	102(1)
		Cl1–H3 ^{II} –N3 ^{II}	168(2)

3. Additional Investigations, Tables and Figures

3.1 Additional tables

Table S15. Determined Rwp values for Pawley refinements of $1/2[M(pt)_2]$ (M = Mn (1), Fe (2), Co (3), Ni (4), Cu (5), Zn (6), Cd (7)). If not stated otherwise, the refinements were performed for diffractograms recorded on the PANalytical X'Pert Pro diffractometer at room temperature.

M in $1/2[M(pt)_2]$	R _{wp} [%]
Mn	3.96
Fe	3.49
Fe ^{a,b}	5.46
Fe ^{a,c}	5.54
Fe ^{a,d}	5.64
Co	1.19
Co ^{a,b}	5.84
Co ^{a,d}	5.59
Ni	2.51
Cu	5.87
Zn	7.49
Zn ^{a,b}	5.76
Zn ^{a,c}	5.88
Zn ^{a,d}	5.90
Cd	4.04

^a Recorded on the Stoe Stadi P diffractometer with HT1 capillary furnace. ^b Recorded during temperature-dependent PXRD investigations at a temperature T = 30 °C. ^c Recorded during temperature-dependent PXRD investigations at a temperature T = 180 °C. ^d Recorded during temperature-dependent PXRD investigations at a temperature T = 305 °C

Table S16. Calculated L*a*b* chromaticity coordinates of the coordination polymers $1/2[M(pt)_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn). Corresponding reflectance spectra are given in Figure S20. The listed values were rounded to two decimal places. The colour of the chromaticity cells corresponds to the colours calculated from reflectance spectra.

M in $1/2[M(pt)_2]$	L*	a*	b*	Chromaticity ^a
Mn ^a	85.82	-3.32	6.59	
Fe	34.14	24.29	26.29	
Co	61.42	14.41	20.75	
Ni	72.43	34.20	-37.54	
Cu	87.95	-26.80	-13.97	
Zn ^a	75.59	-0.37	1.70	

^a It should be noted, that the calculation results in greyish colours for Mn and Zn containing polymers, although their appearance to the bare eye is white. This is explained by the L* value mathematically not reaching 100. The proximity to almost perfect white appearance gets evident by examination of the a* and b* values, which are close to 0 in comparison to the respective values observed for the other coordination polymers.

Table S17. Calculated L*a*b* chromaticity coordinates of $1/2[Fe(pt)_2]$ (2) using UV-VIS reflectance spectra at listed temperatures.

Temperature ^{a,b} T [°C]	L*	a*	b*	Chromaticity ^c
25 °C ▲	47.60	40.03	37.06	
50 °C ▲	53.380	41.03	42.54	
75 °C ▲	59.081	39.69	49.39	
100 °C ▲	64.758	37.20	55.81	
125 °C ▲	68.26	35.97	60.86	
150 °C ▲	71.086	34.81	64.79	
175 °C ▲	73.35	33.42	67.99	
200 °C	73.39	33.26	69.27	
175 °C ▼	71.76	34.66	66.92	
150 °C ▼	70.63	35.25	64.80	
125 °C ▼	67.61	36.63	60.66	
100 °C ▼	63.93	38.24	55.55	
75 °C ▼	59.29	39.54	49.44	
50 °C ▼	54.06	40.14	43.23	
25 °C ▼	48.61	39.64	37.29	

^a ▲ indicates measurement during the heating ramp. ^b ▼ indicates measurement during cooling down. ^c Differences of room temperature chromaticities in comparison to the chromaticity given in Figure 7 within the main paper and Table S16 are explained by using different specimen cells.

Table S18. Excitation wavelength λ_{exc} and CIE chromaticity coordinates xy of 2-(1,2,4-1H-triazol-3-yl)pyridine (Hpt). Given values were rounded to two decimal places. For respective emission spectra, see Figure S22. A graphical depiction of the chromaticity coordinates xy is given in Figure S24.

Excitation wavelength λ_{exc} [nm]	x	y
306	0.21	0.21
311	0.21	0.22
324	0.21	0.22
346	0.22	0.241

Table S19. Excitation wavelength λ_{exc} and CIE chromaticity coordinates xy of $1/2[Zn(pt)_2]$ (6). Given values were rounded to two decimal places. For respective emission spectra, see Figure S23. A graphical depiction of the chromaticity coordinates xy is given in Figure S25.

Excitation wavelength λ_{exc} [nm]	x	y
306	0.19	0.10
311	0.20	0.11
324	0.22	0.16
346	0.23	0.19

Table S20. Solvent utilised for impregnation of $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**), as well as excitation wavelengths λ_{exc} with corresponding CIE chromaticity coordinates xy of emitted. Obtained chromaticity coordinates were rounded to two decimal places.

Solvent	λ_{exc} [nm]	x	y
DMF	306	0.23	0.20
	311	0.24	0.21
	324	0.29	0.29
	346	0.32	0.32
MeCN	306	0.22	0.16
	311	0.23	0.17
	324	0.29	0.26
	346	0.36	0.33
MeOH	306	0.22	0.17
	311	0.28	0.27
	324	0.27	0.26
	346	0.33	0.34

Table S21. Fitting parameters for multi-exponential luminescence intensity decay fits of synthesized light emitting compounds, with listing of respective luminescent constituents of these compounds, emission wavelength λ_{em} , for which the intensity decay was screened, and solvents used for the impregnation, in comparison to determined parameters for pure CP **6** and the pure ligand. The decays of luminescence intensity I were fitted with $I = A + B_1 \cdot \exp(-t/\tau_1) + B_2 \cdot \exp(-t/\tau_2)$ with A being a background factor, B_i as pre-exponential factor of the decay with the luminescence lifetime τ_i , and t as time. The quality of the fit was evaluated with χ^2 . Excitation of the CP and ligand fluorescence was achieved with a pulsed diode with peak wavelength at 340 nm. The lanthanide luminescence was excited with a Xe lamp at 346 nm.

Compound	Luminescent constituent	λ_{em} [nm] ^a	Solvent	A	B_1	τ_1	B_2	τ_2	$\tau_{\text{av}}^{b,c}$	χ^2
EuTb@ $\frac{1}{2}[\text{Zn}(\text{pt})_2]$	Tb3+	698	DMF	3.8(1)	693(9)	0.40(2) ms	1124(4)	1.160(6) ms	1.028(6) ms	1.18
			MeCN	3.2(2)	985(9)	0.40(2) ms	837(4)	1.148(8) ms	0.930(7) ms	1.10
			MeOH	3.0(2)	1908(14)	0.50(2) ms	2043(7)	1.107(6) ms	0.927(5) ms	1.17
EuTb@ $\frac{1}{2}[\text{Zn}(\text{pt})_2]$	Eu3+	544	DMF	1.40(9)	2230(3)	0.48(3) ms	186(2)	1.30(3) ms	1.04(2) ms	1.10
			MeCN	6.8(2)	1182(7)	0.350(6) ms	267(2)	1.34(2) ms	0.81(2) ms	1.10
			MeOH	13.6(2)	519(6)	0.39(2) ms	237(3)	1.19(3) ms	0.86(2) ms	1.08
EuTb@ $\frac{1}{2}[\text{Zn}(\text{pt})_2]$	CP	395	DMF	31.7(3)	6287(20)	1.19(2) ns	1442(7)	3.54(3) ns	2.14(2) ns	1.18
			MeCN	40.0(4)	4132(19)	1.10(2) ns	1636(8)	3.35(3) ns	2.33(2) ns	1.07
			MeOH	26.1(3)	4812(20)	0.699(7) ns	702(6)	2.41(3) ns	1.27(2) ns	1.13
$\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (pure 6)	CP	395	-	25.4(3)	5406(20)	1.00(2) ns	1425(7)	3.10(3) ns	1.95(2) ns	1.26
Hpt (pure ligand)	Ligand	395	-	25.8(3)	6634(21)	1.16(1) ns	863(8)	2.89(3) ns	1.58(2) ns	1.21

^a Since Tb³⁺ also emits light around 617 nm, the luminescence intensity decay of Eu³⁺ was recorded for $\lambda_{\text{em}} = 698$ nm rather than for the most intense emission band at 617 nm. ^b The average luminescence lifetime was calculated according to Equation 4. ^c The standard deviation of the average luminescence lifetime was calculated according to Equation 7

Table S22. Assignments of important vibration bands¹³⁻¹⁹ observed in infrared spectra of the coordination polymers $\frac{1}{2}[\text{M}(\text{pt})_2]$ (M = Mn (1), Fe (2), Co (3), Ni (4), Zn (6), Cd (7)). Corresponding spectra are given in Figure S31. ν = stretching vibration, δ = deformation vibration (in plane), γ = out-of-plane vibration, Tz = triazole ring, Py = pyridine ring.

Assignment	$\frac{1}{2}[\text{Mn}(\text{pt})_2]$ (1)	$\frac{1}{2}[\text{Fe}(\text{pt})_2]$ (2)	$\frac{1}{2}[\text{Co}(\text{pt})_2]$ (3)	$\frac{1}{2}[\text{Ni}(\text{pt})_2]$ (4)	$\frac{1}{2}[\text{Cu}(\text{pt})_2]$ (5)	$\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (6)	$\frac{1}{2}[\text{Cd}(\text{pt})_2]$ (7)
$\nu(\text{O-H})$ of water	3419	3423	3445	3423	3441	3421	3420
$\nu(\text{C-H})$	3101	3104	3111	3115	3104	3108	3097
	3084	3086	3090	3091	3071	3091	3079
	3060	3059	3062	3063	3060	3064	3059
	3026	3026	3028	3030	3028	3030	3023
	3015	3018	3020	3022	3019	3020	3009
	2977	2978	2979	2979	2981	2982	2977
	2944	2945	2947	2950	2954	2952	2944
	1624	1624	1624	1626	1636	1622	1621
	1604	1605	1608	1608	1612	1605	1601
	1570	1568	1570	1571	1598	1572	1571
$\nu(\text{C=N})$ and $\nu(\text{C=C})$	1561	1561	1551	1553	1558	1558	1551
	1513	1516	1516	1519	1526 1514	1517	1510
$\nu(\text{C-N})$	1472	1471	1473	1473	1471	1476	1472
$\nu_{\text{Ring}}(\text{Py})$	1449	1448	1449	1451	1451	1450	1448
$\delta(\text{C-H})$	1437	1435	1438	1438	1439	1438	1437
$\nu(\text{C-N})$	1417	1417	1420	1418	1420	1421	1417
$\delta(\text{C-H})$	1384	1384	1384	1391	1384	1384	1390
$\nu_{\text{Ring}}(\text{Py})$	1350	1357	1360	1367	1370 1353	1363	1350
$\nu(\text{C-N})$	1271	1274	1264	1267	1269	1265	1262
$\nu_{\text{Ring}}(\text{Tz})$	1250	1252	1252	1254	1254	1252	1251
$\delta(\text{C-H})$	1203	1201	1204	1206	1210	1208	1204
$\nu_{\text{Ring}}(\text{Tz})$	1145	1149	1149	1150	1149 1138	1149	1145
$\delta(\text{C-H})$	1112	1115	1118	1126	1121	1125	1116
$\nu(\text{C-N})$	1092	1097	1097	1097	1095	1095	1095
	1048	1050	1050	1051	1051	1050	1048
$\nu_{\text{Ring}}(\text{Py})$	1029	1031	1033	1034	1043	1035	1027
$\delta(\text{Py})$	1007	1009	1009	1012	1016	1007	1006
$\gamma(\text{C-H})$	876	874	874	871	870	876	874
	805	803	805	803	802	806	803
$\delta(\text{C-H})$	755	757	757	757	752	755	752
	717	718	718	718	718	718	717
$\gamma(\text{Tz})$	676	676	674	676	676 667	674	673
	636	636	638	639	642 628	635	635
$\gamma(\text{Py})$	483	490	496	502	490	493	480
$\nu(\text{M-N})^a$	407	409	411	415	418 408	408	405

^a M corresponds to the respective metal atom within the coordination polymers listed in the header row.

Table S23. Assignments of important vibration bands¹³⁻¹⁹ observed in infrared spectra of the complexes [MnCl₂(Hpt)] (**9**), [FeCl₂(Hpt)] (**10**), [CoCl₂(Hpt)] (**11**), and [CoBr₂(Hpt)] (**12**). Corresponding spectra are given in Figure S32. ν = stretching vibration, δ = deformation vibration (in plane), γ = out-of-plane vibration, Tz = triazole ring, Py = pyridine ring.

Assignment	[MnCl ₂ (Hpt)] (9) ^a	[MnCl ₂ (Hpt)] (9) ^b	[FeCl ₂ (Hpt)] (10) ^a	[FeCl ₂ (Hpt)] (10) ^b	[CoCl ₂ (Hpt)] (11) ^a	[CoCl ₂ (Hpt)] (11) ^b	[CoBr ₂ (Hpt)] (12) ^a
ν (N-H) (hydrogen bonding)	3450	3446	3442	3442	3443	3440	3432
ν (C-H)	3200 -2500	3200 -2500	3200 -2500	3200 -2500	3200 -2500	3200 -2500	3200 -2500
ν (C=N) and ν (C=C)	1657	1654	1633	1633	1654	1657	1635
	1603	1603	1605	1605	1608	1608	1606
	1569	1569	1569	1568	1569	1569	1569
ν (C-N)	1477	1477	1482	1476	1477	1479	1477
ν_{Ring} (Py)	1448	1449	1448	1446	1449	1449	1448
ν_{Ring} (Py) and ν_{Ring} (TzH)	1422	1423	1425	1422	1426	1426	1423
ν_{Ring} (TzH)	1289	1289	1288	1285	1289	1289	1285
ν_{Ring} (Py) and ν_{Ring} (TzH)	1272	1272	1271	1265	1271	1271	1265
ν_{Ring} (TzH)	1149	1150	1150	1149	1152	1152	1149
ν (C-N) of Py and TzH	1098	1099	1098	1095	1099	1099	1098
ν (C-N) of TzH	1051	1051	1051	1050	1051	1051	1051
γ (C-N)	899	899	899	897	897	897	899
	797	797	797	797	797	797	797
δ (C-H)	749	749	751	751	752	752	752
γ (Tz)	724	724	724	724	724	724	724
	714	715	715	715	717	715	717
	639	639	639	636	639	639	635
γ (Py)	479	479	486	486	490	490	490
ν (M-N) ^c	412	412	415	415	421	419	419

^a Synthesised from metal halide in pyridine. ^b Synthesised from metal halide hydrate in acetonitrile. ^c M corresponds to the metal contained in the compound as stated in the header row.

Table S24. Compound numbers, sum formulae, theoretical and experimental elemental weight percentages, besides suggested sum formulas considering solvent molecules, and calculated weight percentages according to these sum formula suggestions of the coordination polymers **1** – **7**.

Compound number	XRD sum formulae ^a	Theoretical elemental weight percentages ^b [wt-%]			Sum formulae considering solvents	Calculated elemental weight percentages ^c [wt-%]			Experimental elemental weight percentages [wt-%]		
		C	H	N		C	H	N	C	H	N
1	$\frac{1}{2}[\text{Mn}(\text{pt})_2]$	48.71	2.92	32.46	$\frac{1}{2}[\text{Mn}(\text{pt})_2] \cdot 0.34\text{Py} \cdot 0.21\text{H}_2\text{O}$	50.19	3.25	31.07	50.20	2.99	30.98
2	$\frac{1}{2}[\text{Fe}(\text{pt})_2]$	48.58	2.91	32.37	$\frac{1}{2}[\text{Fe}(\text{pt})_2] \cdot 0.34\text{Py} \cdot 0.21\text{H}_2\text{O}$	50.04	3.24	31.00	50.02	2.96	30.91
3	$\frac{1}{2}[\text{Co}(\text{pt})_2]$	48.15	2.89	32.09	$\frac{1}{2}[\text{Co}(\text{pt})_2] \cdot 0.34\text{Py} \cdot 0.21\text{H}_2\text{O}$	49.65	3.22	30.74	49.82	2.93	30.96
4	$\frac{1}{2}[\text{Ni}(\text{pt})_2]$	48.18	2.89	32.11	$\frac{1}{2}[\text{Ni}(\text{pt})_2] \cdot 0.11\text{Py} \cdot 0.63\text{H}_2\text{O}$	47.38	3.23	30.78	47.37	3.20	30.88
5	$\frac{1}{2}[\text{Cu}(\text{pt})_2]$	47.28	2.83	31.51	$\frac{1}{2}[\text{Cu}(\text{pt})_2] \cdot 0.05\text{Py} \cdot 0.63\text{H}_2\text{O}$	46.38	3.14	30.55	46.07	2.78	29.64
6	$\frac{1}{2}[\text{Zn}(\text{pt})_2]$	47.31	2.84	31.53	$\frac{1}{2}[\text{Zn}(\text{pt})_2] \cdot 0.39\text{Py} \cdot 0.63\text{H}_2\text{O}$	48.15	3.34	29.55	48.31	2.96	29.53
7	$\frac{1}{2}[\text{Cd}(\text{pt})_2]$	41.76	2.50	27.83	$\frac{1}{2}[\text{Cd}(\text{pt})_2] \cdot 0.24\text{Py} \cdot 0.63\text{H}_2\text{O}$	41.96	2.88	26.71	42.15	2.90	26.66

^a Sum formulae of **1** – **7** correspond to the formula of $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**), which was found by SCXRD investigations. ^b Elemental weight percentages were calculated according to given sum formulae in the second column. ^c Elemental weight percentages were calculated according to sum formulae as given in column 9 considering solvent molecules within pore channels.

Table S25. Compound numbers, sum formulae, theoretical and experimental elemental weight percentages of the complexes **9** – **14** synthesised in different solvents (Py = pyridine, MeCN = acetonitrile).

Compound number	SCXRD sum formulae	Solvent for synthesis	Theoretical elemental weight percentages ^a [wt-%]			Experimental elemental weight percentages [wt-%]		
			C	H	N	C	H	N
9	$[\text{MnCl}_2(\text{Hpt})_2]$	Py	40.32	2.30	26.80	40.06	2.70	26.19
10	$[\text{FeCl}_2(\text{Hpt})_2]$		40.13	2.89	26.74	40.87	2.80	26.43
13	$[\text{CoCl}_2(\text{Hpt})_2]$		39.83	2.87	26.54	39.88	2.84	25.62
14	$[\text{CoBr}_2(\text{Hpt})_2]$		32.90	2.37	21.93	32.90	2.37	21.93
9	$[\text{MnCl}_2(\text{Hpt})_2]$	MeCN	40.32	2.30	26.80	40.30	2.89	26.50
10	$[\text{FeCl}_2(\text{Hpt})_2]$		40.13	2.89	26.74	39.38	2.72	26.01
12	$[\text{FeI}_2(\text{Hpt})_2]$		27.93	2.01	18.62	27.83	1.89	17.76
13	$[\text{CoCl}_2(\text{Hpt})_2]$		39.83	2.87	26.54	40.29	2.57	26.47
14	$[\text{CoBr}_2(\text{Hpt})_2]$		32.90	2.37	21.93	32.40	2.23	20.96

^a Elemental percentages were calculated according to given sum formulae in the second column.

Table S26. Onsets (temperature T , and relative mass m_r), besides relative mass losses Δm_r of $\frac{1}{2}[\text{Mn}(\text{pt})_2]$ (**1**), $\frac{1}{2}[\text{Co}(\text{pt})_2]$ (**3**), $\frac{1}{2}[\text{Ni}(\text{pt})_2]$ (**4**), and $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**) determined by STA. The letters a – f resemble the assignments as stated in Figure S33, Figure S34, Figure S35, and Figure S36.

Compound number	Onsets						Relative mass losses Δm_r , wt-%		
	a		b		c		d	e	f
	T [°C]	m_r [wt-%]	T [°C]	m_r [wt-%]	T [°C]	m_r [wt-%]			
1	92	100	410	93	465	65	7	28	40
3	102	100	415	95	465	74	5	21	50
4	123	100	470	94	510	50	6	44	28
6	101	100	460	97	490	39	3	58	14

Table S27. Lattice parameters a , c and cell volume V determined by Pawley refinements (Figure S4) of recorded PXRD patterns of the coordination polymers $\frac{1}{2}[\text{M}(\text{pt})_2]$ ($\text{M} = \text{Mn} - \text{Cd}$; Figure 2 in the main paper). Standard deviations are given in brackets.

Compound	M ($\frac{1}{2}[\text{M}(\text{pt})_2]$)	a [pm]	c [pm]	V [10^6 pm^3]
1	Mn	2283.10(8)	1305.60(9)	6805.5(7)
2	Fe	2256.0(2)	1279.2(1)	6510.8(8)
3	Co	2263.96(6)	1269.95(7)	6509.1(5)
4	Ni	2254.8(2)	1262.2(2)	6417(2)
5	Cu	2302.3(6)	1237.8(2)	6560(4)
6	Zn	2275.79(7)	1275.20(7)	6604.6(5)
7	Cd	2299.14(7)	1325.4(2)	7005.9(7)

Table S28. Weight percentages of lanthanides within $\text{EuTb}@\frac{1}{2}[\text{Zn}(\text{pt})_2]$ impregnated in stated solvents. Amounts were determined by inductively coupled plasma mass spectrometry (ICP-MS).

Solvent for utilized for impregnation of $\frac{1}{2}[\text{Zn}(\text{pt})_2]$	Eu [wt-%]	Tb [wt-%]
DMF	1.71	1.97
MeOH	2.16	2.29
MeCN	1.72	1.99

3.2 Depictions of single crystal structures

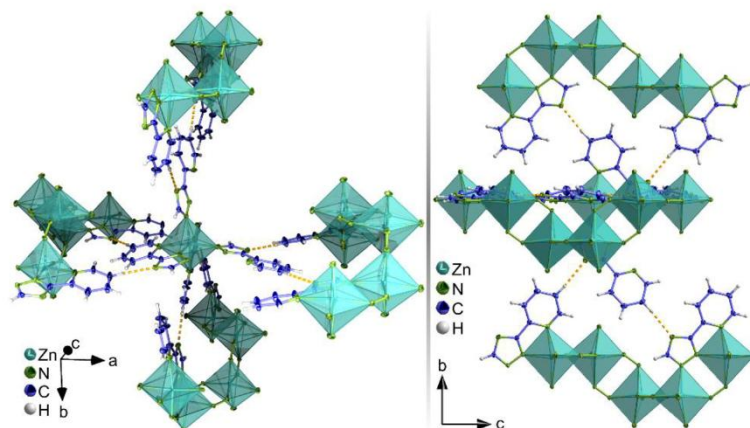


Figure S1. Depiction of C-H...N interactions between polymeric strands of $\frac{1}{3}[\text{Zn}(\text{pt})_2]$ (**6**). Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. For clarity, some of the ligand molecules are omitted and only the neighbored nitrogen atoms of the triazole ring are shown. Only one of the two disorders of the ligand is depicted.

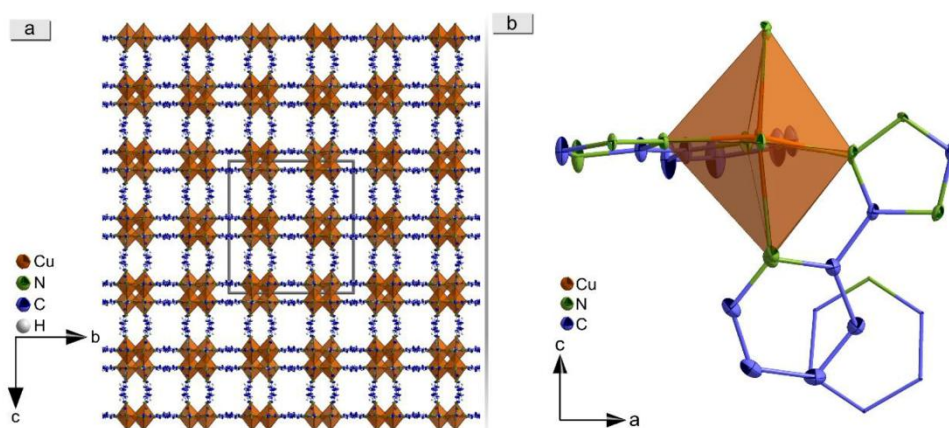


Figure S2. Excerpt of the crystal structure of $\frac{1}{3}[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (**8**) along the crystallographic a axis (**a**; intercalated solvent molecules are omitted), besides depiction of the stacking of pyridine and the ligand (**d**; hydrogen atoms are omitted). Polyhedra around Cu are highlighted in orange. Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. Crystallographic data is summarised in Table S3.

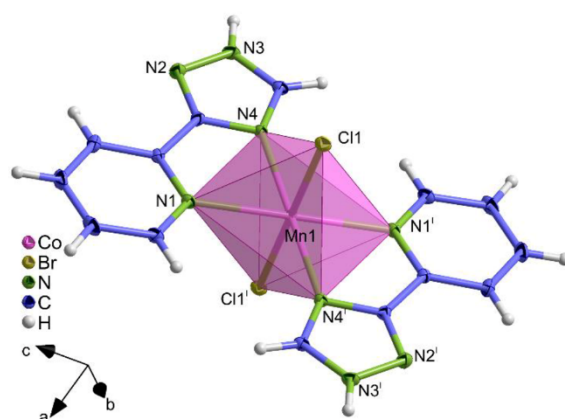


Figure S3. Extended octahedral coordination of Mn^{2+} in $[\text{MnCl}_2(\text{Hpt})]$ (**9**). The octahedral coordination of Mn^{2+} is highlighted in pink. Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. N–H $\cdots$ Cl hydrogen bonds are shown with dashed orange lines. Crystallographic data is summarised in Table S5. Symmetry operations: $1 = 1-x, 1-y, 1-z$.

3.3 PXRD Investigation

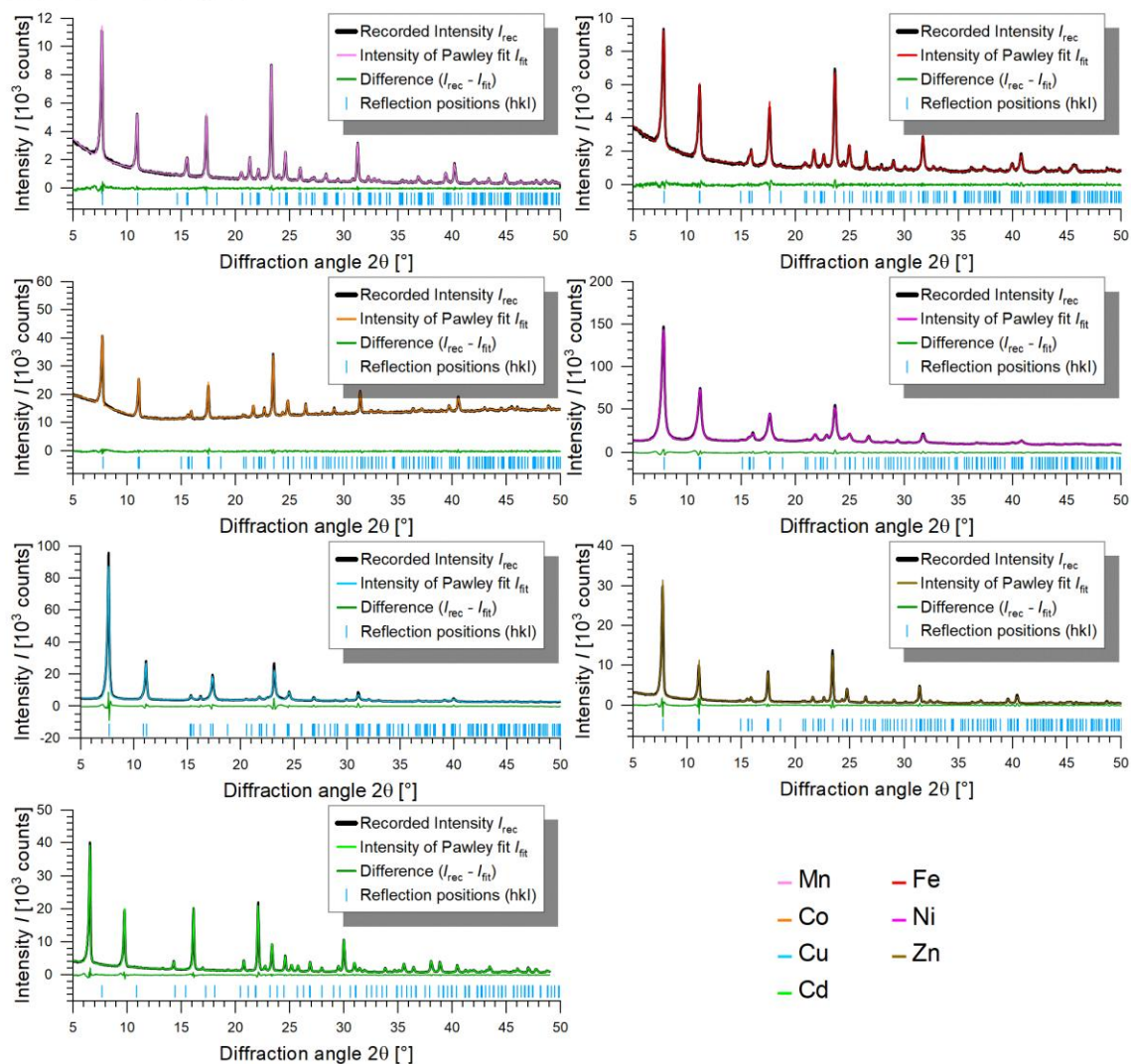


Figure S4. Difference plots for Pawley refinements of one-dimensional coordination polymers $[M(pt)_2]$ (M = Mn (1), Fe (2), Co (3), Ni (4), Cu (5), Zn (6), Cd (7)). Determined cell parameters are listed in Table 5 within the main paper. Reached R_{wp} values are given in Table S15.

When taking a closer look at the cell constants (Table S278), it gets clear that the length of cell axis *a* does not follow a simple trend being expected for exchanging the metal ions according to their respective ionic radii⁴² (Figure S5). The *a* axis of $\frac{1}{2}[\text{Fe}(\text{pt})_2]$ (**2**) is shorter than assumed. This may be explained by simultaneous existence of both, high and low spin configuration, as described later in this manuscript. Due to a smaller ionic radius of octahedrally coordinated Fe^{II} in low spin configuration,⁴² the overall length of cell axis *a* is reduced. Therefore, the cell parameter *a* should prolong upon heating, which was observed in Pawley refinements of temperature-dependent PXRD investigations (Figures S5, S9, and S10, Table S15). The effect of the temperature on the length of *a* thereby is too low to explain the prominent elongation of *a* for $\frac{1}{2}[\text{Fe}(\text{pt})_2]$ (**2**) upon heating. This gets clear when comparing respective lengths for temperature-dependent PXRD measurement refinements of $\frac{1}{2}[\text{Co}(\text{pt})_2]$ (**3**) and $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**) (Figure S5). Hence, this further substantiates the assumption of simultaneous existence of both, high and low spin configuration, and a continuous spin crossover, which also coincides with observed absorption properties of $\frac{1}{2}[\text{Fe}(\text{pt})_2]$ (**2**) (see following discussion).

Table S29. Lattice parameters *a*, *c* and cell volume *V* determined by Pawley refinements (Figure S4) of recorded PXRD patterns of the coordination polymers $\frac{1}{2}[\text{M}(\text{pt})_2]$ (*M* = Mn - Cd); Figure 2 in the main paper). Standard deviations are given in brackets.

Compound	<i>M</i> ($\frac{1}{2}[\text{M}(\text{pt})_2]$)	<i>a</i> [pm]	<i>c</i> [pm]	<i>V</i> [10 ⁶ pm ³]
1	Mn	2283.10(8)	1305.60(9)	6805.5(7)
2	Fe	2256.0(2)	1279.2(1)	6510.8(8)
3	Co	2263.96(6)	1269.95(7)	6509.1(5)
4	Ni	2254.8(2)	1262.2(2)	6417(2)
5	Cu	2302.3(6)	1237.8(2)	6560(4)
6	Zn	2275.79(7)	1275.20(7)	6604.6(5)
7	Cd	2299.14(7)	1325.4(2)	7005.9(7)

Furthermore, the cell parameters of $\frac{1}{2}[\text{Cu}(\text{pt})_2]$ (**5**) deviate from the expected trend, as well (Figure S5), since the cell axis *a* is longer, and *c* is shorter than assumed. This indicates enhanced attractive interactions between ligand and transition metal, reducing interatomic distances and hence shortening *c* axis. Contrary, due to reduced attractive forces between the polymeric strands, cell axis *a* is elongated (Figure S5). This is further substantiated by observed IR bands corresponding to vibrations of the ligand. Vibrations of the pyridine ring are shifted to higher energy in comparison to bands of $\frac{1}{2}[\text{M}(\text{pt})_2]$ (*M* = Mn, Fe, Co, Ni, Zn, Cd), resulting from increased Cu–N interaction and hence reduced electron density within the ring.

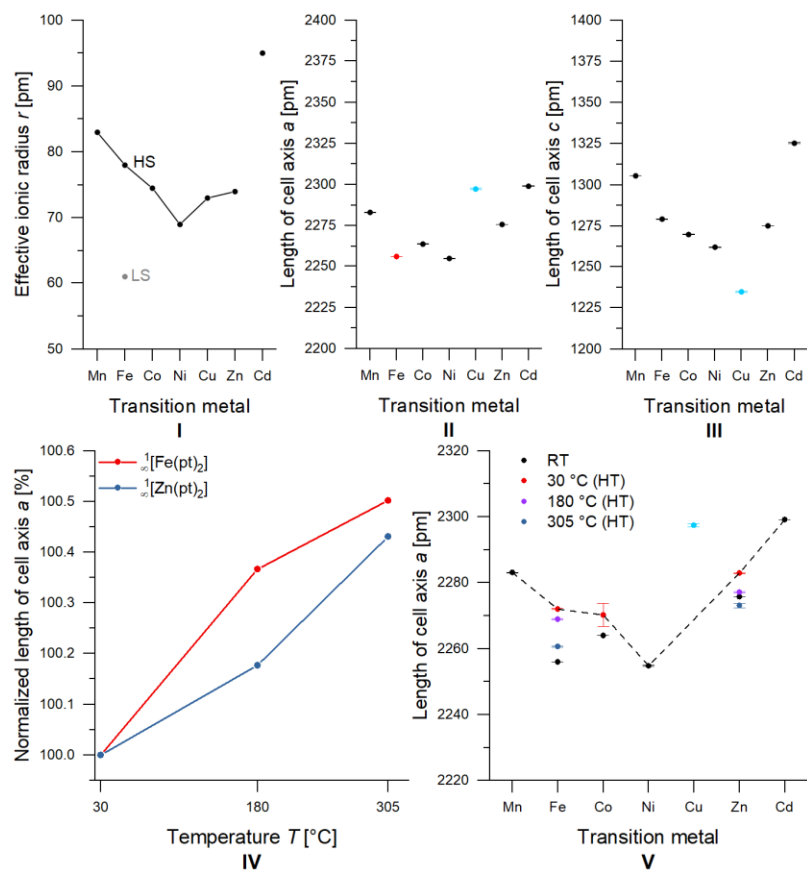


Figure S5. Comparison of effective ionic radii of divalent transition metal ions in octahedral coordination²⁰ with cell parameters of CP 1–7 obtained by Pawley refinement.

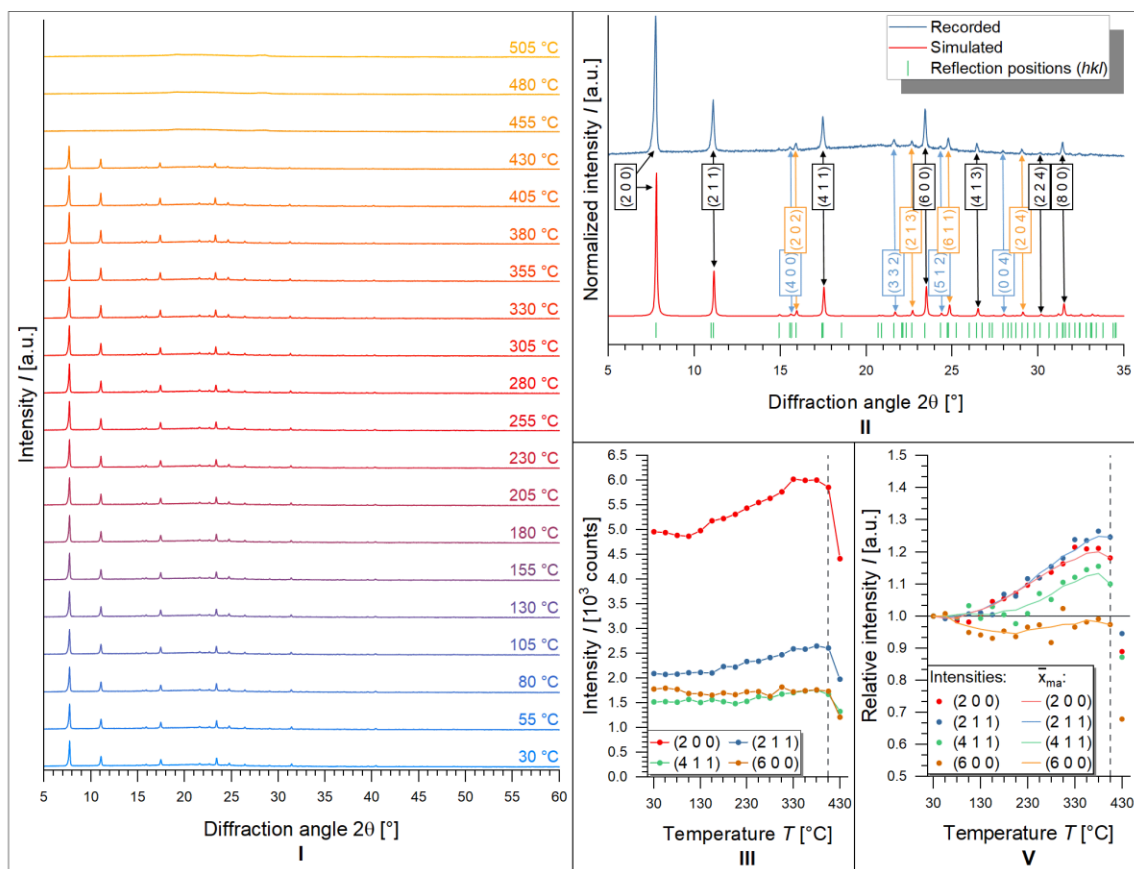


Figure S6. I: Temperature-dependent PXRD patterns of $[Zn(pt)_2]$ (**6**) recorded from 30 °C to 505 °C in steps of 25 °C (left). II: Diffractogram of **6** recorded at 30 °C and pattern of **6** simulated from SCXRD data, besides the (hkl) assignments of identifiable reflections. Calculated reflection positions are marked with green bars. III: Intensities of the four most prominent reflections of **6** in dependence of measurement temperature. IV: Intensities as given in III, relative to the intensity of respective reflections at 30 °C, besides the corresponding moving average $\bar{x}_{ma}$. The dashed line marks the temperature at which the decomposition of the coordination polymer begins (here 405 °C).

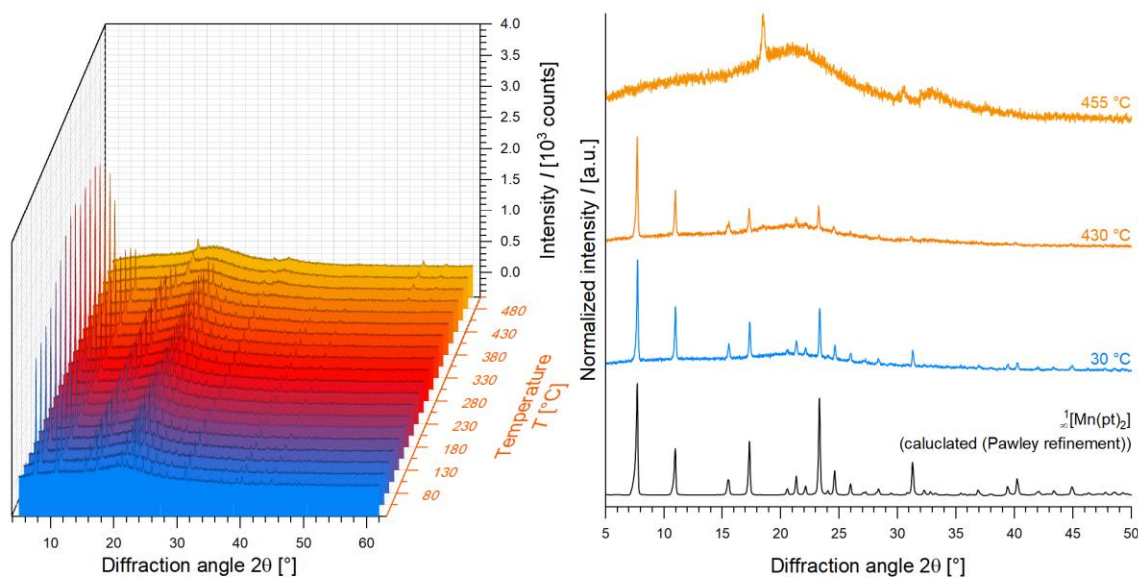


Figure S7. Waterfall plot of temperature-dependent PXRD patterns of $\frac{1}{2}[\text{Mn}(\text{pt})_2]$ (**1**) recorded from 30 °C to 505 °C in steps of 25 °C (left), besides respective diffractograms of **1** at 30 °C, 430 °C and 455 °C in comparison to a pattern of **1** obtained by Pawley refinement (right). $\frac{1}{2}[\text{Mn}(\text{pt})_2]$ (**1**) is identifiable by PXRD for temperatures up to 430 °C. At 455 °C, CP **1** has complete decomposed to an unknown phase.

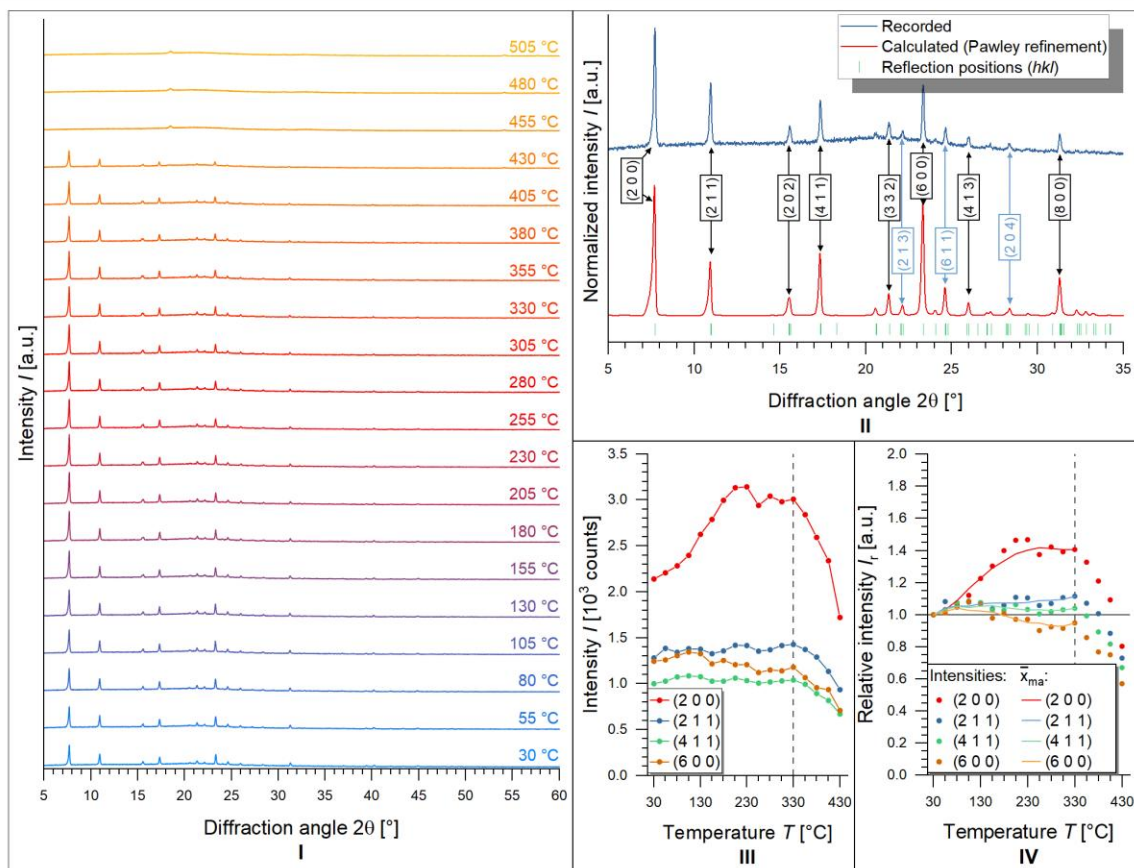


Figure S8. I: Temperature-dependent PXRD patterns of $\frac{1}{2}[\text{Mn}(\text{pt})_2]$ (**1**) recorded from 30 °C to 505 °C in steps of 25 °C (left). II: Diffractogram of **1** recorded at 30 °C and pattern of **1** obtained by Pawley refinement, besides the (hkl) assignments of identifiable reflections. Calculated reflection positions are marked with green bars. III: Intensities of the four most prominent reflections of **1** in dependence of measurement temperature. IV: Intensities as given in III, relative to the intensity of respective reflections at 30 °C, besides the corresponding moving average $\bar{x}_{\text{ma}}$. The dashed line marks the temperature at which the decomposition of the coordination polymer begins (here 330 °C).

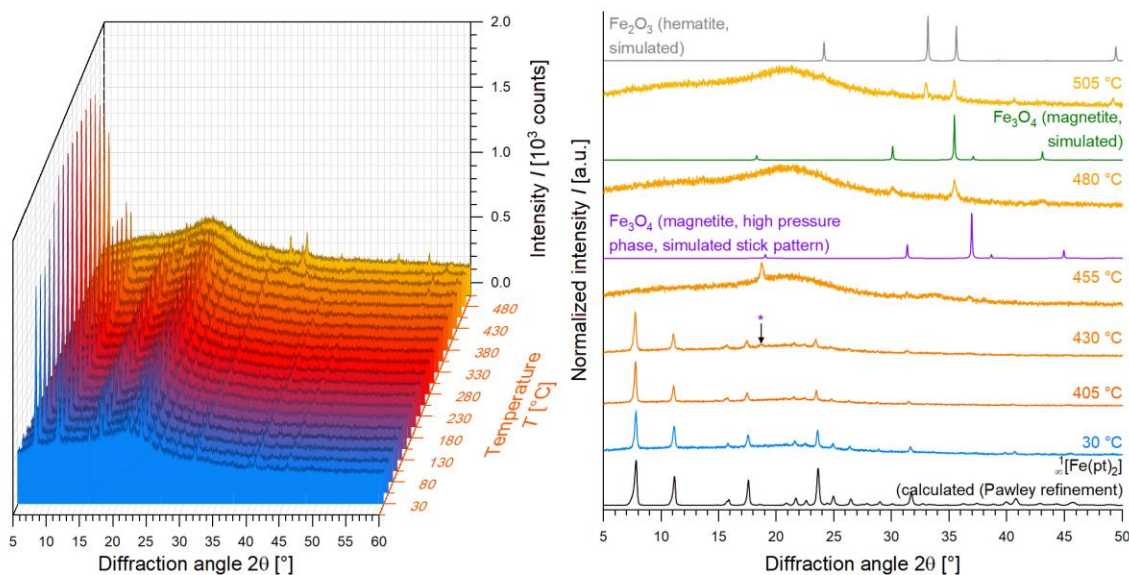


Figure S9. Waterfall plot of temperature-dependent PXRD patterns of $[Fe(pt)_2]$ (**2**) recorded from 30 °C to 505 °C in steps of 25 °C (left), besides respective diffractograms of **2** at 30 °C, and 405—505 °C in comparison to a pattern of **2** obtained by Pawley refinement (right). $[Fe(pt)_2]$ (**2**) is identifiable by PXRD for temperatures up to 430 °C. At 430 °C, a reflection of most likely a high pressure modification of magnetite²¹ begins to emerge (marked with *) indicating a beginning decomposition. At 455 °C, CP **2** has complete decomposed to that phase. Upon further heating to 480 °C, a phase transition to magnetite²² occurs. At 505 °C the majority phase of the product is identified as hematite.²³

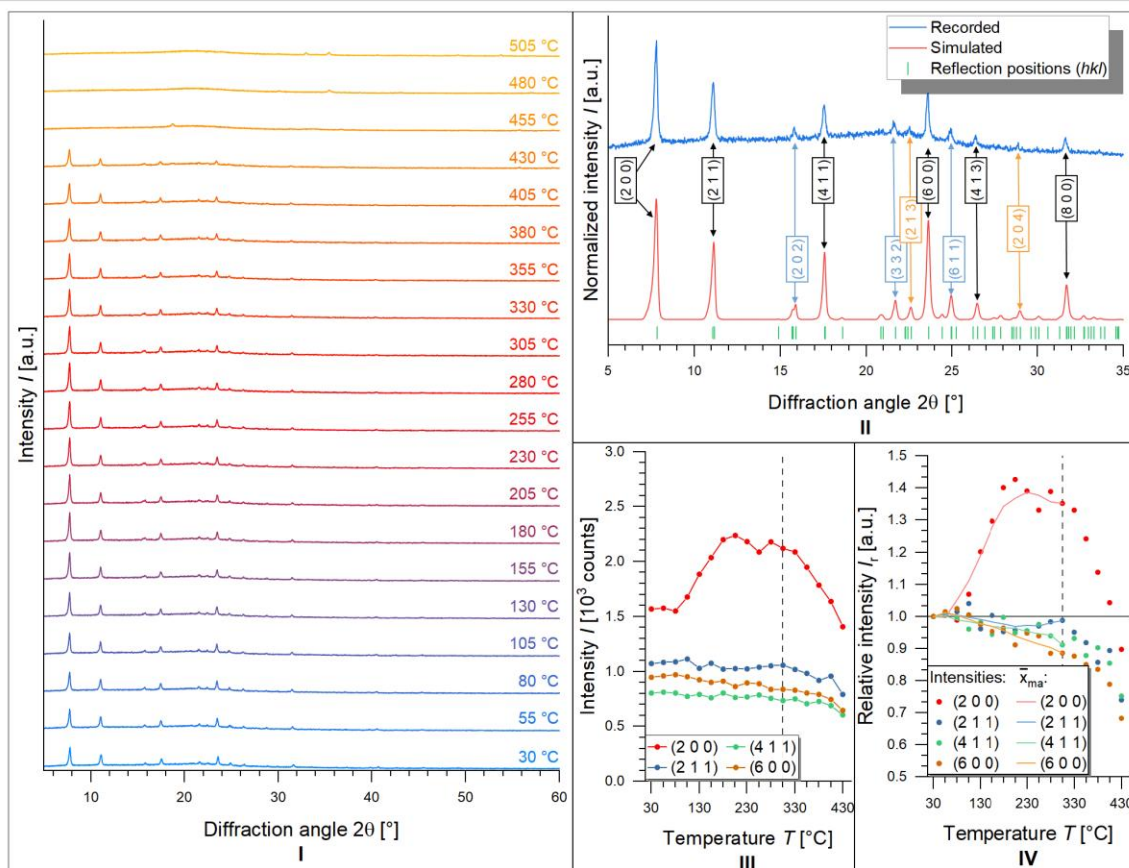


Figure S10. I: Temperature-dependent PXRD patterns of $[Fe(pt)_2]$ (**2**) recorded from 30 °C to 505 °C in steps of 25 °C (left). II: Diffractogram of **2** recorded at 30 °C and pattern of **2** obtained by Pawley refinement, besides the (hkl) assignments of identifiable reflections. Calculated reflection positions are marked with green bars. III: Intensities of the four most prominent reflections of **2** in dependence of measurement temperature. IV: Intensities as given in III, relative to the intensity of respective reflections at 30 °C, besides the corresponding moving average $\bar{x}_{ma}$. The dashed line marks the temperature at which the decomposition of the coordination polymer begins (here 305 °C).

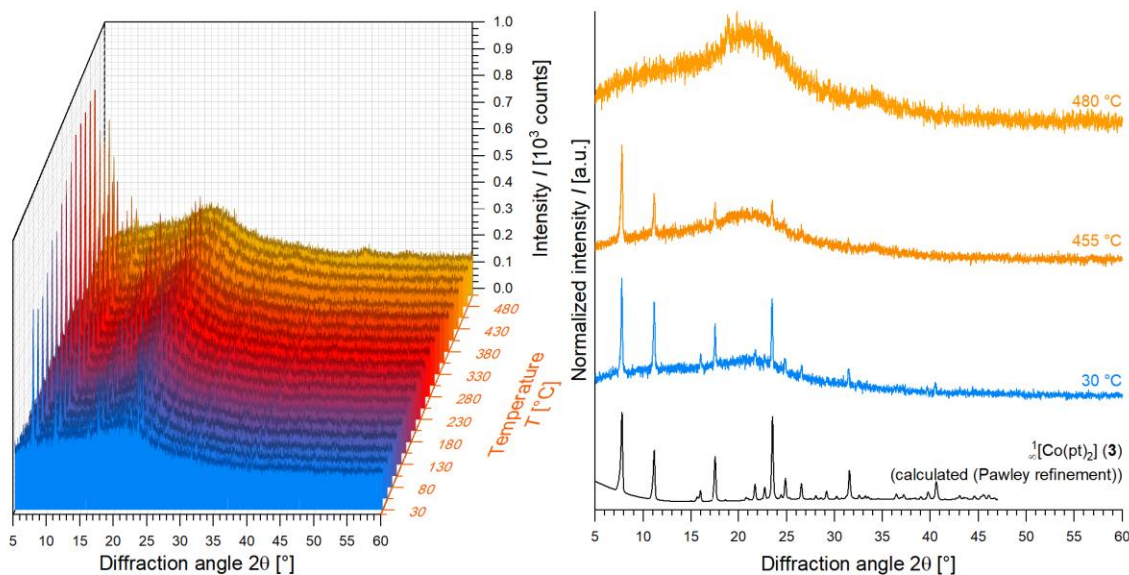


Figure S11. Waterfall plot of temperature-dependent PXRD patterns of $[\text{Co}(\text{pt})_2]$ (**3**) recorded from 30 °C to 505 °C in steps of 25 °C (left), besides respective diffractograms of **3** at 30 °C, 455 °C, and 480 °C in comparison to a pattern of **5** obtained by Pawley refinement (right). $[\text{Co}(\text{pt})_2]$ (**3**) is identifiable by PXRD for temperatures up to 455 °C. At 480 °C, CP **3** has completely decomposed resulting in an amorphous product.

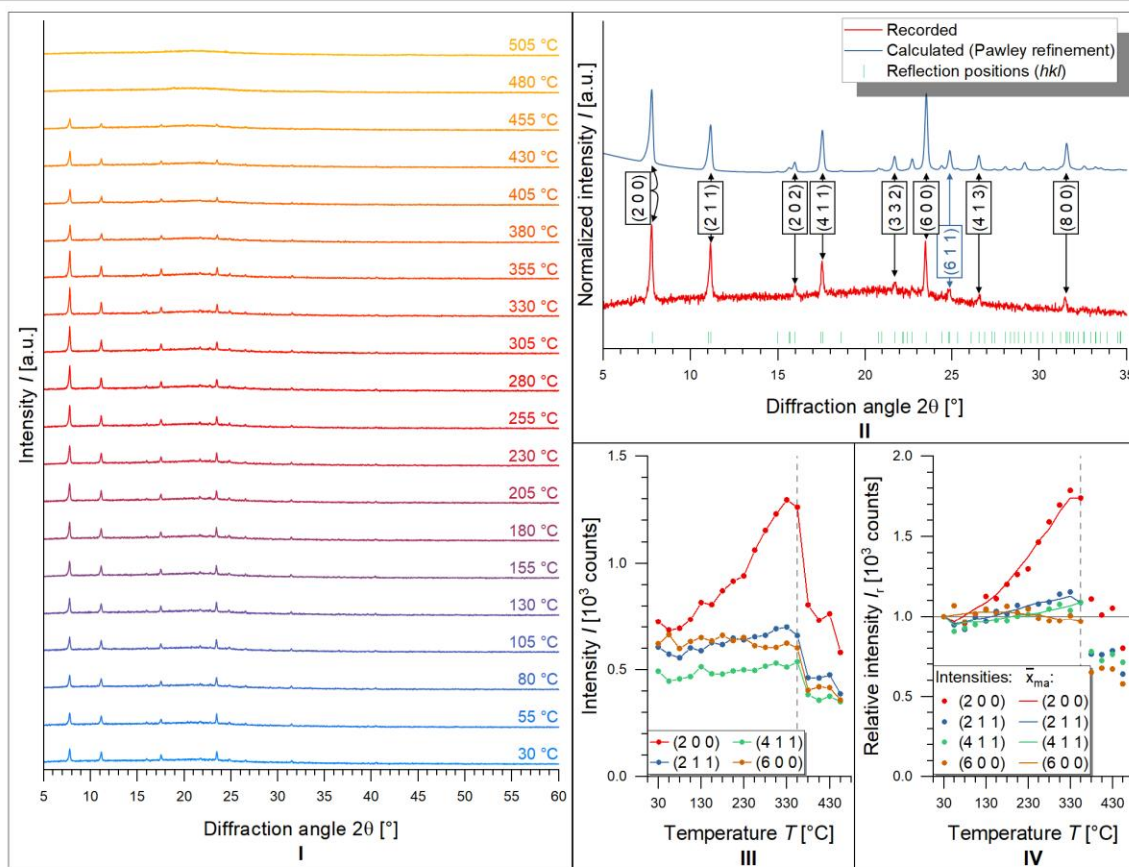


Figure S12. I: Temperature-dependent PXRD patterns of $[\text{Co}(\text{pt})_2]$ (**3**) recorded from 30 °C to 505 °C in steps of 25 °C (left). II: Diffractogram of **3** recorded at 30 °C and pattern of **3** obtained by Pawley refinement, besides the (hkl) assignments of identifiable reflections. Calculated reflection positions are marked with green bars. III: Intensities of the four most prominent reflections of **3** in dependence of measurement temperature. IV: Intensities as given in III, relative to the intensity of respective reflections at 30 °C, besides the corresponding moving average $\bar{x}_{\text{ma}}$. The dashed line marks the temperature at which the decomposition of the coordination polymer begins (here 355 °C).

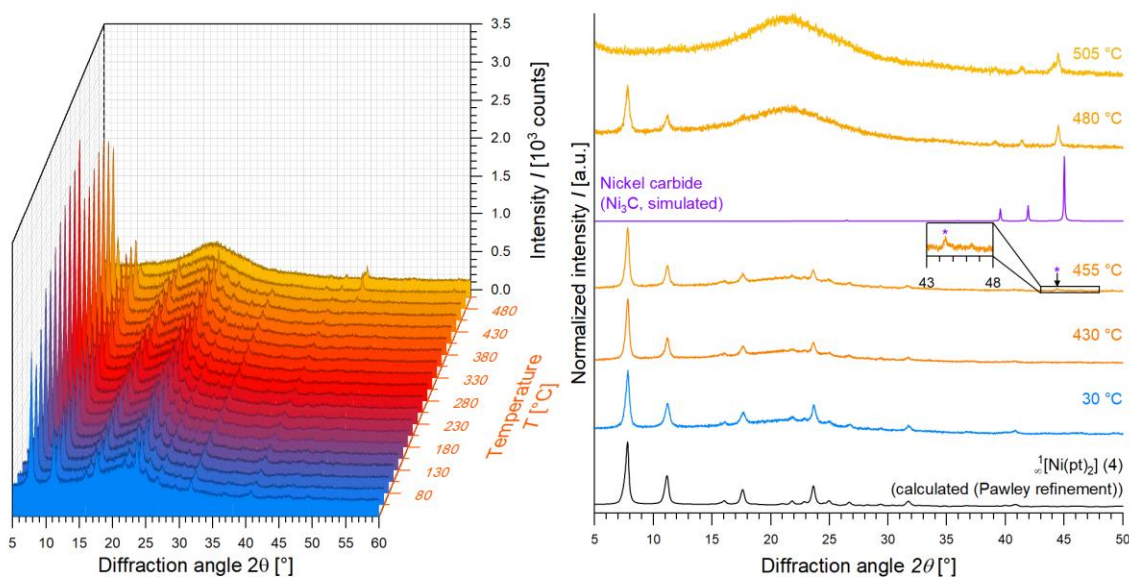


Figure S13. Waterfall plot of temperature-dependent PXRD patterns of $[Ni(pt)_2]$ (4) recorded from 30 °C to 505 °C in steps of 25 °C (left), besides respective diffraction patterns of 4 at 30 °C, 430—505 °C in comparison to a pattern of 4 obtained by Pawley refinement (right). $[Ni(pt)_2]$ (4) is identifiable by PXRD for temperatures up to 480 °C. At 455 °C, the most intense reflection of Ni_3C begins to emerge (marked with *) indicating a beginning decomposition. At 480 °C, reflections of Ni_3C are clearly observable. Upon further heating to 505 °C, CP 4 completely decomposes.

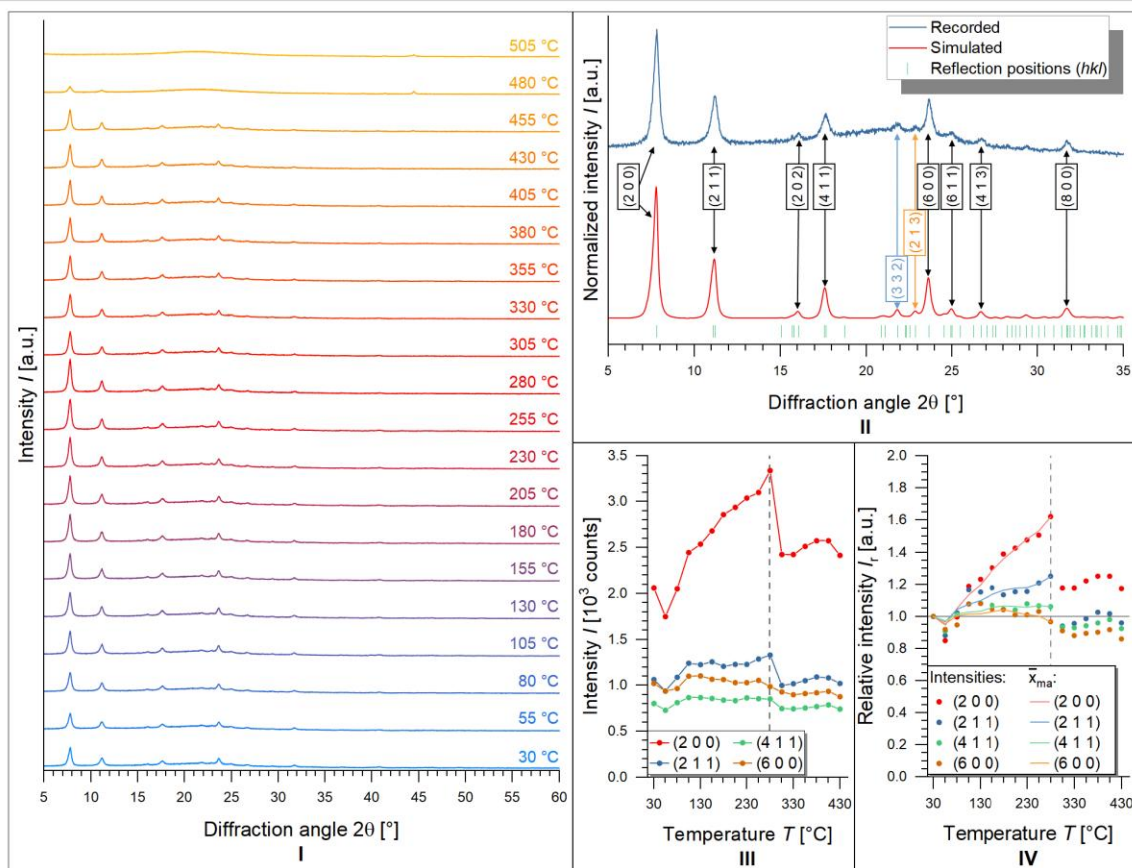


Figure S14. I: Temperature-dependent PXRD patterns of $[Ni(pt)_2]$ (4) recorded from 30 °C to 505 °C in steps of 25 °C (left). II: Diffraction pattern of 4 recorded at 30 °C and pattern of 4 obtained by Pawley refinement, besides the (hkl) assignments of identifiable reflections. Calculated reflection positions are marked with green bars. III: Intensities of the four most prominent reflections of 4 in dependence of measurement temperature. IV: Intensities as given in III, relative to the intensity of respective reflections at 30 °C, besides the corresponding moving average $\bar{x}_{ma}$. The dashed line marks the temperature at which the decomposition of the coordination polymer begins (here 280 °C).

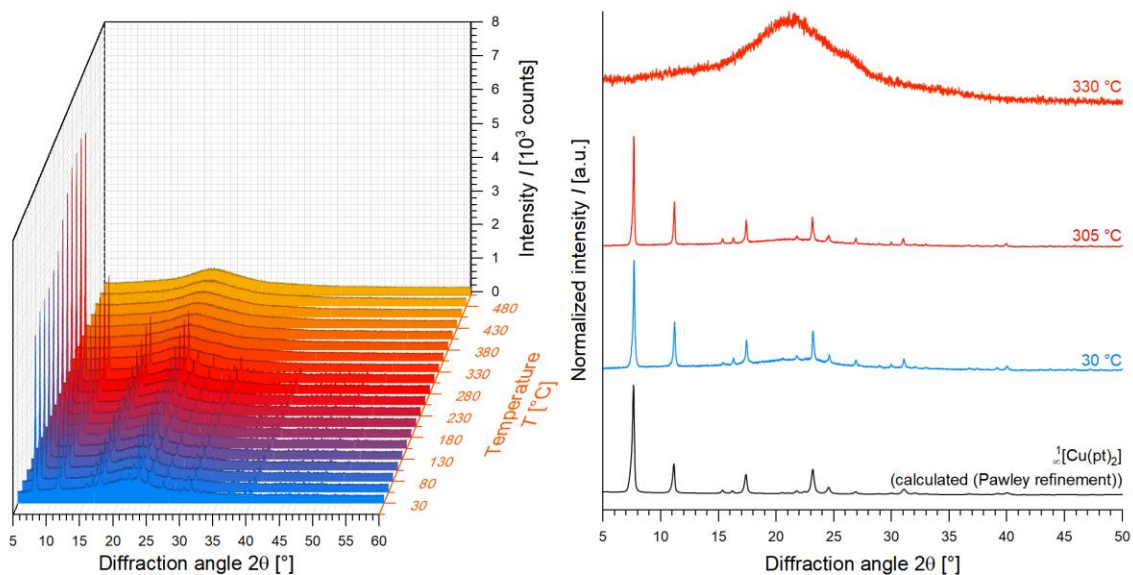


Figure S15. Waterfall plot of temperature-dependent PXRD patterns of $\frac{1}{2}[\text{Cu}(\text{pt})_2]$ (**5**) recorded from 30 °C to 505 °C in steps of 25 °C (left), besides respective diffractograms of **5** at 30 °C, 305 °C, and 330 °C in comparison to a pattern of **5** obtained by Pawley refinement (right). $\frac{1}{2}[\text{Cu}(\text{pt})_2]$ (**5**) is identifiable by PXRD for temperatures up to 305 °C. At 330 °C, CP **5** has complete decomposed to an amorphous product.

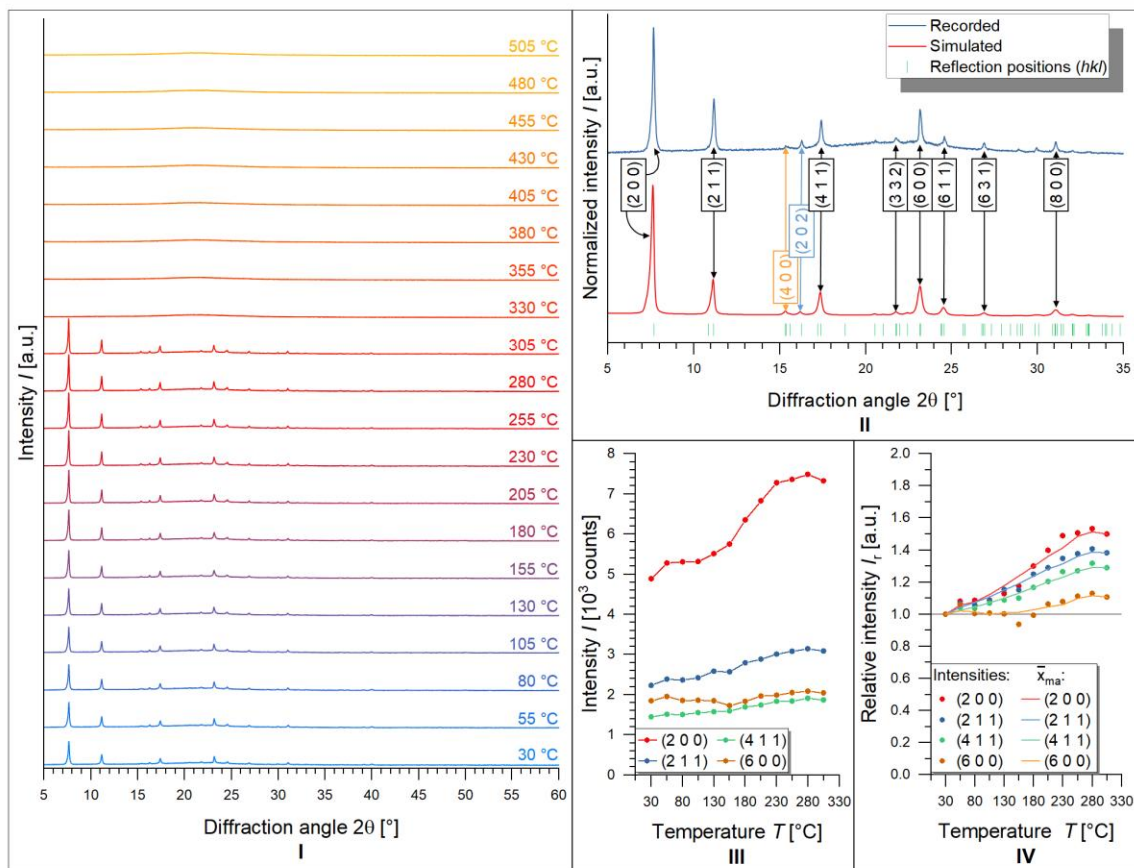


Figure S16. I: Temperature-dependent PXRD patterns of $\frac{1}{2}[\text{Cu}(\text{pt})_2]$ (**5**) recorded from 30 °C to 505 °C in steps of 25 °C (left). II: Diffractogram of **5** recorded at 30 °C and pattern of **5** obtained by Pawley refinement, besides the (hkl) assignments of identifiable reflections. Calculated reflection positions are marked with green bars. III: Intensities of the four most prominent reflections of **5** in dependence of measurement temperature. IV: Intensities as given in III, relative to the intensity of respective reflections at 30 °C, besides the corresponding moving average $\bar{x}_{\text{ma}}$.

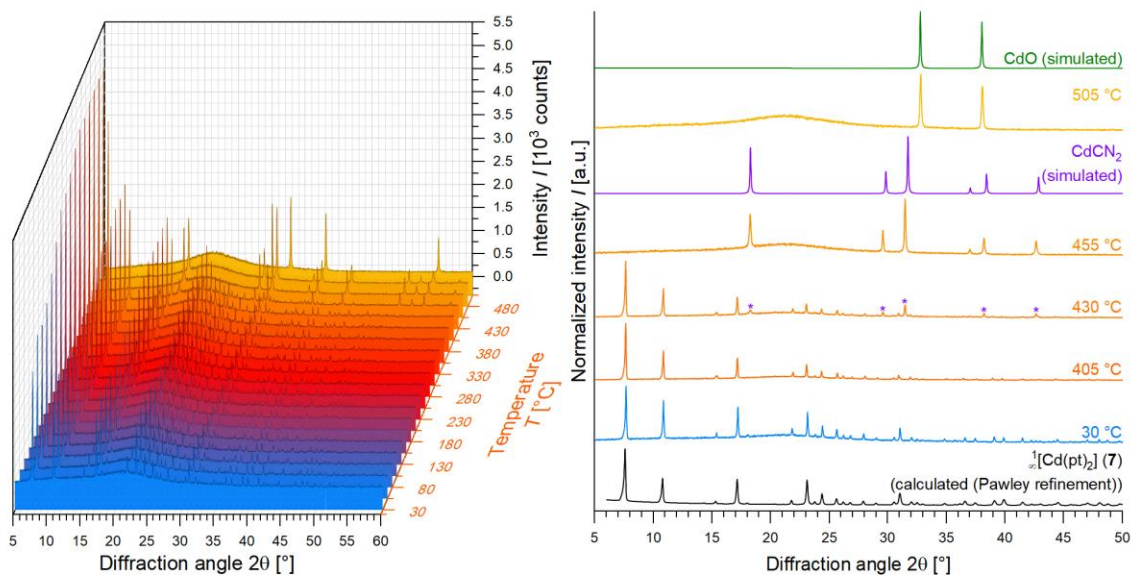


Figure S17. Waterfall plot of temperature-dependent PXRD patterns of $[Cd(pt)_2]$ (7) recorded from 30 °C to 505 °C in steps of 25 °C (left), besides respective diffractograms of 7 at 30 °C, and 405—505 °C in comparison to a pattern of 7 obtained by Pawley refinement (right). $[Cu(pt)_2]$ (5) is identifiable by PXRD for temperatures up to 430 °C. At 430 °C, reflections of $CdCN_2$ begin to emerge (marked with *) indicating a beginning decomposition. At 455 °C, CP 5 is complete decomposed to $CdCN_2$. Upon further heating to 505 °C, the majority phase can be identified as CdO .²⁶

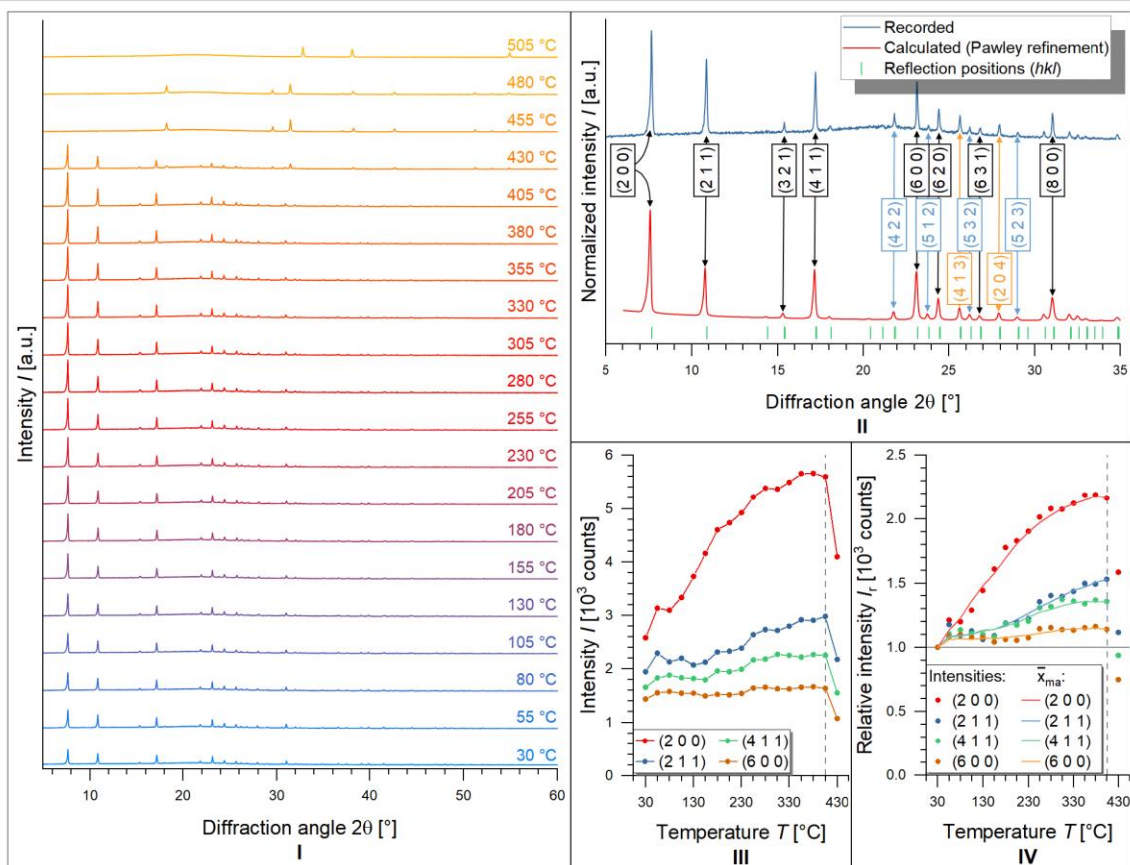


Figure S18. I: Temperature-dependent PXRD patterns of $[Cd(pt)_2]$ (7) recorded from 30 °C to 505 °C in steps of 25 °C (left). II: Diffractogram of 7 recorded at 30 °C and pattern of 7 obtained by Pawley refinement, besides the (hkl) assignments of identifiable reflections. Calculated reflection positions are marked with green bars. III: Intensities of the four most prominent reflections of 7 in dependence of measurement temperature. IV: Intensities as given in III, relative to the intensity of respective reflections at 30 °C, besides the corresponding moving average $\bar{x}_{ma}$.

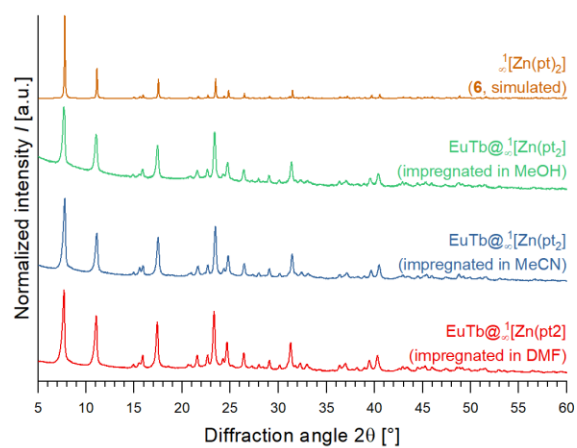


Figure S19. Powder X-ray diffraction patterns of $\text{EuTb}@{}^1[\text{Zn}(\text{pt})_2]$ (**6**) impregnated in different solvents.

3.4 UV-VIS Spectroscopy

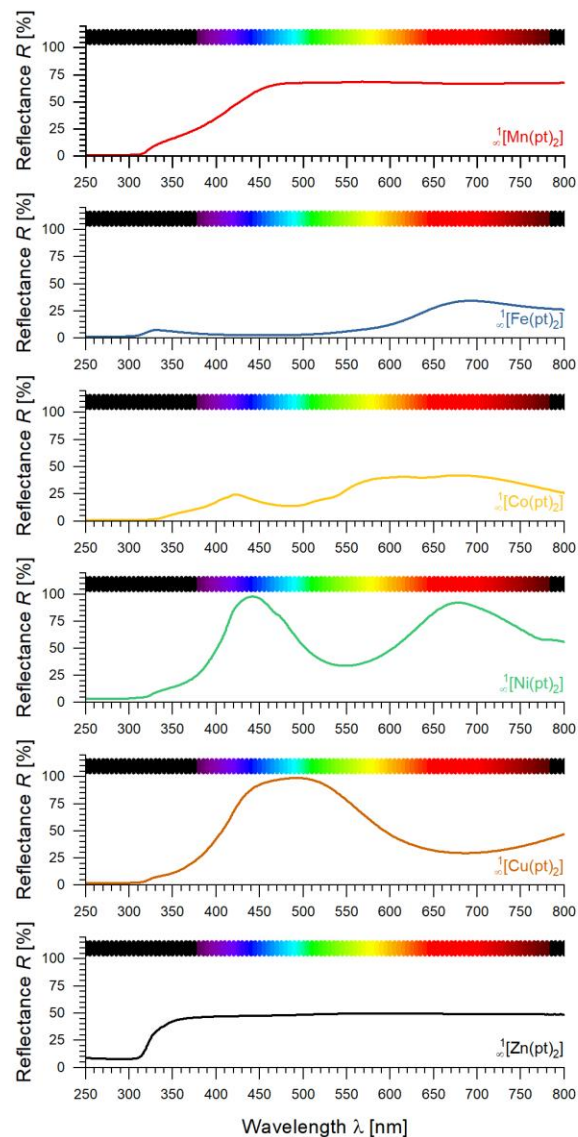


Figure S20. UV-VIS reflectance spectra of the coordination polymers $1[M(pt)_2]$ ($M = \text{Mn}$ (1), Fe (2), Co (3), Ni (4), Cu (5), Zn (6)).

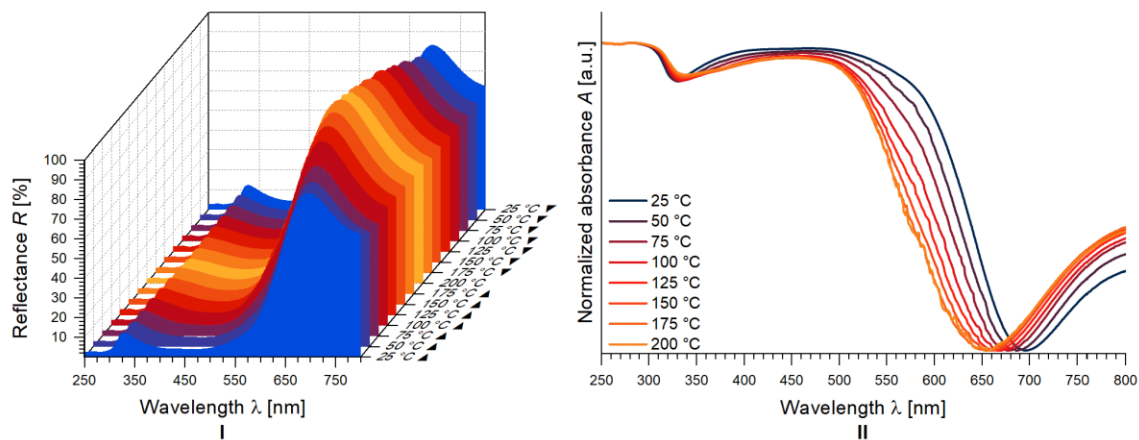


Figure S21. Reflectance spectra as waterfall diagram (I), besides calculated absorbance spectra (II) of temperature-dependent UV-VIS characterization of $[Fe(pt)_2]$ (CP 2). Triangles pointing upwards indicate spectra being recorded during heating up to 200 °C. Accordingly, triangles pointing downwards indicate spectra recorded while cooling down.

3.5 Photoluminescence Spectroscopy

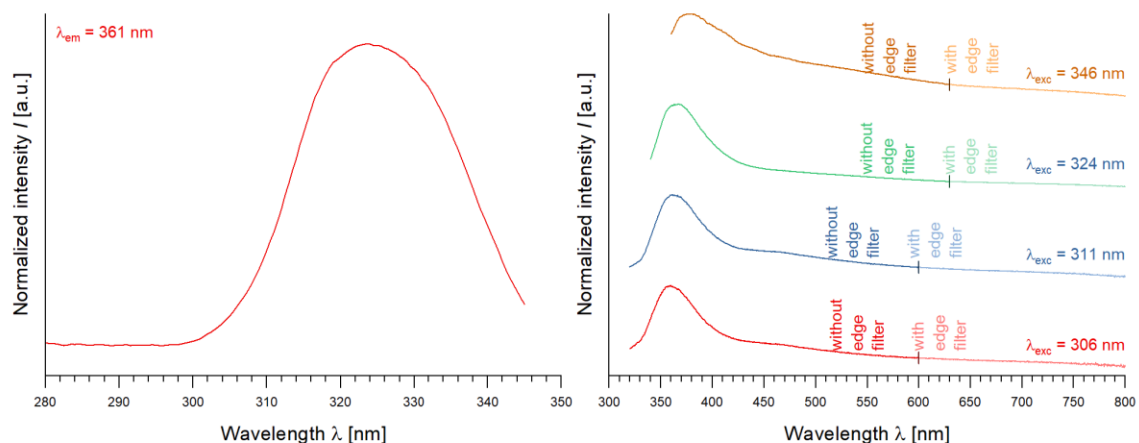


Figure S22. Excitation (left) and emission spectra (right) of the pure ligand 2-(1,2,4-1H-triazol-3-yl)pyridine (Hpt) as purchased. For recording of emission spectra at high wavelengths, a 395 nm edge filter was added to the beam path to prevent detection of excitation light of higher orders.

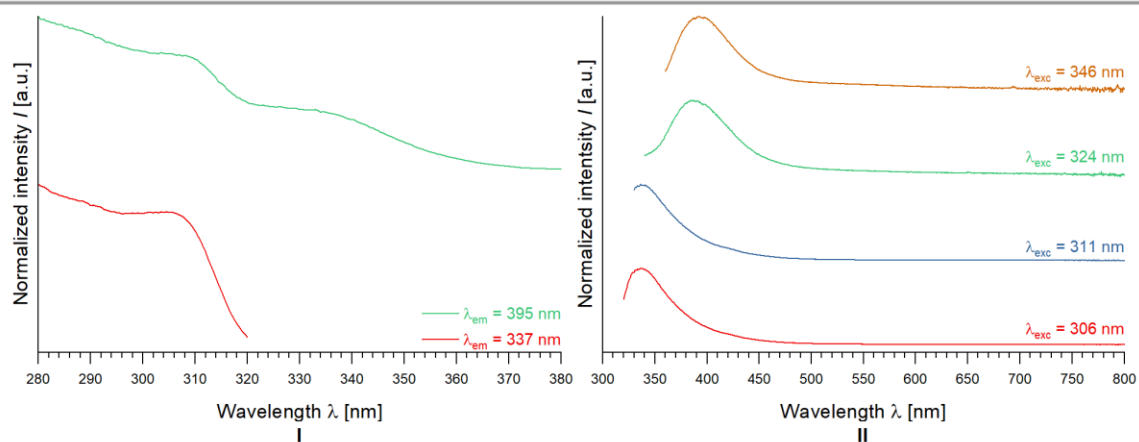


Figure S23. Excitation (left) and emission spectra (right) of a sample of activated $[\text{Zn}(\text{pt})_2]$ (CP 6).

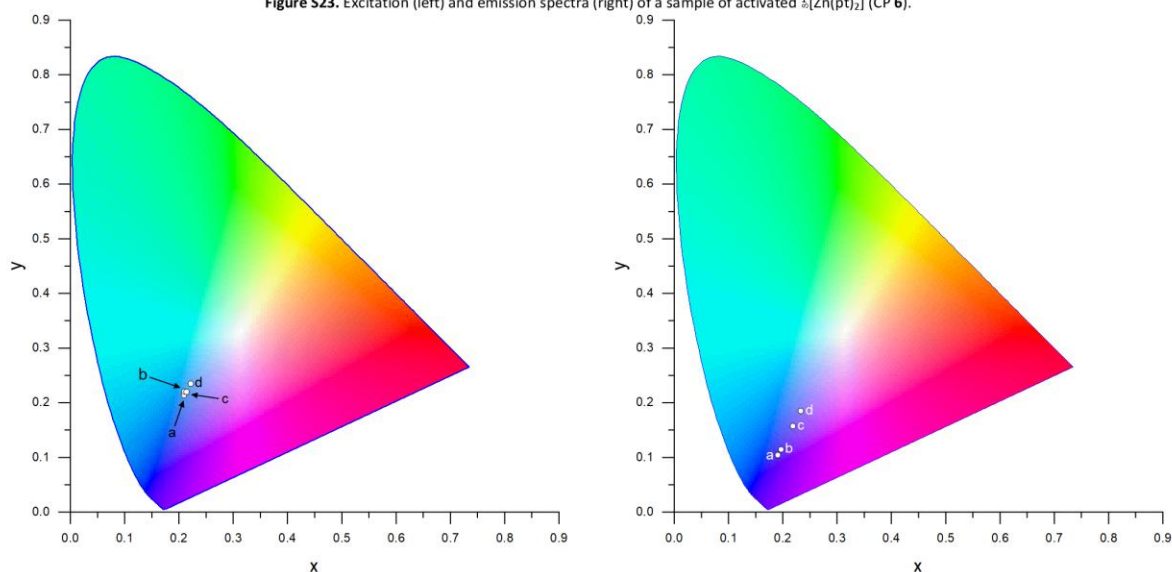


Figure S24. CIE chromaticity diagram of the ligand Hpt with inserted chromaticity coordinates xy for emission at different excitation wavelengths. a: $\lambda_{\text{exc}} = 306$ nm, b: $\lambda_{\text{exc}} = 311$ nm, c: $\lambda_{\text{exc}} = 324$ nm, d: $\lambda_{\text{exc}} = 337$ nm, e: $\lambda_{\text{exc}} = 346$ nm. For respective emission and excitation spectra, see Figure S22.

Figure S25. CIE chromaticity diagram of $[\text{Zn}(\text{pt})_2]$ (CP 6) with inserted chromaticity coordinates xy for emission at different excitation wavelengths. a: $\lambda_{\text{exc}} = 306$ nm, b: $\lambda_{\text{exc}} = 311$ nm, c: $\lambda_{\text{exc}} = 324$ nm, d: $\lambda_{\text{exc}} = 337$ nm, e: $\lambda_{\text{exc}} = 346$ nm. For respective emission and excitation spectra, see Figure S23.

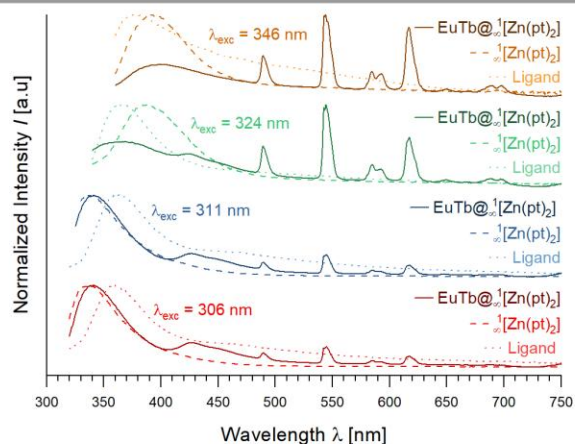


Figure S26. Comparison of emission profiles of the ligand Hpt (dotted lines), CP 6 ($[\text{Zn}(\text{pt})_2]$, dashed lines), and $\text{EuTb}@[\text{Zn}(\text{pt})_2]$ at different wavelengths.

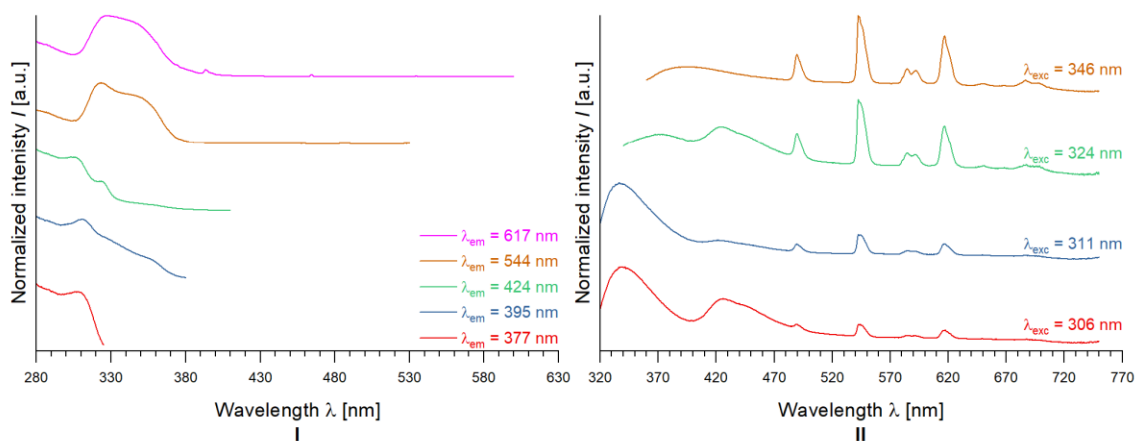


Figure S27. Excitation (left) and emission spectra (right) of $[Zn(pt)_2]$ impregnated with Eu and Tb ions for eight days using MeOH as solvent.

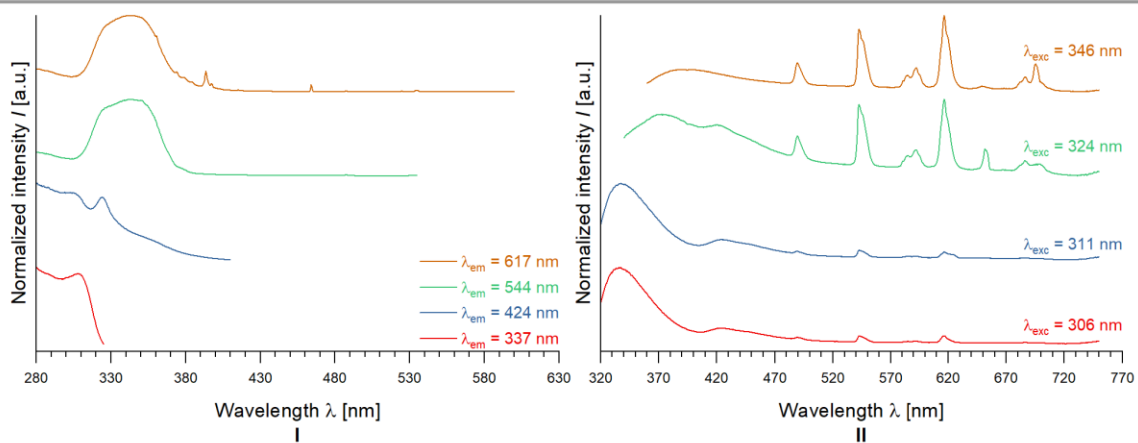


Figure S28. Excitation (left) and emission spectra (right) of $[Zn(pt)_2]$ impregnated with Eu and Tb ions for eight days using MeCN as solvent.

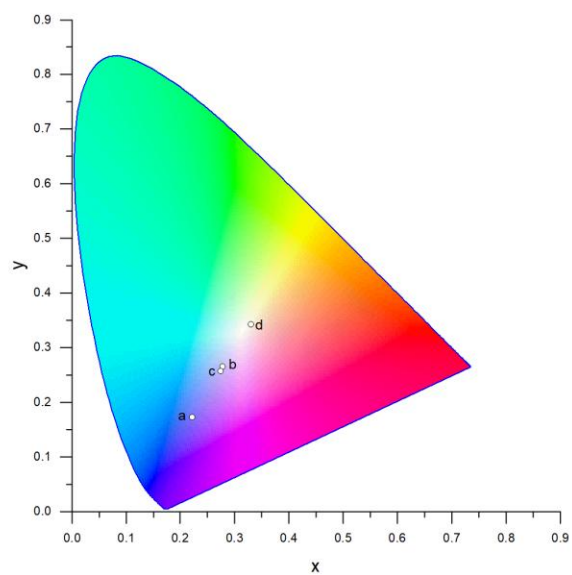


Figure S29. CIE chromaticity diagram with inserted chromaticity coordinates xy of $\frac{1}{3}[\text{Zn}(\text{pt})_2]$ impregnated with Eu and Tb ions for eight days using MeOH as solvent.

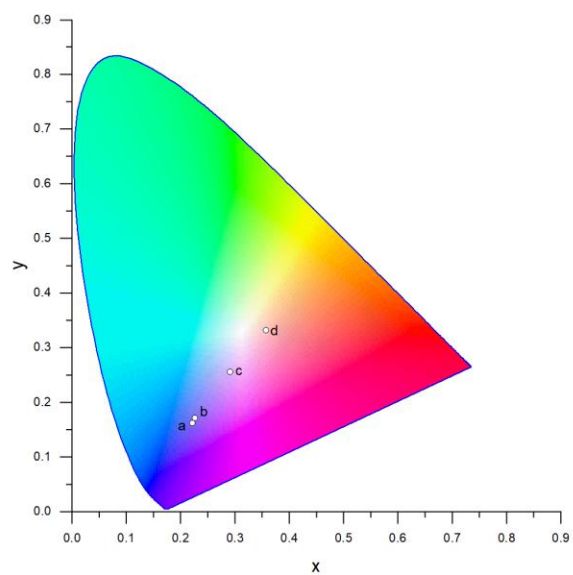


Figure S30. CIE chromaticity diagram with inserted chromaticity coordinates xy of $\frac{1}{3}[\text{Zn}(\text{pt})_2]$ impregnated with Eu and Tb ions for eight days using MeCN as solvent

3.6 Infrared spectroscopy

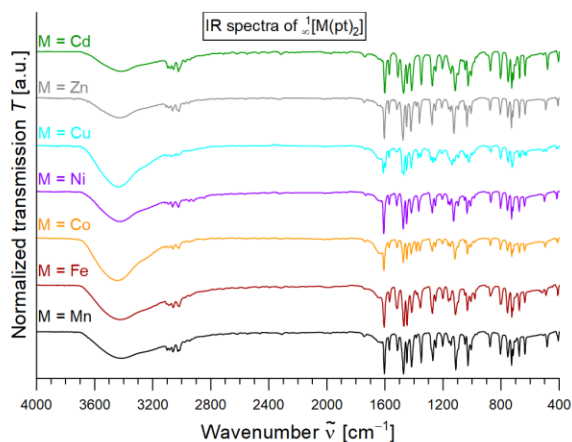


Figure S31. Infrared transmission spectra of the coordination polymers $[M(pt)_2]$ (M = Mn (**1**), Fe (**2**), Co (**3**), Ni (**4**), Zn (**6**), Cd (**7**)). The observed bands are assigned to vibrations listed in Table S22.

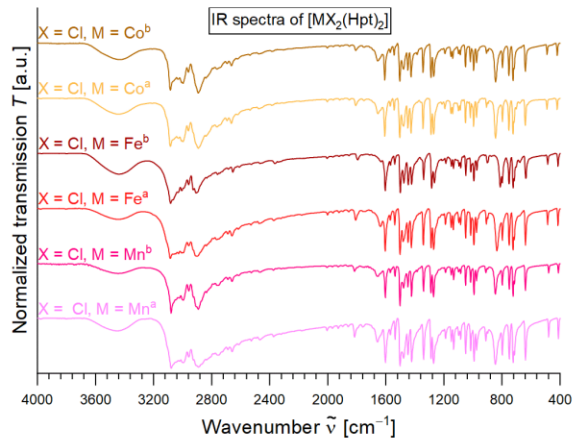


Figure S32. Infrared transmission spectra of the complexes $[MX_2(Hpt)_2]$ synthesized in pyridine (superscript a) or acetonitrile (superscript b) with MX_2 = $MnCl_2$ (**9**), $FeCl_2$ (**10**), $FeBr_2$ (**11**), $CoCl_2$ (**13**), $CoBr_2$ (**14**). The observed bands are assigned to vibrations listed in Table S23.

3.7 Simultaneous thermal analyses (STA)

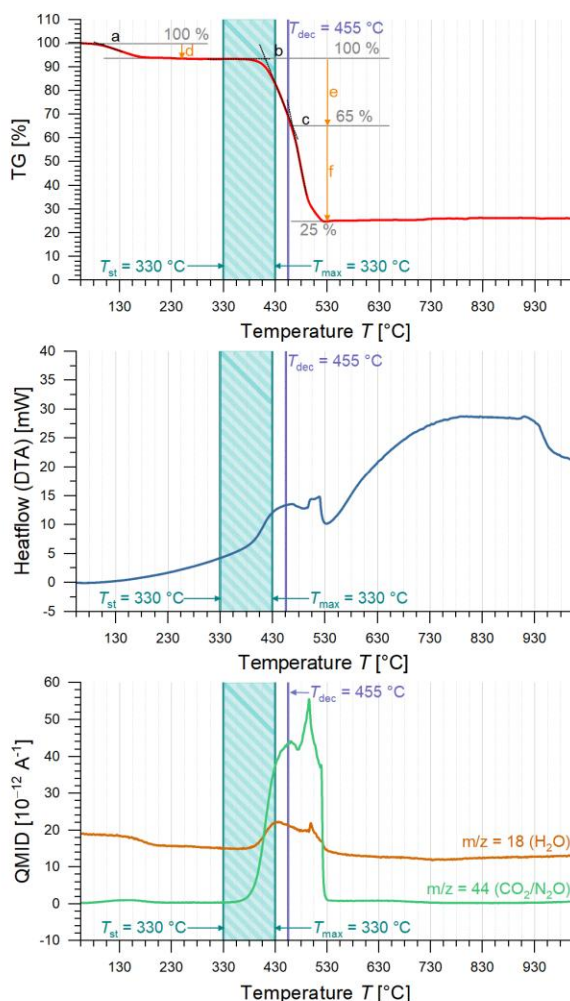


Figure S33. Simultaneous thermal analysis (STA) of $1[\text{Mn}(\text{pt})_2]$ (**1**). The grid lines and T_{st} , T_{max} , as well as T_{dec} are in analogy to temperature dependent PXRD (Figure S8) **Top:** Thermogravimetric (TG) relative mass loss. Onset a: 90 °C, 100 %; Onset b: 410 °C, 93 %; Onset c: 465 °C, 65 %; mass loss d: 7 %; mass loss e: 28 %, mass loss f: 40 %. **Centre:** Heatflow, differential thermal analysis (DTA). **Bottom:** Temperature-dependent mass spectrometry (MS) signals. Data is summarized within Table S26.

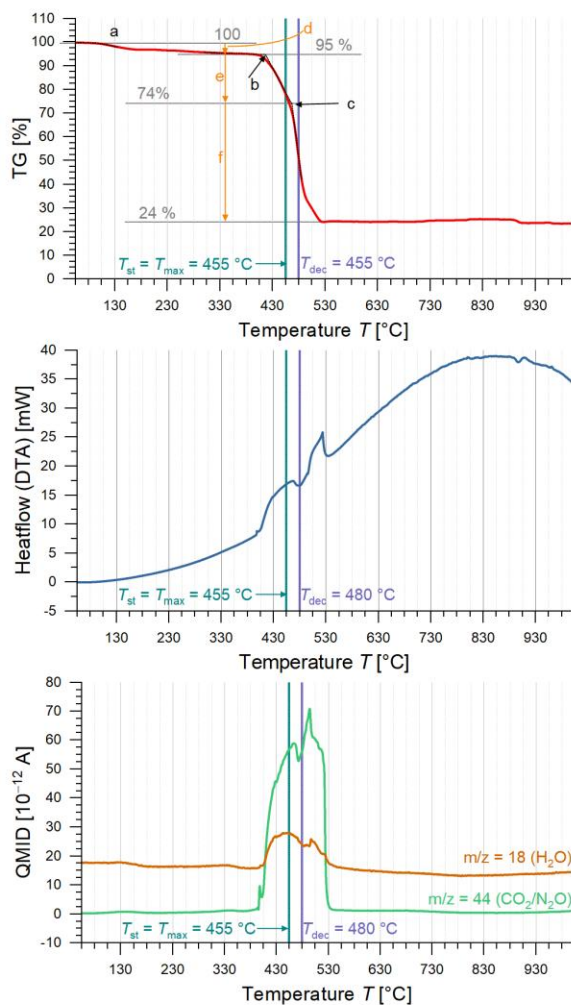


Figure S34. Simultaneous thermal analysis (STA) of $1[\text{Co}(\text{pt})_2]$ (**3**). The grid lines and T_{st} , T_{max} , as well as T_{dec} are in analogy to temperature dependent PXRD (Figure S12). **Top:** Thermogravimetric (TG) relative mass loss. Onset a: 100 °C, 100 %; onset b: 415 °C, 95 %; onset c: 465 °C, 74 %; mass loss d: 5 %; mass loss e: 21 %, mass loss f: 50 %. **Centre:** Heatflow, differential thermal analysis (DTA). **Bottom:** Temperature-dependent mass spectrometry (MS) signals. Data is summarized within Table S26.

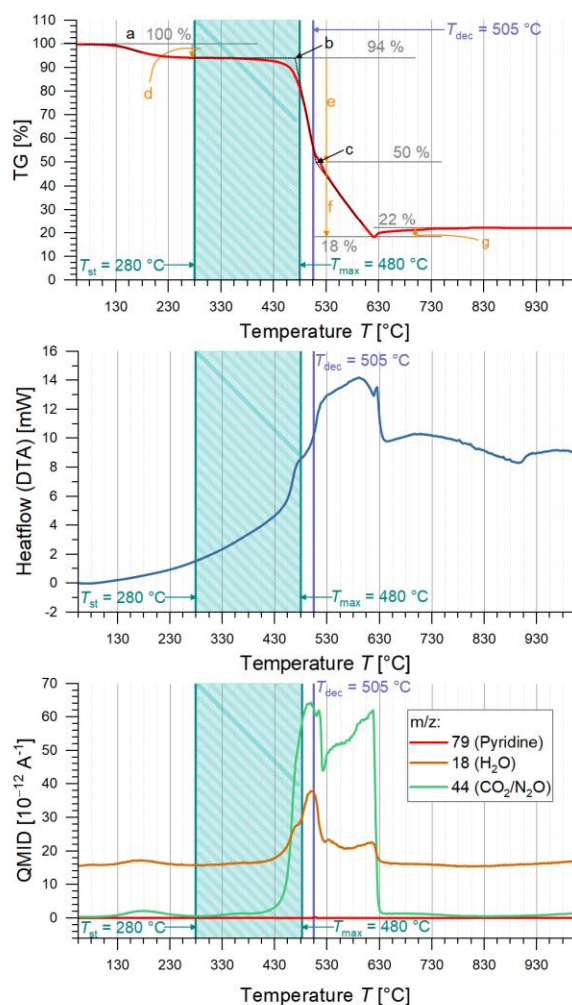


Figure S35. Simultaneous thermal analysis (STA) of $1[\text{Ni}(\text{pt})_2]$ (**4**). The grid lines and T_{st} , T_{max} as well as T_{dec} are in analogy to temperature dependent PXRD (Figure S14). **Top:** Thermogravimetric (TG) relative mass loss. Onset a: 128 °C, 100 %; onset b: 470 °C; 94 %; onset c: 510 °C, 50 %; mass loss d: 6 %; mass loss e: 44 %, mass loss f: 28 %, mass gain: 4 % **Centre:** Heatflow, differential thermal analysis (DTA). **Bottom:** Temperature-dependent mass spectrometry (MS) signals. Data is summarized within Table S26.

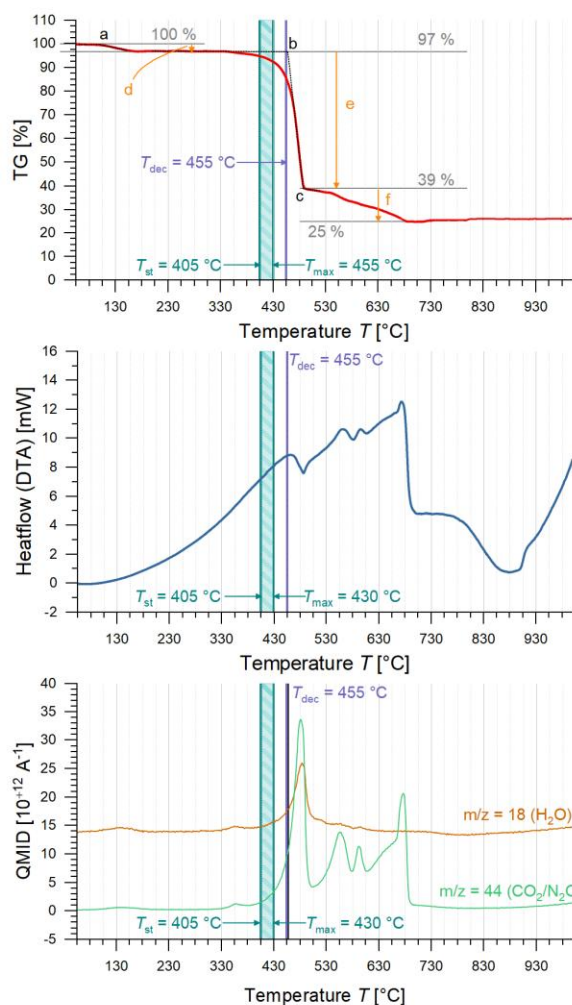


Figure S36. Simultaneous thermal analysis (STA) of $1[\text{Zn}(\text{pt})_2]$ (**6**). The grid lines and T_{st} , T_{max} as well as T_{dec} are in analogy to temperature dependent PXRD (Figure S6). **Top:** Thermogravimetric (TG) relative mass loss. Onset a: 100 °C, 100 %; onset b: 460 °C; 97 %; onset c: 490 °C, 39 %; mass loss d: 3 %; mass loss e: 58 %; mass loss f: 14 % **Centre:** Heatflow, differential thermal analysis (DTA). **Bottom:** Temperature-dependent mass spectrometry (MS) signals. Data is summarized within Table S26.

3.8 Sorption isotherms

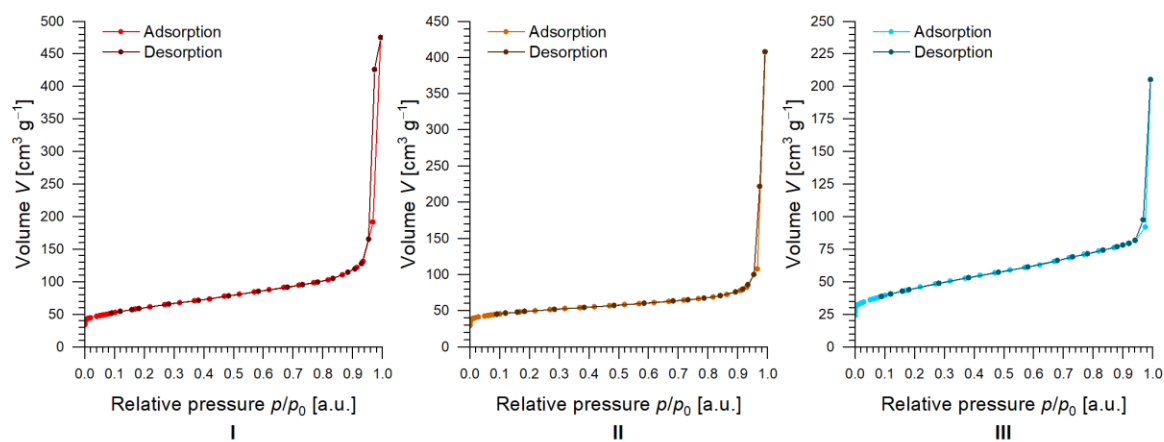


Figure S37. N_2 sorption isotherms of $\frac{1}{3}[\text{Fe}(\text{pt})_2]$ (I), $\frac{1}{3}[\text{Co}(\text{pt})_2]$ (II), and $\frac{1}{3}[\text{Zn}(\text{pt})_2]$ (III) recorded at 77 K.

3.9 Scanning Electron Micrographs

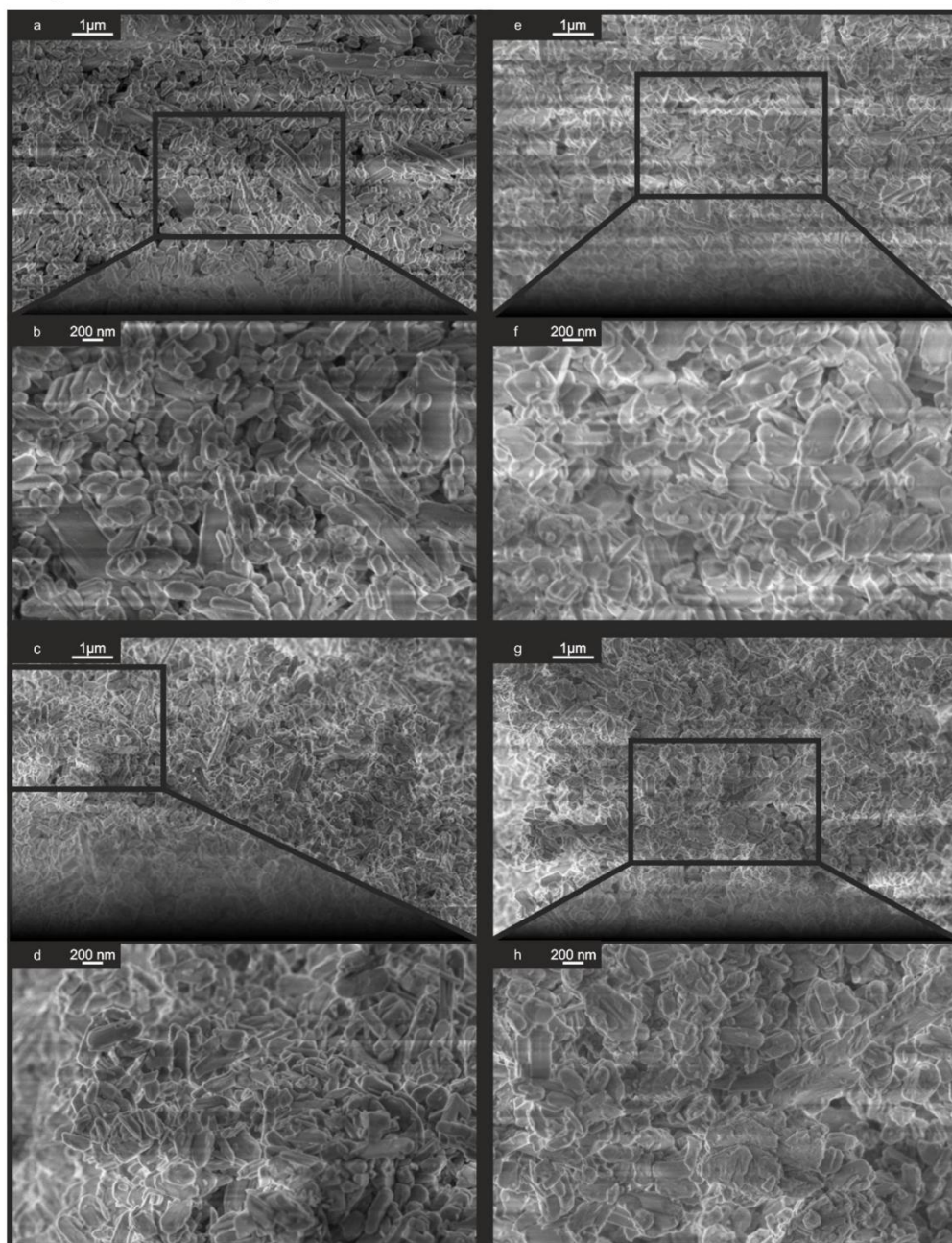


Figure S38. Scanning electron micrographs of [Zn(pt)₂] (6, a, b), as well as of EuTb@[Zn(pt)₂] synthesized in DMF (c, d), MeCN (e,f), and MeOH (g, h).

4. Additional experiments and single crystal structures

4.1 Crystal structure of the complex [Zr(pt)₄] (14)

The complex [Zr(pt)₄] crystallizes in the monoclinic crystal system in the space group *C2/c*. Contained Zr is coordinated by four deprotonated η^2 -pt ligand molecules in a trigondodecahedral coordination. Each ligand coordinates by the nitrogen atom of the pyridine ring (N1) and one nitrogen atom of the triazole ring (N2) ring. Crystallographic data is summarized in Table S30. Interatomic distances and angles are listed in Table S31. A depiction of the crystal structure is given in Figure S39.

Table S30. Crystallographic data for [Zr(pt)₄] (complex **16**). Deviations are given in brackets.

Empirical formula	C ₂₈ H ₂₀ N ₁₆ Zr
Formula weight [g · mol ⁻¹]	671.82
Crystal colour and shape	colourless block
Crystal size	0.379 x 0.273 x 0.218 mm ³
Crystal system	monoclinic
Space group	<i>C2/c</i>
a [pm]	1701.2(2)
b [pm]	9955.3(9)
c [pm]	1716.4(2)
V [10 ⁶ pm ³]	2863.9(4)
α [°]	90
β [°]	99.871(3)
γ [°]	90
Z	4
ρ_{calc} [g · cm ⁻³]	1.558
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	0.436
X-ray radiation	MoK α , λ = 71.073 pm
Measurement temperature [K]	100(2)
Absorption correction type	multi-scan
2 θ range [°]	4.76 to 54.198
No. of measured reflections	32490
No. of independent reflections	3161
R _{int}	0.0495
No. of independent reflections (<i>I</i> > 2 σ (<i>I</i>))	3161
No. of parameters	204
R ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0437
wR ₂ (all data)	0.1117
GOF	1.085
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ [e · 10 ⁻⁶ pm ⁻³]	0.870, -0.513

Table S31. Interatomic distances and angles for [Zr(pt)₄] (complex **16**). Deviations are given in brackets. Symmetry operation: *l* = 1 - *x*, *y*, 1/2 - *z*.

Atoms	Distance [pm]	Atoms	Angles [°]
Zr1-N1	239.6(3)	N1-Zr1-N1 ^{<i>l</i>}	74(1)
Zr1-N1 ^{<i>l</i>}	239.6(3)	N1-Zr1-N2	70(1)
Zr1-N2	221.8(2)	N1-Zr1-N2 ^{<i>l</i>}	79(1)
Zr1-N2 ^{<i>l</i>}	221.8(2)	N1-Zr1-N3	135(1)
Zr1-N3	238.9(2)	N1-Zr1-N3 ^{<i>l</i>}	125(1)
Zr1-N3 ^{<i>l</i>}	238.9(2)	N1-Zr1-N4	75(1)
Zr1-N4	222.4(2)	N1-Zr1-N4 ^{<i>l</i>}	146(1)
Zr1-N4 ^{<i>l</i>}	222.4(2)	N2-Zr1-N1 ^{<i>l</i>}	79(1)
		N2-Zr1-N2 ^{<i>l</i>}	140(2)
		N2-Zr1-N3	147(1)
		N2-Zr1-N3 ^{<i>l</i>}	73(1)
		N2-Zr1-N4	104.(1)
		N2-Zr1-N4 ^{<i>l</i>}	90(1)
		N3-Zr1-N1 ^{<i>l</i>}	125(1)
		N3-Zr1-N2 ^{<i>l</i>}	73(1)
		N3-Zr1-N3 ^{<i>l</i>}	74(2)
		N3-Zr1-N4	70(1)
		N3-Zr1-N4 ^{<i>l</i>}	77(1)
		N4-Zr1-N1 ^{<i>l</i>}	146(1)
		N4-Zr1-N2 ^{<i>l</i>}	90(1)
		N4-Zr1-N3 ^{<i>l</i>}	77(1)
		N4-Zr1-N4 ^{<i>l</i>}	138(2)
		N1 ^{<i>l</i>} -Zr1-N2 ^{<i>l</i>}	70(1)
		N1 ^{<i>l</i>} -Zr1-N3 ^{<i>l</i>}	135(1)
		N1 ^{<i>l</i>} -Zr1-N4 ^{<i>l</i>}	75(1)
		N2 ^{<i>l</i>} -Zr1-N4 ^{<i>l</i>}	104(1)
		N2 ^{<i>l</i>} -Zr1-N3 ^{<i>l</i>}	147(1)
		N3 ^{<i>l</i>} -Zr1-N4 ^{<i>l</i>}	70(1)

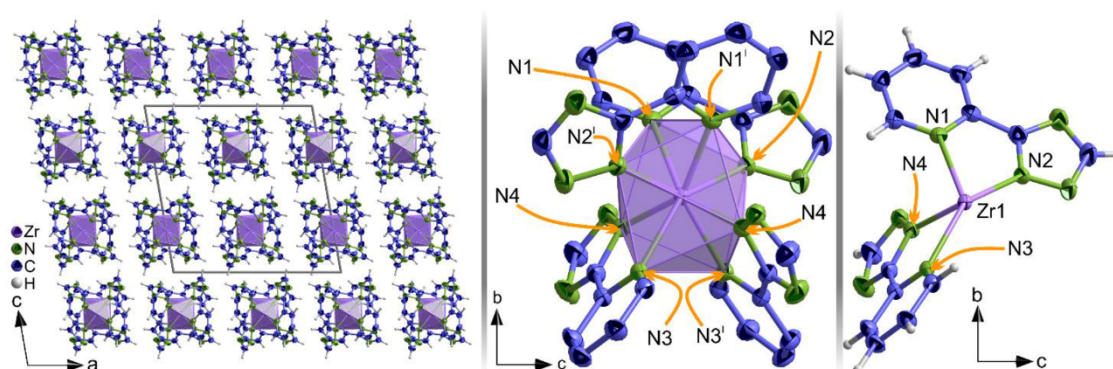


Figure S39. Depiction of the crystal structure of $[\text{Zr}(\text{pt})_4]$ (**14**). Presented are: An excerpt of the crystal structure along the crystallographic b-axis (left), the extended coordination of Zr^{4+} (centre, hydrogen atoms are omitted), and the asymmetric unit of $[\text{Zr}(\text{pt})_4]$ (right). Polyhedra around Zr are highlighted in purple. Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. Symmetry operation: $l = 1-x, y, 1/2-z$.

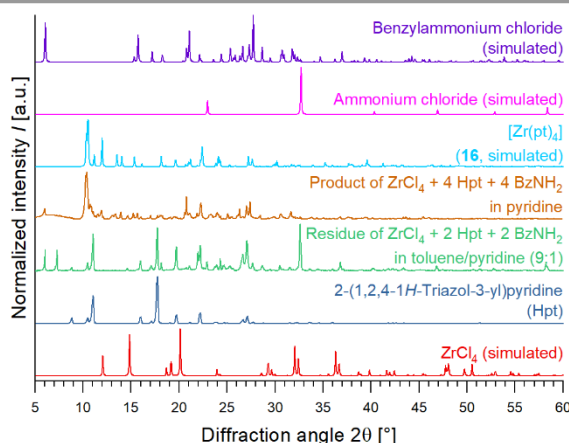


Figure S40. Powder X-ray diffractograms of the reaction product of ZrCl_4 , Hpt, and benzylamine in both, pyridine and a mixture of toluene/pyridine (9:1) in comparison to a recorded pattern of Hpt, and simulated patterns of ZrCl_4 ,²⁷ $[\text{Zr}(\text{pt})_4]$ (**14**), ammonium chloride,²⁸ and benzylammonium chloride²⁹ utilizing corresponding SCXRD data.

Single crystals of the complex $[\text{Zr}(\text{pt})_4]$ (**14**) were obtained by solvothermal reaction of 50 μmol (12 mg) ZrCl_4 , 0.10 mmol (15 mg) Hpt, and 2 droplets of benzylamine in 1 mL of toluene/pyridine (9:1). Following the synthesis principle for coordination compounds described within the main paper. The reaction mixture was heated with $2^\circ\text{C}\cdot\text{h}^{-1}$ to 180°C , which was held constant for 480 h. After cooling down to room temperature with $2^\circ\text{C}\cdot\text{h}^{-1}$, colourless crystals were found within the product, which were suitable for single crystal X-ray diffraction. However, the PXRD of the dried residue after SCXRD experiments shows reflections of the ligand, benzylammonium chloride, and ammonium chloride, indicating decomposition and therefore air sensitivity of complex **14**. Additionally, reflections of unknown phase(s) are present (see Figure S40). The PXRD pattern of a product (handled under inert conditions) of the reaction of the reagents (in stoichiometric amounts) in pyridine exhibits reflections of the complex $[\text{Zr}(\text{pt})_4]$ (**14**) confirming assumed air sensitivity, besides reflections of ZrCl_4 , Hpt, benzylammonium chloride and again, additional reflections of unknown phase(s). Therefore, $[\text{Zr}(\text{pt})_4]$ (**14**) is reported within this work as single crystal structure, only.

4.2 Crystal structure of the dinuclear complexes $[\text{Fe}_2\text{X}_2(\text{pt})_2(\text{Py})_4]$ ($\text{X} = \text{Cl}$ (15), Br (16))

The dinuclear complex with the sum formula $[\text{Fe}_2\text{Cl}_2(\text{pt})_2(\text{Py})_4]$ (Py = pyridine, **15**) crystallises in the triclinic crystal system in the space group $P\bar{1}$. Each Fe atom is coordinated by one halido ligand, two *trans* pyridine molecules (coordination *via* N5, respectively N6), and a η^2 -pt molecule coordinating *via* N1 of the pyridine ring and N2 of the triazole ring. The distorted octahedral coordination of Fe is completed by coordination of N3 of the symmetry generated pt molecule interlinking two metal atoms and thus resulting in formation of a dinuclear complexes. This structure was also found for the bromide analogue $[\text{Fe}_2\text{Br}_2(\text{pt})_2(\text{Py})_4]$ (**16**). A depiction for each crystal structure is shown in Figure S41 and Figure S42. Crystallographic details of complexes **15** and **16** are listed in Table S32 and Table S34. Interatomic distances and angles are given in Table S33 and Table S35. Fe–N– distances of 217.5(2) – 225.0(2) pm are in agreement with 213 – 223 pm in $[\text{Fe}(\text{Hpt})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$, which contains Fe^{II} octahedrally coordinated by three η^2 -Hpt ligands.³⁰

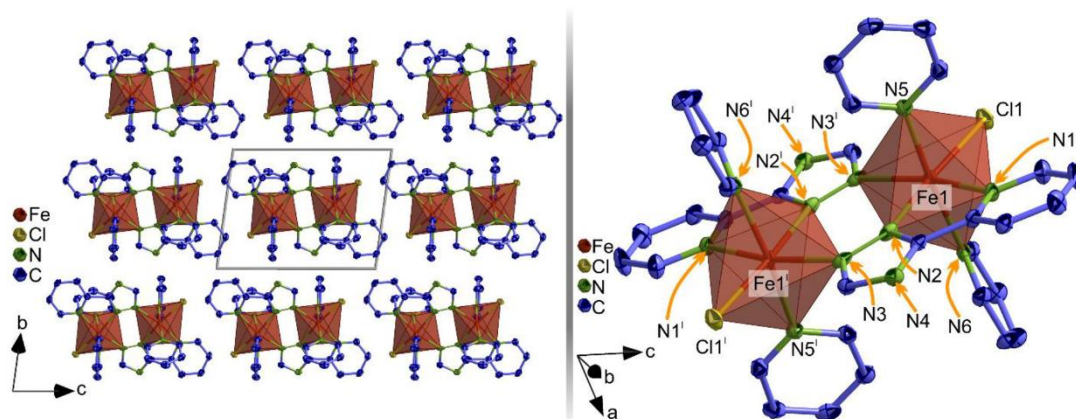


Figure S41. Depiction of the crystal structure of $[\text{Fe}_2\text{Cl}_2(\text{pt})_2(\text{Py})_4]$ (**15**) along the crystallographic a axis (left), besides extended coordination of Fe^{2+} (right). The octahedral coordination polyhedra are highlighted in red. Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. For better clarity, the hydrogen atoms are omitted. Symmetry operation: $1 = 1 - x, 1 - y, 1 - z$.

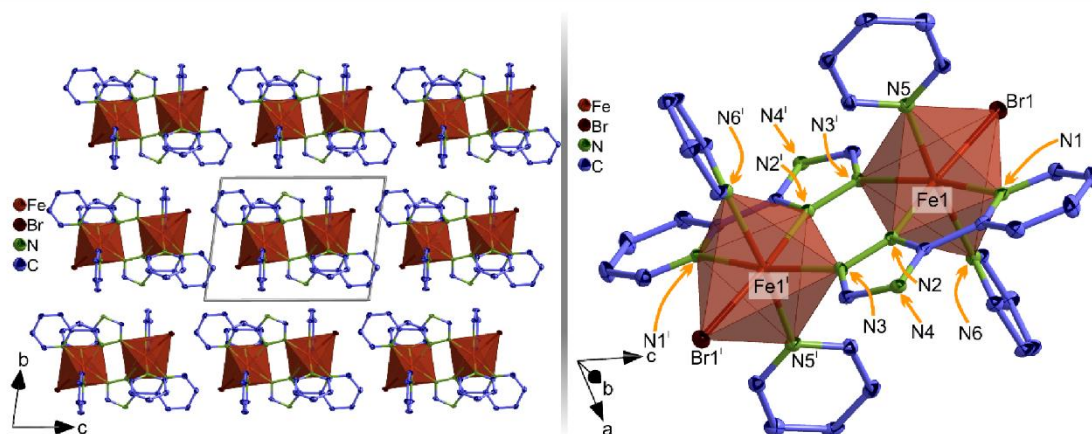


Figure S42. Depiction of the crystal structure of $[\text{Fe}_2\text{Br}_2(\text{pt})_2(\text{Py})_4]$ (**16**) along the crystallographic a axis (left), besides extended coordination of Fe^{2+} (right). The octahedral coordination polyhedra are highlighted in red. Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. For better clarity, the hydrogen atoms are omitted. Symmetry operation: $1 = 1 - x, 1 - y, 1 - z$.

Table S32. Crystallographic data for $[\text{Fe}_2\text{Cl}_2(\text{pt})_2(\text{Py})_4]$ (complex **15**). Deviations are given in brackets.

Empirical formula	$\text{C}_{34}\text{H}_{30}\text{Cl}_2\text{Fe}_2\text{N}_{12}$
Formula weight $[\text{g} \cdot \text{mol}^{-1}]$	789.3
Crystal colour and shape	orange block
Crystal size	0.358 x 0.283 x 0.256 mm ³
Crystal system	triclinic
Space group	$P\bar{1}$
a [pm]	891.58(8)
b [pm]	966.20(8)
c [pm]	121.03(2)
V [10 ⁶ pm ³]	863.4(2)
α [°]	74.277(3)
β [°]	69.785(3)
γ [°]	62.978(3)
Z	1
$\rho_{\text{calc}} [\text{g} \cdot \text{cm}^{-3}]$	1.518
$\mu(\text{MoK}\alpha) [\text{mm}^{-1}]$	1.04
X-ray radiation	$\text{MoK}\alpha$, $\lambda = 71.073 \text{ pm}$
Measurement temperature [K]	100(2)
Absorption correction type	multi-scan
2 θ range [°]	3.62 to 57.4
No. of measured reflections	27124
No. independent reflections	4451
R_{int}	0.0648
No. of independent reflections ($I > 2\sigma(I)$)	4451
No. of parameters	226
R_1 ($I > 2\sigma(I)$)	0.0368
wR ₂ (all data)	0.0844
GOF	1.064
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} [\text{e} \cdot 10^{-6} \text{ pm}^{-3}]$	0.650, -0.502

Table S33. Interatomic distances and angles for $[\text{Fe}_2\text{Cl}_2(\text{pt})_2(\text{Py})_4]$ (complex **15**). Deviations are given in brackets. Symmetry operation: $l = 1-x, 1-y, 1-z$.

Atoms	Distance [pm]	Atoms	Angle [°]
Fe1–N1	222.4(2)	N1–Fe1–N2	76(1)
Fe1–N2	218.2(2)	N1–Fe1–N5	85(1)
Fe1–N5	223.8(2)	N1–Fe1–N6	89(1)
Fe1–N6	225.0(2)	N1–Fe1–Cl1	96(1)
Fe1–Cl1	240.7(2)	N1–Fe1–N3 ^l	166(1)
Fe1–N3 ^l	217.5(2)	N2–Fe1–N5	88(1)
		N2–Fe1–N6	91(1)
		N2–Fe1–Cl1	172(1)
		N2–Fe1–N3 ^l	90(1)
		N5–Fe1–N6	173(1)
		N5–Fe1–Cl1	90(1)
		N5–Fe1–N3 ^l	95(1)
		N6–Fe1–Cl1	91(1)
		N6–Fe1–N3 ^l	92(1)
		Cl1–Fe1–N3 ^l	98(1)

Table S34. Crystallographic data for $[\text{Fe}_2\text{Br}_2(\text{pt})_2(\text{Py})_4]$ (complex **16**). Deviations are given in brackets.

Empirical formula	$\text{C}_{34}\text{H}_{30}\text{Br}_2\text{Fe}_2\text{N}_{12}$
Formula weight $[\text{g} \cdot \text{mol}^{-1}]$	878.22
Crystal colour and shape	yellow plate
Crystal size	$0.130 \times 0.075 \times 0.028 \text{ mm}^3$
Crystal system	triclinic
Space group	$P\bar{1}$
a [pm]	887.82(8)
b [pm]	967.38(9)
c [pm]	121.39(2)
V [10^6 pm^3]	872.1(2)
α [°]	74.666(3)
β [°]	70.793(3)
γ [°]	63.437(3)
Z	1
$\rho_{\text{calc}} [\text{g} \cdot \text{cm}^{-3}]$	1.672
$\mu(\text{MoK}\alpha) [\text{mm}^{-1}]$	3.168
X-ray radiation	$\text{MoK}\alpha, \lambda = 71.073 \text{ pm}$
Measurement temperature [K]	100(2)
Absorption correction type	multi-scan
2θ range [°]	4.754 to 58.894
No. of measured reflections	41511
No. of independent reflections	4838
R_{int}	0.0488
No. of independent reflections ($I > 2\sigma(I)$)	4838
No. of parameters	226
R_1 ($I > 2\sigma(I)$)	0.0388
wR_2 (all data)	0.0793
GOF	1.111
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} [\text{e} \cdot 10^{-6} \text{ pm}^{-3}]$	0.663, -1.000

Table S35. Interatomic distances and angles for $[\text{Fe}_2\text{Br}_2(\text{pt})_2(\text{Py})_4]$ (complex **16**). Deviations are given in brackets. Symmetry operation: $l = 1-x, 1-y, 1-z$.

Atoms	Distance [pm]	Atoms	Angle [°]
Fe1–N1	221.8(2)	N1–Fe1–N2	76(1)
Fe1–N2	218.1(2)	N1–Fe1–N5	84(1)
Fe1–N5	223.0(2)	N1–Fe1–N6	88(1)
Fe1–N6	224.3(2)	N1–Fe1–Br1	95(1)
Fe1–Br1	259.51(5)	N1–Fe1–N3 ^l	168(1)
Fe1–N3 ^l	214.3(2)	N2–Fe1–N5	88(1)
		N2–Fe1–N6	92(1)
		N2–Fe1–Br1	171(1)
		N2–Fe1–N3 ^l	91(1)
		N5–Fe1–N6	173(1)
		N5–Fe1–Br1	90(1)
		N5–Fe1–N3 ^l	95(1)
		N6–Fe1–Br1	90(1)
		N6–Fe1–N3 ^l	93(1)
		Br1–Fe1–N3 ^l	97(1)

The dinuclear complexes $[\text{Fe}_2\text{X}_2(\text{pt})_2]$ ($\text{X} = \text{Cl}$ (**15**), Br (**16**)) were found within products of reactions of 0.05 mmol of the respective iron halide (6 mg FeCl_2 ; 11 mg FeBr_2), 0.10 mmol (15 mg) 2-(1,2,4-1*H*-triazol-3-yl)pyridine, and two droplets of benzylamine in 1 mL toluene/pyridine (9:1), which were performed following the synthesis principle for coordination compounds described within the main paper. The reaction mixture was heated with $2^\circ\text{C}\cdot\text{h}^{-1}$ to 180°C , held constant for 480 h, followed by cooling to room temperature with $2^\circ\text{C}\cdot\text{h}^{-1}$. The PXRD pattern of the obtained, dried solid of a reaction of FeCl_2 with Hpt and benzylamine shows reflections of the dinuclear complex $[\text{Fe}_2\text{Cl}_2(\text{pt})_2(\text{Py})_4]$ (**15**), the complex $[\text{FeCl}_2(\text{Hpt})]$ (**10**), the one-dimensional coordination polymer $\frac{1}{2}[\text{Fe}(\text{pt})_2]$ (**2**), which is isotypic to $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**) and benzylammonium chloride (see Figure S43). Therefore, the dinuclear complexes $[\text{Fe}_2\text{X}_2(\text{pt})_2]$ ($\text{X} = \text{Cl}$ (**15**), Br (**16**)) are assumed to be intermediates during the formation of CP **2**. Hence **15**, and **16** are reported as single crystal structures, only.

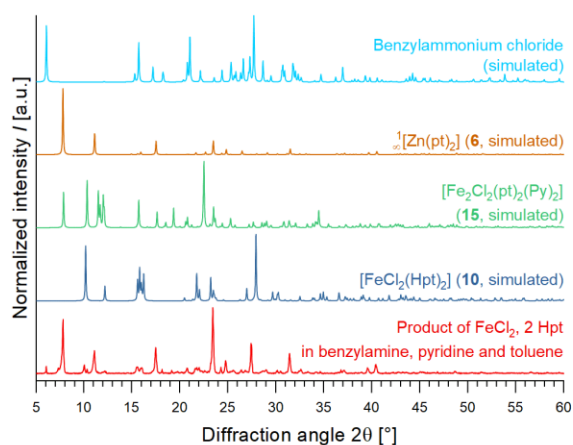


Figure S43. Powder X-ray diffractograms of the reaction product of FeCl_2 , 2 Hpt, and benzylamine in a 9:1 mixture of toluene:pyridine, besides simulated patterns of $[\text{FeCl}_2(\text{Hpt})_2]$ (**10**), $[\text{Fe}_2\text{Cl}_2(\text{pt})_2(\text{Py})_2]$ (**15**), $[\text{Zn}(\text{pt})_2]$ (**6**), and benzylammonium chloride,²⁹ Simulated patterns were created utilizing respective SCXRD data.

4.3 Crystal structure of the two-dimensional coordination polymer $\frac{2}{3}[\text{Cu}_2\text{Cl}(\text{pt})]$ (**17**)

The two-dimensional CP $\frac{2}{3}[\text{Cu}_2\text{Cl}(\text{pt})]$ (**17**) crystallizes in the monoclinic crystal system in the space group *Cc*. The structure contains two crystallographically independent copper atoms, Cu1 and Cu2, both coordinated in a trigonal planar geometry. In case of Cu1, this coordination geometry is formed by two molecules of pt. The first molecule coordinates *via* N1 of the pyridine ring and N4 of the triazolyl ring. The second molecule coordinates *via* N3 of the triazole ring. Therefore, pt molecules interconnect Cu1 atoms by coordination of the nitrogen atoms N1, N3 and N4 forming polymeric Cu1-pt-Cu1-pt strand. The remaining nitrogen atom of the ligands (N2) are coordinating to Cu2. The trigonal planar coordination geometry of Cu2 is completed by coordination of two chlorido ligands, interconnecting Cu2 atoms in polymeric Cu2-Cl-Cu2-Cl zig-zag chains, resulting in an overall two-dimensional polymeric structure. A depiction of the crystal structure is given in Figure S44. Crystallographic data is listed in Table S36. Interatomic distances and angles are given in Table S37. The Cu–N distances (187.6(3) pm to 223.9(3) pm) are comparable to distances within $[\text{Cu}(\text{bbtmp})](\text{NO}_3)$ (bbtmp = 2,6-bis(benzimidazol-2'-ylthiomethyl)pyridine). It contains Cu^I trigonal planarly coordinated by the ligand. Interatomic Cu–N distances range from 191 pm to 208 pm.³¹ The distances in **17** are also comparable to those in $\frac{1}{3}[\text{Cu}(\text{pt})_2]\cdot\text{H}_2\text{O}$, which contains Cu based octahedra interconnected by pt-ligands and forms polymeric zig-zag chains with two different orientations within the unit cell. Interatomic Cu–N distances for this compound range from 197 pm to 254 pm.³²

In analogy to the single crystal synthesis of $\frac{1}{3}[\text{Zn}(\text{pt})_2]$ (**6**) described in the manuscript, few yellow single crystals of CP **17** were obtained by solvothermal combination of 0.05 mmol (7 mg) CuCl₂, 0.10 mmol (15 mg) Hpt, and two droplets of benzylamine in 1 mL of a 9:1 mixture of toluene:pyridine according to the synthesis principle for coordination compounds described within the main paper. The reaction mixture was heated to 180 °C with 2 °C·h⁻¹, which was held constant for 480 h, followed by cooling to room temperature with 2 °C·h⁻¹. However, **17** is sensitive against oxidation at air, since over time a colour change from yellow to turquoise was observable, indicating an oxidation of Cu^I to Cu^{II}. By PXRD, the resulting product is identified as a mixture of multiple phases. The majority phases are identified as compounds isotypic to benzylammonium chloride, $\frac{2}{3}[\text{Cu}_2\text{Cl}(\text{pt})]$ (**17**), which contains Cu^I, and $\frac{1}{3}[\text{Cu}(\text{pt})_2]\cdot 0.5\text{Py}$ (**8**), which contains Cu^{II}, as well as unidentified additional phase(s) (see Figure S45). A bulk synthesis of phase pure $\frac{2}{3}[\text{Cu}_2\text{Cl}(\text{pt})]$ (**17**) was not possible, wherefore it is reported as single crystal structure, only.

Table S36. Crystallographic data for $\frac{1}{2}[\text{Cu}_2\text{Cl}(\text{pt})]$ (**17**). Deviations are given in brackets.

Empirical formula	$\text{C}_7\text{H}_5\text{ClCu}_2\text{N}_4$
Formula weight [$\text{g} \cdot \text{mol}^{-1}$]	307.68
Crystal colour and shape	yellow needle
Crystal size	$0.844 \times 0.152 \times 0.098 \text{ mm}^3$
Crystal system	monoclinic
Space group	<i>Cc</i>
<i>a</i> [pm]	370.57(2)
<i>b</i> [pm]	2401.34(8)
<i>c</i> [pm]	995.78(4)
<i>V</i> [10^6 pm^3]	881.10(5)
α [°]	90
β [°]	96.097(2)
γ [°]	90
<i>Z</i>	4
ρ_{calc} [$\text{g} \cdot \text{cm}^{-3}$]	2.319
$\mu(\text{MoK}\alpha)$ [mm^{-1}]	5.085
X-ray radiation	$\text{MoK}\alpha$, $\lambda = 71.073 \text{ pm}$
Measurement temperature [K]	100(2)
Absorption correction type	multi-scan
2θ range [°]	5.332 to 62.026
No. of measured reflections	16153
No. of independent reflections	2785
R_{int}	0.0664
No. of independent reflections ($I > 2\sigma(I)$)	2785
No. of parameters	128
R_1 ($I > 2\sigma(I)$)	0.0301
wR_2 (all data)	0.0481
GOF	1.03
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ [$\text{e} \cdot 10^{-6} \text{ pm}^{-3}$]	0.410, −0.512

Table S37. Interatomic distances and angles for $\frac{1}{2}[\text{Cu}_2\text{Cl}(\text{pt})]$ (**17**). Deviations are given in brackets. Symmetry operations: I = $-1+x, y, z$; II = $-1+x, 1-y, -1/2+z$; III = $1+x, y, z$.

Atoms	Distance [pm]	Atoms	Angle [°]
Cu1–N3	187.6(3)	N3–Cu1–N1 ^{II}	120(1)
Cu1–N1 ^{II}	223.9(3)	N3–Cu1–N4 ^{II}	160(1)
Cu1–N4 ^{II}	192.2(3)	N1 ^{III} –Cu1–N4 ^{II}	80(1)
Cu2–N2	192.6(3)	N2–Cu2–Cl1	107(1)
Cu2–Cl1	245.7(2)	N2–Cu2–Cl1 ^I	147(1)
Cu2–Cl1 ^I	218.6(1)	Cl1–Cu2–Cl1 ^I	106(1)
		Cu2–Cl1–Cu2 ^{III}	106(1)

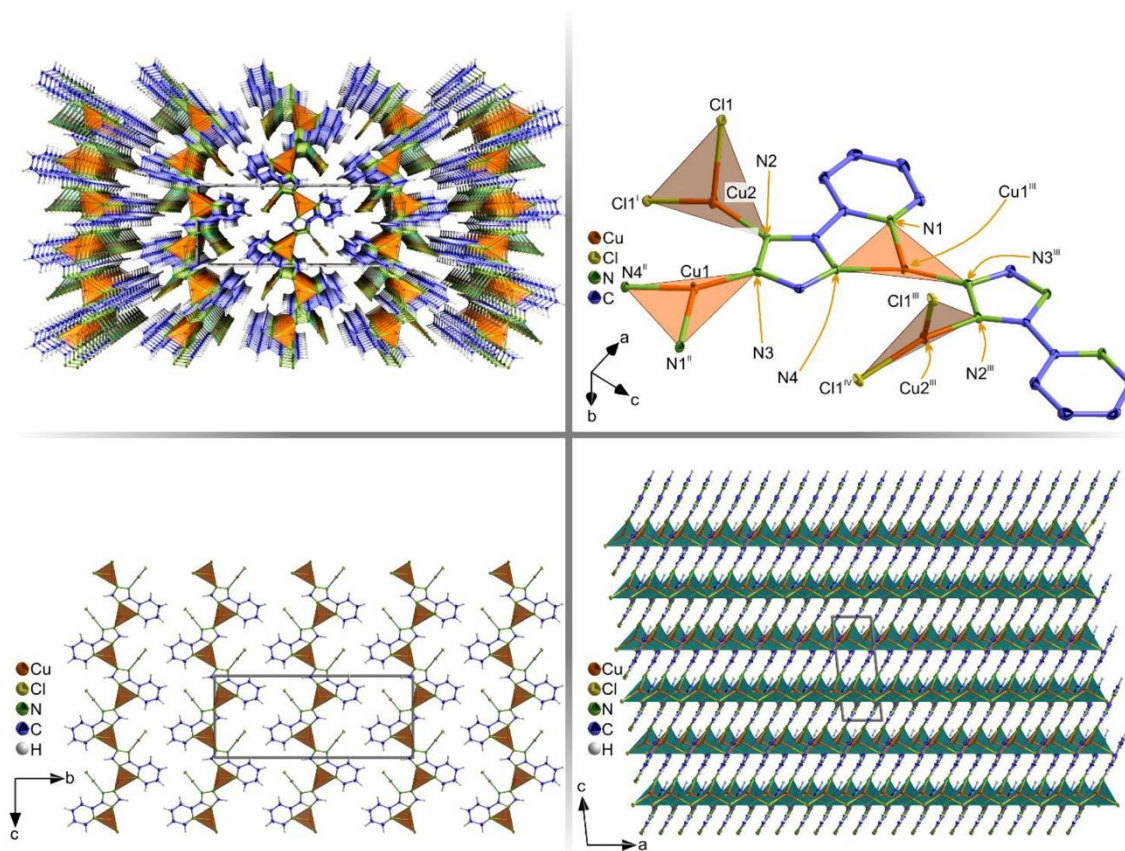


Figure S44. Depiction of the crystal structure of $\frac{1}{2}[\text{Cu}_2\text{Cl}(\text{pt})]$ (**17**). Presented are: A three-dimensional depiction of the stacked polymeric layers (top left), the extended coordination of Cu^+ (top right, hydrogen atoms are omitted), an excerpt of the crystal structure along the crystallographic a axis (bottom left), besides an excerpt along the crystallographic b -axis (bottom right). The trigonal planar coordination of Cu1 is highlighted in orange. The coordination of Cu2 is highlighted in teal. Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. Symmetry operations: I = $-1+x, y, z$; II = $-1+x, 1-y, -1/2+z$; III = $1+x, 1-y, 1/2+z$; IV = $x, 1-y, 1/2+z$.

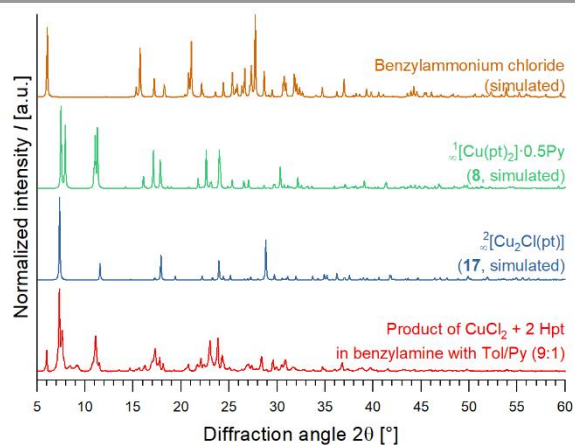


Figure S45. PXRD pattern of the product obtained by reaction of CuCl_2 and Hpt in presence of benzylamine with toluene/pyridine (9:1) as solvent in comparison to simulated patterns (utilizing SCXRD data) of benzylammonium chloride, $\frac{1}{2}[\text{Cu}_2\text{Cl}(\text{pt})]$ (**17**), and $[\text{Cu}(\text{pt})_2] \cdot 0.5\text{Py}$ (**8**).

4.4 Crystal structure of the one-dimensional coordination polymer $\frac{1}{3}[\text{MnCl}(\text{bpt})]$ (**18**)

The one-dimensional CP $\frac{1}{3}[\text{MnCl}(\text{bpt})]$ (bpt = 3,5-bis(2-pyridyl)-1,2,4-triazolate, **18**) crystallizes in the trigonal crystal system in the space group $R\bar{3}$. Contained Mn is coordinated by two ligand bpt molecules. The first coordinates *via* one nitrogen atom (N1) of the triazole ring and the nitrogen atom of one of the two pyridine rings (N4). The second, symmetry generated ligand coordinates by another nitrogen atom of the triazole ring (N2) and the nitrogen atom of the second pyridine ring (N5). Distorted octahedral coordination of Mn is completed by two *cis* chlorido ligands (one of them being symmetry generated). The ligand molecules and respective chlorido ligand, which is in one plane with the ligand, coordinate to a neighbouring Mn atom. Thereby, the nitrogen atom of the second pyridine ring and the neighbouring nitrogen atom of the triazole ring, as well as the chlorido ligand, interconnect Mn atoms to form one-dimensional polymeric strands along the crystallographic *c* axis. A depiction of the crystal structure is shown in Figure S46. Crystallographic data is given in Table S38. Interatomic distances and angles are listed in Table S39. Interatomic Mn–N distances range from 212.6(3) pm to 241.4(3) pm, which are close to distances reported for $[\text{Mn}_2\text{Cl}_2(\text{bpt})_2(\text{H}_2\text{O})_2]$ containing Mn^{II} based octahedra interconnected by bpt ligand and for which Mn–N distances range from 217 pm to 238 pm.³³

In analogy to single crystal synthesis of $\frac{1}{3}[\text{Zn}(\text{pt})_2]$ (**6**) elucidated in the main paper, few colourless single crystals of CP **18** were obtained by reaction of 50 μmol (6.3 mg) MnCl_2 , 0.15 mmol (22 mg) Hpt, 2 droplets of benzylamine in 1 mL of a 9:1 mixture of toluene:pyridine following the synthesis principle for coordination compounds described within the main paper. A powder X-ray diffraction pattern of a dried sample of reaction product shows reflections of $\frac{1}{3}[\text{Mn}(\text{pt})_2]$ (**1**), $\frac{1}{3}[\text{MnCl}(\text{bpt})]$ (**18**), $[\text{MnCl}_2(\text{Hpt})]$ (**9**), Hpt, benzylammonium chloride, and additional unknown phase(s) (see Figure S47). Therefore CP **18** is considered as byproduct and is reported as single crystal structure, only. It is noteworthy that – since Hpt was initially used – this ligand reacted with pyridine being present within the solvent mixture. Thus, the ligand contained in $\frac{1}{3}[\text{MnCl}(\text{bpt})]$ (**18**), namely 3,5-bis(2-pyridyl)-1,2,4-triazolate was formed *in situ*. The structure contains solvent-accessible voids, which are occupied by five pyridine molecules per unit cell.

Table S38. Crystallographic data for $\frac{1}{3}[\text{MnCl}(\text{bpt})]$ (**18**). Deviations are given in brackets.

Empirical formula	$\text{C}_{37}\text{H}_{33}\text{ClMnN}_{10}$
Formula weight [$\text{g} \cdot \text{mol}^{-1}$]	708.12
Crystal colour and shape	colourless needle
Crystal size	0.520 x 0.084 x 0.027 mm ³
Crystal system	trigonal
Space group	$R\bar{3}$
a [pm]	2845.0(2)
b [pm]	2845.0(2)
c [pm]	1055.52(9)
V [10^6 pm^3]	7399(2)
α [°]	90
β [°]	90
γ [°]	120
Z	18
ρ_{calc} [$\text{g} \cdot \text{cm}^{-3}$]	2.861
$\mu(\text{MoK}\alpha)$ [mm^{-1}]	1.056
X-ray radiation	$\text{MoK}\alpha$, $\lambda = 71.073 \text{ pm}$
Measurement temperature [K]	100(2)
Absorption correction type	multi-scan
2θ range [°]	2.864 to 58.252
No. of measured reflections	39820
No. of independent reflections	4435
R_{int}	0.0948
No. of independent reflections ($I > 2\sigma(I)$)	4435
No. of parameters	172
R_1 ($I > 2\sigma(I)$)	0.0706
wR_2 (all data)	0.1364
GOF	1.127
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ [$\text{e} \cdot 10^{-6} \text{ pm}^{-3}$]	0.683, -0.681

Table S39. Interatomic distances and angles for $\frac{1}{3}[\text{MnCl}(\text{bpt})]$ (**18**). Deviations are given in brackets. Symmetry operations: I = $2/3-x+y$, $4/3-x$, $1/3+z$; II = $4/3-y$, $2/3+x-y$, $-1/3+z$.

Atoms	Distance [pm]	Atoms	Angle [°]
Mn1–N1	212.8(3)	N1–Mn1–N4	70(1)
Mn1–N4	241.4(3)	N1–Mn1–N2 ^I	166(1)
Mn1–N2 ^I	212.6(3)	N1–Mn1–N5 ^I	102(1)
Mn1–N5 ^I	236.5(3)	N1–Mn1–Cl1	86(1)
Mn1–Cl1	255.0(1)	N1–Mn1–Cl1 ^I	100(1)
Mn1–Cl1 ^I	260.4(1)	N4–Mn1–N2 ^I	96(1)
		N4–Mn1–N5 ^I	85(1)
		N4–Mn1–Cl1	155(1)
		N4–Mn1–Cl1 ^I	94(1)
		N2 ^I –Mn1–N5 ^I	71(1)
		N2 ^I –Mn1–Cl1	107(1)
		N2 ^I –Mn1–Cl1 ^I	85(1)
		N5 ^I –Mn1–Cl1	93(1)
		N5 ^I –Mn1–Cl1 ^I	156(1)
		Cl1–Mn1–Cl1 ^I	98(1)
		Mn1–Cl1–Mn1 ^{II}	106(1)

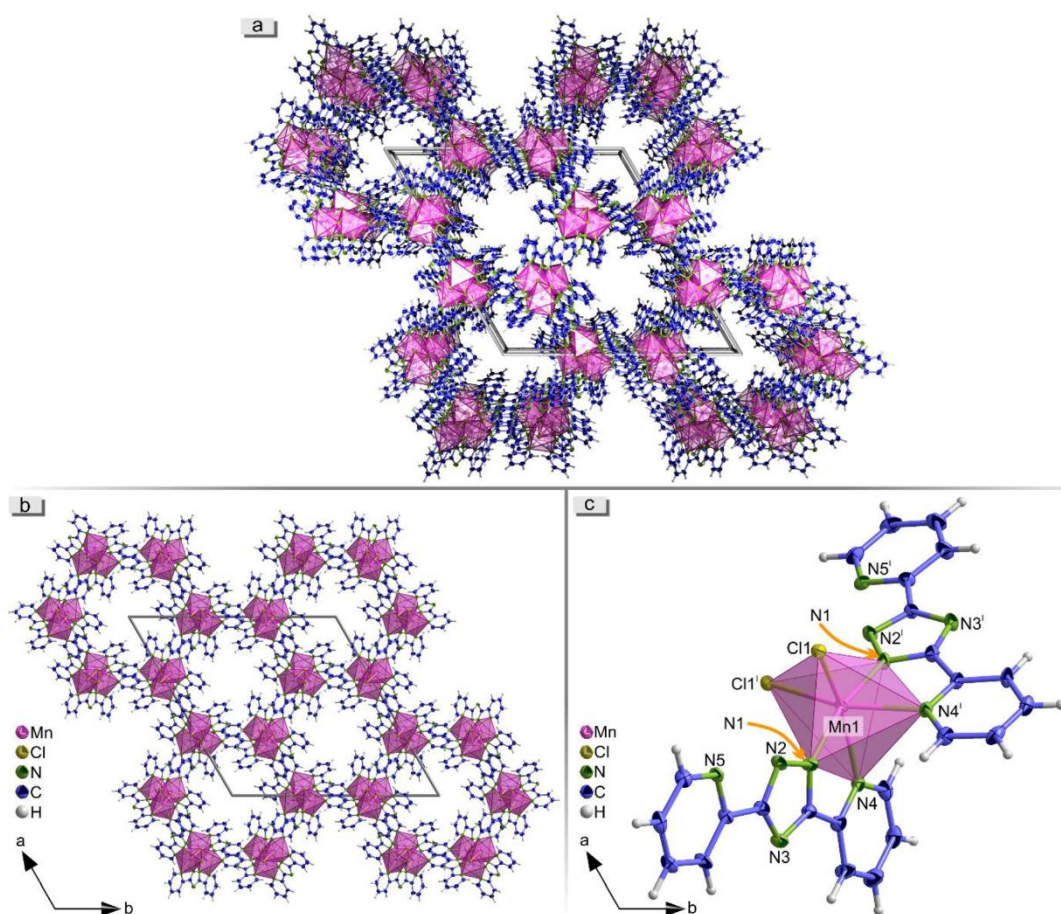


Figure S46. Depiction of the crystal structure of $\frac{1}{3}[\text{MnCl}(\text{bpt})]$ (**18**). Presented are: A three-dimensional depiction of the polymeric strands (a), an excerpt of the crystal structure along the crystallographic c axis (b), besides the extended coordination of Mn^{2+} (c). The distorted octahedral coordination of Mn is highlighted in pink. Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. Symmetry operations: I: $2/3-x+y, 4/3-x, 1/3+z$; II: $4/3-y, 2/3+x-y, -1/3+z$.

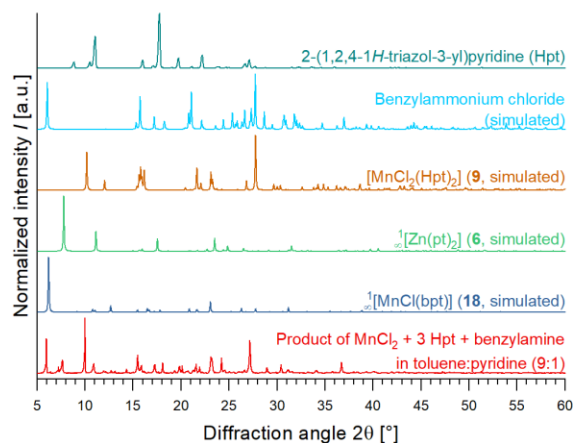


Figure S47. Powder X-ray diffraction pattern of the dried reaction product of MnCl_2 , Hpt, and benzylamine in a 9:1 mixture of toluene:pyridine in comparison to simulated diffraction patterns of $[\text{MnCl}(\text{bpt})]$ (**18**), $[\text{Zn}(\text{pt})_2]$ (**6**), $[\text{MnCl}_2(\text{Hpt})_2]$ (**9**), and benzylammonium chloride,²⁹ as well as a recorded pattern of 2-(1,2,4-1*H*-triazol-3-yl)pyridine (Hpt). Simulated patterns were created utilizing respective SXCRD data.

4.5 Crystal structure of the one-dimensional coordination polymer $\frac{1}{6}[\text{Co}_2\text{Cl}_3(\text{pt})(\text{H}_2\text{O})_2]\cdot 4\text{CyOH}$ (**19**)

Within the scope of experiments performed for this work, a solvothermal reaction of 50 μmol (12 mg) $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, 0.15 mmol (22 mg) Hpt, and 0.15 mmol (16 mg, 0.02 mL) NEt_3 was performed following the synthesis principle of coordination compounds described within the main paper. As a solvent of higher viscosity in comparison to pyridine, 1 mL of cyclohexanol was utilized. The reaction mixture was heated to 180 $^\circ\text{C}$ with 4 $^\circ\text{C}\cdot\text{h}^{-1}$. This temperature was held constant for 120 h, followed by cooling to room temperature with 4 $^\circ\text{C}\cdot\text{h}^{-1}$. Few blue single crystals within orange microcrystalline product were found, which were suitable for SCXRD and consisting of the one-dimensional coordination polymer $\frac{1}{6}[\text{Co}_2\text{Cl}_3(\text{pt})(\text{H}_2\text{O})_2]\cdot 4\text{CyOH}$ (CyOH = cyclohexanol, **19**).

It crystallizes in the monoclinic crystal system in the space group $C2/c$ and contains two crystallographically independent Co atoms. The first (Co1) is coordinated octahedrally by two pt^- molecules, two water molecules and one chlorido ligand. One of the pt^- molecules coordinates *via* N1 of the pyridine ring and N2 of the triazole ring. The second (symmetry generated) molecule coordinates by N3 of the triazole ring, interconnecting Co1 atoms. Two water molecules coordinate in *trans* geometry. These establish hydrogen bonds to two solvent molecules (cyclohexanol), each. The octahedral coordination is completed by a chlorido ligand, which interconnects Co1 and Co2 atoms. The tetrahedral coordination of Co2 is complemented by another two (non-bridging) chlorido ligands and N4 of pt^- . A depiction of the crystal structure is given in Figure S48. Crystallographic data is listed in Table S40. Interatomic distances and angles are listed in Table S41. The Co–N distances range from 201.3(5) pm to 215.1(6) pm and are close to distances within $[\text{Co}(\text{L})](\text{H}_2\text{O})_2][\text{H}_2\text{Mo}_{12}\text{O}_{40}]_{0.5}$ ($\text{L} = 4\text{-[2-(5-Pyridin-2-yl-[1,2,4]triazol-1-yl)-ethyl]-morpholine}$; 208 pm to 214 pm).³⁴ Only the Co2–N4 distances, with 201.3(5) pm is significantly shorter, which is explained by the chlorido ligands coordinating to this cobalt atom, reducing electron density and hence strengthening the metal–ligand bond.

Due to low crystal quality and heavily disordered cyclohexanol molecules, the determined C–C bond precision is low (PLAT341_ALERT_3_B) and the U3/U1 ratio for $\langle \text{U}(i,j) \rangle$ tensor deviates significantly from 1 (reached value = 4.5; PLAT250_ALERT_2_B). Since the crystals already differ visually from the remaining solid product, and the crystal quality was low, this compound is presented as single crystal structure, only.

Table S40. Crystallographic data for $\frac{1}{3}[\text{Co}_2\text{Cl}_3(\text{pt})(\text{H}_2\text{O})_2] \cdot 4\text{CyOH}$ (**19**). Deviations are given in brackets.

Empirical formula	$\text{C}_{31}\text{H}_{57}\text{Cl}_3\text{Co}_2\text{N}_4\text{O}_6$
Formula weight [$\text{g} \cdot \text{mol}^{-1}$]	806.01
Crystal colour and shape	violet block
Crystal size	0.170 x 0.104 x 0.103 mm ³
Crystal system	monoclinic
Space group	$C2/c$
a [pm]	2846.6(2)
b [pm]	9836.0(6)
c [pm]	2840.2(2)
V [10^6 pm^3]	7942.2(8)
α [°]	90
β [°]	92.869(2)
γ [°]	90
Z	8
ρ_{calc} [$\text{g} \cdot \text{cm}^{-3}$]	1.348
$\mu(\text{MoK}\alpha)$ [mm^{-1}]	1.08
X-ray radiation	$\text{MoK}\alpha$, $\lambda = 71.073 \text{ pm}$
Measurement temperature [K]	200(2)
Absorption correction type	multi-scan
2 θ range [°]	3.954 to 52.042
No. of measured reflections	64649
No. of independent reflections	7820
R_{int}	0.0596
No. of independent reflections ($I > 2\sigma(I)$)	7821
No. of parameters	553
R_1 ($I > 2\sigma(I)$)	0.0925
wR_2 (all data)	0.2401
GOF	1.034
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ [$\text{e} \cdot 10^{-6} \text{ pm}^{-3}$]	1.012, -0.695

Table S41. Interatomic distances and angles for $\frac{1}{3}[\text{Co}_2\text{Cl}_3(\text{pt})(\text{H}_2\text{O})_2] \cdot 4\text{CyOH}$ (**19**). Deviations are given in brackets. Symmetry operations: I = x, 1+y, z; II = 3/2-x, 3/2-y, 1-z.

Atoms	Distance [pm]	Atoms	Angle [°]
Co1–N1	215.2(5)	N1–Co1–N2	78(1)
Co1–N2	209.9(5)	N1–Co1–N3 ^{II}	175(1)
Co1–N3 ^{II}	207.7(5)	N1–Co1–O1	91(1)
Co1–O1	209.1(7)	N1–Co1–O2	89(1)
Co1–O2	210.3(7)	N1–Co1–Cl3 ^I	95(1)
Co1–Cl3 ^I	252.0(2)	N2–Co1–N3 ^{II}	97(1)
Co2–N4	201.4(5)	N2–Co1–O1	90(1)
Co2–Cl3	230.6(2)	N2–Co1–O2	91(1)
Co2–Cl4	224.5(3)	N2–Co1–Cl3 ^I	173(1)
Co2–Cl5	223.9(2)	O1–Co1–N3 ^{II}	90(1)
O3–H1A	204(7)	O1–Co1–O2	179(1)
O4–H2A	178(9)	O1–Co1–Cl3 ^I	89(1)
O5–H1B	178(6)	O2–Co1–N3 ^{II}	91(1)
O6–H1B	186(7)	O2–Co1–Cl3 ^I	89(1)
O7–H2B	195(9)	N3 ^{II} –Co1–Cl3 ^I	90(1)
O8–H2B	191(7)	Cl1–Co2–Cl2	111(1)
		Cl1–Co2–Cl3	109(1)
		Cl1–Co2–N4	113(1)
		Cl2–Co2–Cl3	110(1)
		Cl2–Co2–N4	113(1)
		Cl3–Co2–N4	100(1)
		O1–H1A–O3	142(3)
		O1–H1B–O6	176(6)
		O1–H1B–O5	177(6)
		O2–H2A–O4	174(7)
		O2–H2B–O7	149(4)
		O2–H2B–O8	163(4)

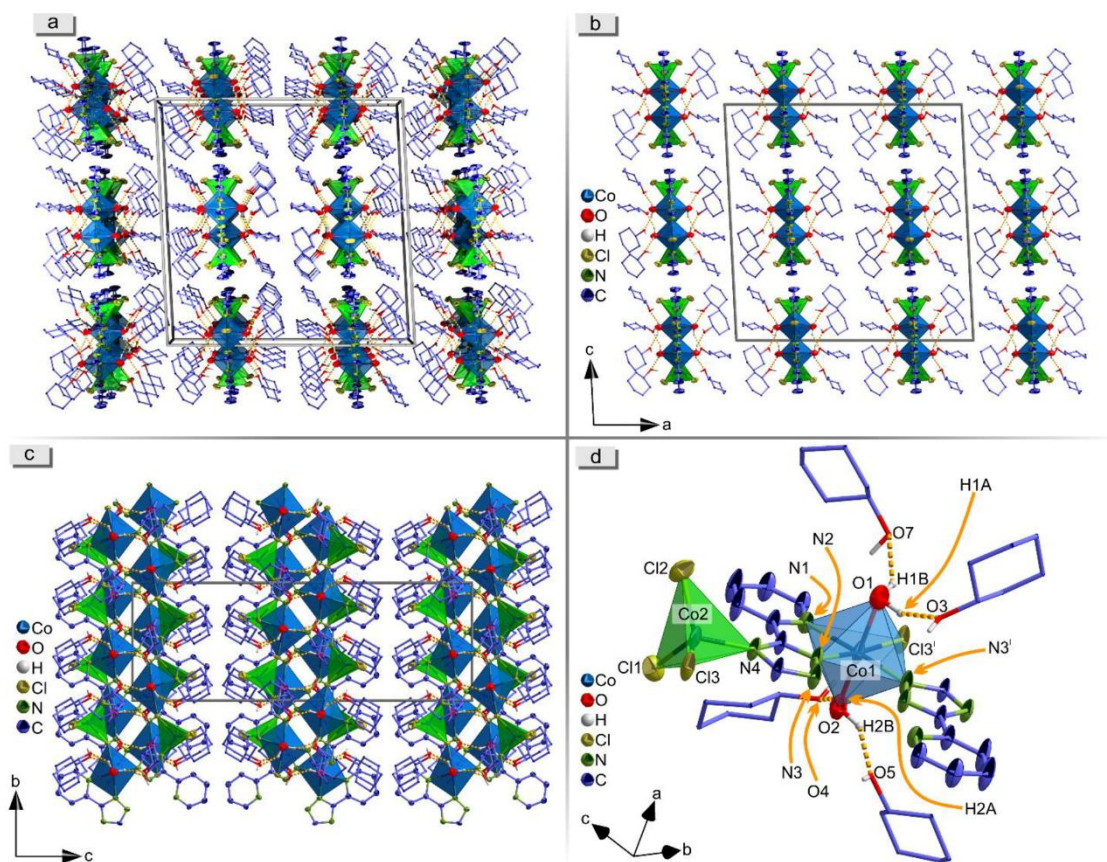


Figure S48. Depiction of the crystal structure of $[Co_2Cl_3(pt)(H_2O)_2] \cdot 4CyOH$ (19). Presented are: A three-dimensional depiction of the polymeric strands along crystallographic b axis (a), excerpts of the crystal structure along the crystallographic b (b) and a axis (c) in parallel projection, besides the extended coordination of Co atoms (d). The distorted octahedral coordination of Co1 is highlighted in blue. The tetrahedral coordination of Co2 is highlighted in green. Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. Cyclohexanol molecules are depicted in wire frame representation. For two of the four cyclohexanol molecules, only one disorder is shown, each. For clarity, all hydrogen atoms, except the ones bound to oxygen atoms, are omitted. Symmetry operations: I = $x, 1+y, z$; II = $3/2-x, 3/2-y, 1-z$.

4.6 Single crystal structure of the two-dimensional coordination polymer $\frac{2}{3}[\text{Co}_2\text{Br}_2(\text{pt})_2]$ (**20**)

A reaction of 0.5 mmol (109 mg) CoBr_2 , 1.2 mmol (175 mg) Hpt, and 1.2 mmol (123 mg, 0.17 mL) NEt_3 in 8 mL pyridine was performed at room temperature as an attempt to obtain a single crystal of $\frac{1}{3}[\text{Co}(\text{pt})_2]$. During the addition of triethylamine, the formation of an orange solid can be observed indicating the formation of $\frac{1}{3}[\text{Co}(\text{pt})_2]$. The reaction mixture was stirred overnight at room temperature, and the resulting solid was allowed to sediment. The solvent was manually removed, and the solid was redispersed in fresh pyridine followed by sedimentation and manual removal of the liquid phase. The product was dried in vacuum. A recorded powder X-ray diffraction pattern of this product shows reflections of triethylammonium bromide, indicating the deprotonation of Hpt and ligand exchange of Br^- , and side phase(s) of poor crystallinity. The broad reflection around 8° in 2θ indicates the formation of $\frac{1}{3}[\text{Co}(\text{pt})_2]$ (**3**, see Figure S49). Therefore, an attempt was made to recrystallize the product in naphthalene at 300°C for several days, resulting in a few blue crystals suitable for SCXRD. Interatomic Co–N distances range from 207.2(9) pm to 216(2) pm lying in a typical range as reported for $[\text{Co}(\text{Hpt})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (215 and 216 pm)³⁵ or $[\text{Co}(\text{L})](\text{H}_2\text{O})_2[\text{H}_2\text{Mo}_{12}\text{O}_{40}]_{0.5}$ ($\text{L} = 4\text{-}[2\text{-(5-Pyridin-2-yl-[1,2,4]triazol-1-yl)-ethyl]}\text{-morpholine}$; 208 to 214 pm).³⁴

The crystals obtained consist of the two-dimensional coordination polymer $\frac{2}{3}[\text{Co}_2\text{Br}_2(\text{pt})_2]$ (**20**), which crystallizes in the orthorhombic crystal system in the space group *Pbcm*. It contains two crystallographically independent cobalt atoms. One of them is octahedrally coordinated by four pt^- molecules. Two of them coordinate *via* N1 of the pyridine ring and N2 of the triazole ring in a way, that N2 atoms are in *trans* geometry, and N1 atoms are in *cis* geometry. The remaining two ligand molecules coordinate *via* N3 of the triazole ring. Therefore, two Co1 atoms are interconnected by two pt^- molecules, resulting in polymeric strands along the crystallographic *b* axis. Each ligand molecule interconnects Co1 atoms to Co2 atoms by coordination to Co2 *via* the remaining N4 atom of the triazole ring. In that way, Co2 is coordinated by two pt^- molecules resulting in polymeric Co2– pt –Co1– pt chains along crystallographic *c* axis. The tetrahedral coordination of Co2 is completed by two bromido ligands. Crystallographic data is summarized in Table S42. Interatomic distances and angles are listed in Table S43. A depiction of the crystal structure is given in Figure S50. Because of low crystal quality, the determined C–C bond precision is low (PLAT341_ALERT_3_B). The position of residual electron density indicates slight twinning. Thus, and since only few crystals were found within the microcrystalline product, $\frac{2}{3}[\text{Co}_2\text{Br}_2(\text{pt})_2]$ (**20**) is reported as single crystal structure, only.

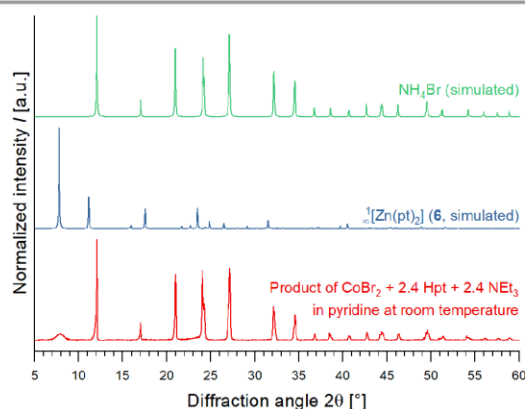


Figure S49. Powder X-ray diffractogram of the reaction product of CoBr_2 , 2.5 Hpt, and 2.4 NEt_3 in pyridine at room temperature besides simulated patterns (utilizing respective single crystal data) of NH_4Br ,³⁶ and $\frac{1}{3}[\text{Zn}(\text{pt})_2]$ (**6**).

Table S42. Crystallographic data for $\frac{1}{2}[\text{Co}_2\text{Br}_2(\text{pt})_2]$ (**20**). Deviations are given in brackets.

Empirical formula	$\text{C}_7\text{H}_5\text{BrCoN}_4$
Formula weight [$\text{g} \cdot \text{mol}^{-1}$]	283.99
Crystal colour and shape	blue needle
Crystal size	$0.099 \times 0.039 \times 0.023 \text{ mm}^3$
Crystal system	orthorhombic
Space group	<i>Pbcm</i>
a [pm]	1318.5(2)
b [pm]	7181.3(6)
c [pm]	1924.8(2)
V [10^6 pm^3]	1822.4(3)
α [°]	90
β [°]	90
γ [°]	90
Z	8
ρ_{calc} [$\text{g} \cdot \text{cm}^{-3}$]	2.07
$\mu(\text{MoK}\alpha)$ [mm^{-1}]	6.221
X-ray radiation	$\text{MoK}\alpha$, $\lambda = 71.073 \text{ pm}$
Measurement temperature [K]	200(2)
Absorption correction type	multi-scan
2 θ range [°]	4.232 to 51.354
No. of measured reflections	13390
No. of independent reflections	1792
R_{int}	0.108
No. of independent reflections ($I > 2\sigma(I)$)	1792
No. of parameters	123
R_1 ($I > 2\sigma(I)$)	0.0904
wR_2 (all data)	0.1832
GOF	1.21
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ [$\text{e} \cdot 10^{-6} \text{ pm}^{-3}$]	2.019, -1.342

Table S43. Interatomic distances and angles for $\frac{1}{2}[\text{Co}_2\text{Br}_2(\text{pt})_2]$ (**20**). Deviations are given in brackets. Symmetry operations: I = x, 3/2-y, 1-z; II = 1-x, 1-y, 1-z; III = 1-x, 1/2+y, z; IV = x, y, 1/2-z

Atoms	Distance [pm]	Atoms	Angle [°]
Co1–N1	216(1)	N1–Co1–N1 ^I	82(1)
Co1–N1 ^I	216(1)	N1–Co1–N2	76(1)
Co1–N2	211(1)	N1–Co1–N2 ^I	96(1)
Co1–N2 ^I	211(1)	N1–Co1–N3 ^{II}	171(1)
Co1–N3 ^{II}	211(1)	N1–Co1–N3 ^{III}	93(1)
Co1–N3 ^{III}	211(1)	N1 ^I –Co1–N2	96(1)
Co2–Br1	240.8(3)	N1 ^I –Co1–N2 ^I	76(1)
Co2–Br2	238.2(3)	N1 ^I –Co1–N3 ^{II}	93(1)
Co2–N4	207.3(9)	N1 ^I –Co1–N3 ^{III}	171(1)
Co2–N4 ^{IV}	207.3(9)	N2–Co1–N2 ^I	170(1)
		N2–Co1–N3 ^{II}	98(1)
		N2–Co1–N3 ^{III}	89(1)
		N2 ^I –Co1–N3 ^{II}	89(1)
		N2 ^I –Co1–N3 ^{III}	98(1)
		N3 ^{II} –Co1–N3 ^{III}	93(1)
		Br1–Co2–Br2	1101(1)
		Br1–Co2–N4	102(1)
		Br1–Co2–N4 ^{IV}	102(1)
		Br2–Co2–N4	112(1)
		Br2–Co2–N4 ^{IV}	112(1)
		N4–Co2–N4 ^{IV}	118(1)

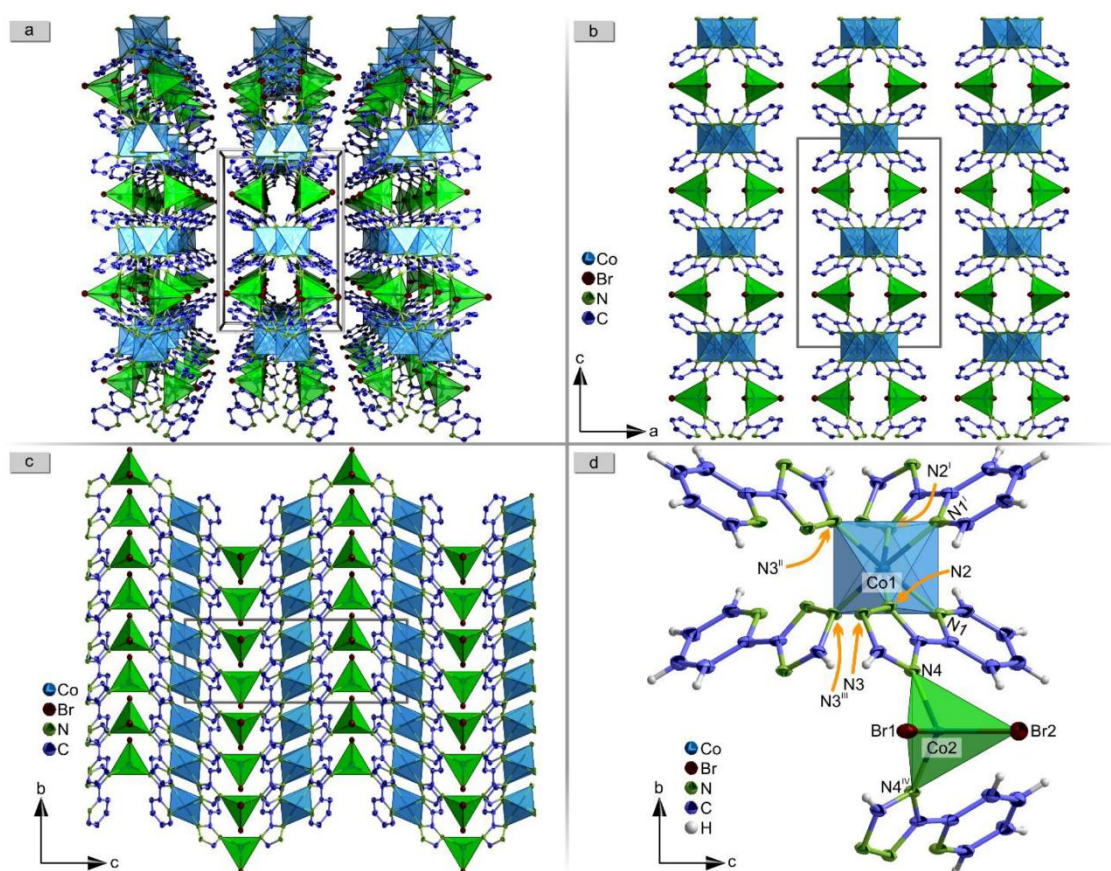


Figure S50. Depiction of the crystal structure of $\frac{1}{2}[\text{Co}_2\text{Br}_2(\text{pt})_2]$ (**20**). Presented are: a three-dimensional depiction of the structure along the crystallographic *b* axis (**a**), excerpts along the crystallographic *b* (**b**) and *a* (**c**) axis in parallel projection, as well as the extended coordination of contained Co atoms (**d**). Octahedral coordination of Co1 is highlighted in blue. Tetrahedral coordination of Co2 is highlighted in green. Displayed thermal ellipsoids correspond to 50 % probability level of the atoms. For all depictions except for extended coordination, hydrogen atoms are omitted for clarity. Symmetry operations: I = $x, 3/2-y, 1-z$; II = $1-x, 1-y, 1-z$; III = $1-x, 1/2+y, z$; IV = $x, y, 1/2-z$.

4.7. Investigations on synthesis of heteroleptic complexes $[\text{MX}_2(\text{Hpt})_2]$

As mentioned in the main paper, reactions of corresponding divalent transition metal halides with an excess of Hpt in pyridine lead to phase-pure complexes $[\text{MnCl}_2(\text{Hpt})_2]$ (**9**), $[\text{FeCl}_2(\text{Hpt})_2]$ (**10**), $[\text{CoCl}_2(\text{Hpt})_2]$ (**11**), and $[\text{CoBr}_2(\text{Hpt})_2]$ (**12**) (see Figure S51). According to the product powder pattern, the reaction of FeBr_2 and Hpt in pyridine yielded in a mixture of multiple phases, including $[\text{FeBr}_2(\text{Hpt})_2]$ (**11**), $[\text{Fe}_2\text{Br}_2(\text{pt})_2(\text{Py})_4]$ (**16**), and $\frac{1}{2}[\text{Fe}(\text{pt})_2]$ (**2**). In case of reaction of FeI_2 and Hpt, the product contains $\frac{1}{2}[\text{Fe}(\text{pt})_2]$ (**2**) and $[\text{SiI}_2(\text{Py})_4]\text{I}_2$ (Py = pyridine)³⁷ indicating reaction of the formal intermediate HI with the glass of the ampoule (see Figure S51). Considering the spectrochemical series of ligands, both, iodide and bromide, are weaker ligands in comparison to chloride with regard to ligand field strength. Thus, they eliminate from respective complexes more easily. Thereby, the N–H bond of the ligand is acidified, and it is possible to abstract the proton with pyridine followed by coordination of the deprotonated ligand to another coordinatively unsaturated metal ion. Since Zn^{2+} , in addition as d^{10} ion, exhibits no crystal field stabilization energy in an octahedral coordination environment, the complex $[\text{ZnCl}_2(\text{Hpt})_2]$ (**13**) is not stable in presence of pyridine under solvothermal conditions, as well. Hence, $\frac{1}{2}[\text{Zn}(\text{pt})_2]$ (**6**) is obtained by combination of ZnCl_2 and Hpt in pyridine.

Analogous syntheses performed in acetonitrile reveal, that all of the complexes $[\text{MnCl}_2(\text{Hpt})_2]$ (**9**), $[\text{FeCl}_2(\text{Hpt})_2]$ (**10**), $[\text{FeBr}_2(\text{Hpt})_2]$, $[\text{FeI}_2(\text{Hpt})_2]$, $[\text{CoCl}_2(\text{Hpt})_2]$ (**11**), $[\text{CoBr}_2(\text{Hpt})_2]$ (**12**), $[\text{ZnCl}_2(\text{Hpt})_2]$ (**13**), were obtained by reaction of the corresponding transition metal halide. Thereby, the product of a reaction of MnCl_2 shows additional reflections, indicating the presence of additional unknown phase(s). Within the diffractograms of the product of reactions of FeBr_2 , and ZnCl_2 , a reflection around 7.8° of low intensity is observable indicating the formation of low amounts of the corresponding one-dimensional coordination polymer (Figure S51). Due to lower solubility in MeCN compared to pyridine, the ligand needs to be separated by sublimation.

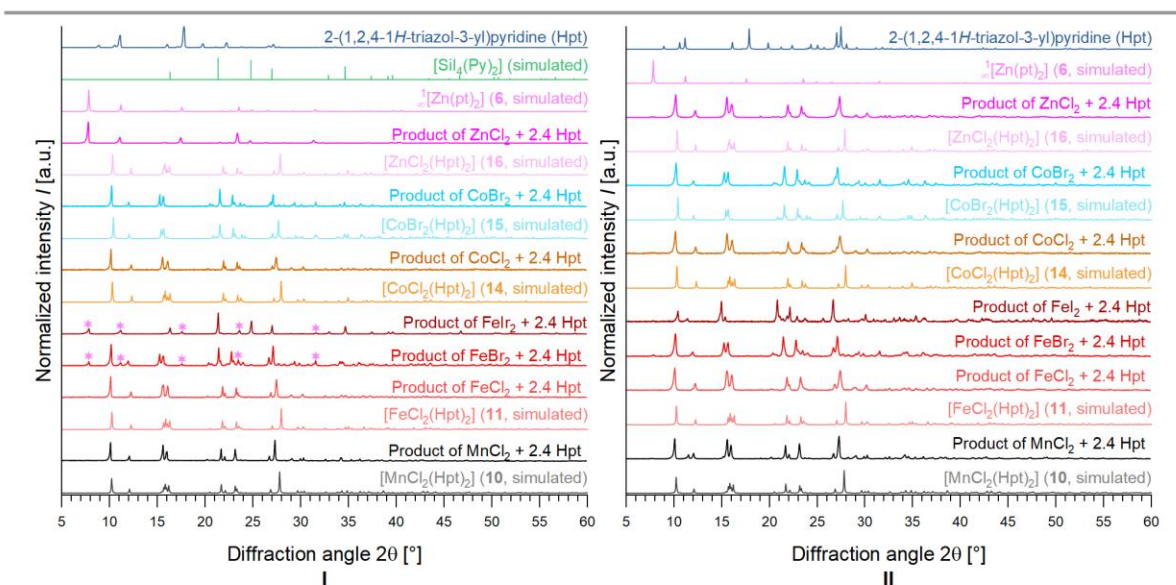


Figure S51. PXRD pattern of products obtained by solvothermal reaction of divalent transition metal halides and an excess of Hpt in pyridine (left) and acetonitrile (right) in comparison to diffractograms of $[\text{Zn}(\text{pt})_2]$ (**6**), $[\text{MnCl}_2(\text{Hpt})_2]$ (**9**), $[\text{FeCl}_2(\text{Hpt})_2]$ (**10**), $[\text{CoCl}_2(\text{Hpt})_2]$ (**11**), $[\text{CoBr}_2(\text{Hpt})_2]$ (**12**), and $[\text{ZnCl}_2(\text{Hpt})_2]$ (**13**), each simulated from SCXRD data, besides a stick pattern of $\text{SiI}_4(\text{Py})_2$.³⁷

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8 Abkürzungsverzeichnis

B

BDC - Benzol-1,4-dicarboxylat

Bipy - 4,4'-Bipyridin

BTC - Benzol-1,3,5-tricarboxylat

C

CP - *coordination polymer*, engl. Koordinationspolymer

D

DMF - *N,N*-Dimethylformamid

DOBDC - *2,5-Dioxidobenzol-1,4-dicarboxylat*

E

ET - Energietransfer

H

H₂BDC - Benzol-1,4-dicarbonsäure, Terephthalsäure

HKUST - *Hong Kong University of Science and Technology*. engl. Hongkong-Universität für Wissenschaft und Technologie

Hpt - 2-(1,2,4-*1H*-Triazol-3-yl)pyridin

I

IC - *internal conversion*, engl. innere Umwandlung

im - Imidazolat

ImH - Imidazol

ISC - *inter system crossing*, engl. Interkombination

IUPAC - *International Union of Pure and Applied Chemistry*, engl. Internationale Union für reine und angewandte Chemie

M

MFC - *magnetic framework composite*, engl. magnetisches Netzwerk-Komposit

MIL - *Matériaux de l'Institut Lavoisier*, franz. Materialien des Lavoisier-Instituts

N

NIR - *near-infrared*, engl. nahes Infrarot

P

PSM - Postsynthetische Modifizierung

R

RFID *radio frequency identification*, engl. Funkfrequenzidentifikation

S

SBU - *secondary building unit*, zentrale Einheit (Metallatom, -ion oder Cluster) in Koordinationspolymeren, welche von Linkern miteinander verknüpft werden.

SPIONs - *superparamagnetic iron oxide nanoparticles*, engl. superparamagnetische Eisenoxid-Nanopartikel

T

TzH - 1,2,4-1*H*-Triazol

U

UiO - *Universitetet i Oslo*, norw. Universität von Oslo

V

VR - *vibronic relaxation*, engl. vibronische Relaxation bzw. Schwingungsrelaxation

Z

ZIF - *zeolitic imidazolate framework*, engl. zeolithische Imidazolat-Gerüstverbindung

9 Wissenschaftliche Beiträge

9.1 Publikationen als Erstautor

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9.2 Publikationen als Koautor

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