

Phosphorescence Afterglow and Thermal Properties of [ScCl₃(ptpy)] (ptpy: 4'-phenyl-2,2',6',2''-terpyridine)

Alexander E. Sedykh,^[a] Dirk G. Kurth,^[c] and Klaus Müller-Buschbaum^{*[a, b]}

Dedicated to Professor Thomas M. Klapötke on the Occasion of his 60th birthday

A trivalent scandium complex with 4'-phenyl-2,2':6',2''-terpyridine [ScCl₃(ptpy)] has been synthesized and characterized. At low temperatures, [ScCl₃(ptpy)] shows a luminescence afterglow of green color in the crystalline form and of cyan color in a glass matrix, caused by phosphorescence of long triplet state

emission lifetime (1.63(2) s in a glass matrix, 0.56(3) s in the crystalline form). In addition, the complex is thermally remarkably stable up to 495 °C, especially in comparison with previously reported similar lanthanide and group 3 metal chloride complexes containing ptpy.

Introduction

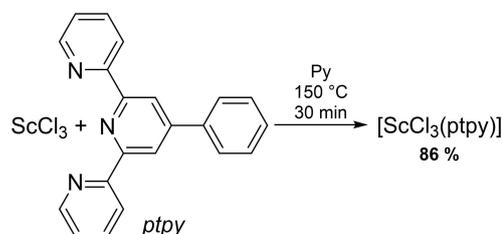
Lanthanide coordination compounds with terpyridine and its derivatives have been known for decades,^[1–19] and namely with 4'-phenyl-2,2':6',2''-terpyridine (ptpy) several reports were published.^[20–28] Recently, we have presented two series of lanthanide coordination polymers and complexes including organic ligand sensitized 4f-4f emission of NIR and visible emitters.^[28] Despite the wide usage of terpyridine and other tridentate N-ligands in the coordination chemistry of lanthanides, only a few examples of coordination compounds obtained with scandium have been published, so far: with 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine^[29] and 2,6-bis(4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl)pyridine,^[30] which have an NNN coordination site similar to terpyridine, and two with 2,2':6',2''-terpyridine itself.^[31,32] Other examples are *in situ* generated trivalent scandium complexes with terpyridine or related molecules for catalysis,^[33,34] or monitoring the changes of organic-based luminescence of 2,3,5,6-tetrakis(2-pyridyl)pyrazine in presence of Sc³⁺ and other metal ions.^[35,36] However,

for trivalent scandium complexes obtained with 2,2':6',2''-terpyridine, no luminescence properties have been investigated. Here we present a new trivalent scandium complex [ScCl₃(ptpy)], which exhibits a ligand-based phosphorescence at low temperatures in both crystalline form and glass matrix. We have thereby completed the row of trivalent lanthanide and group 3 complexes from metal chlorides and 4'-phenyl-2,2':6',2''-terpyridine.^[28] The new Sc complex is the only example of the series exhibiting an afterglow effect, even though terpyridine and its derivatives are known to have a phosphorescence at 77 K with a long lifetime up to several seconds.^[37–42] Additionally, we present photoluminescence properties of ptpy, for which the phosphorescence was not reported previously.

Results and Discussion

[ScCl₃(ptpy)] forms in a reaction between anhydrous scandium trichloride and ptpy in pyridine upon heating with good yield of 86% (Scheme 1). It crystallizes in space group C2/c, with three chlorides and a ligand being coordinated to the metal center, resulting in a coordination number of six and distorted octahedral coordination polyhedra (Figure 1), with the difference between angles of the ideal and observed polyhedra coming from the rigid structure of terpyridine (for more details see SI Table S2).

The molecular structure of [ScCl₃(ptpy)] is quite similar to trichlorido(2,2':6',2''-terpyridine)scandium (crystallizing in space group P2₁/n), the main difference between two complexes



Scheme 1. Synthesis of [ScCl₃(ptpy)].

[a] A. E. Sedykh, Prof. Dr. K. Müller-Buschbaum
Institute of Inorganic and Analytical Chemistry
Justus-Liebig-University Giessen
Heinrich-Buff-Ring 17, 35392 Giessen, Germany
E-mail: kmbac@uni-giessen.de

[b] Prof. Dr. K. Müller-Buschbaum
Center for Materials Research (LAMA)
Justus-Liebig-University Giessen
Heinrich-Buff-Ring 16, 35392 Giessen, Germany

[c] Prof. Dr. D. G. Kurth
Lehrstuhl für Chemische Technologie der Materialsynthese
Julius-Maximilians-University Würzburg
Röntgenring 11, 97070 Würzburg, Germany

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/zaac.202000347>

© 2020 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

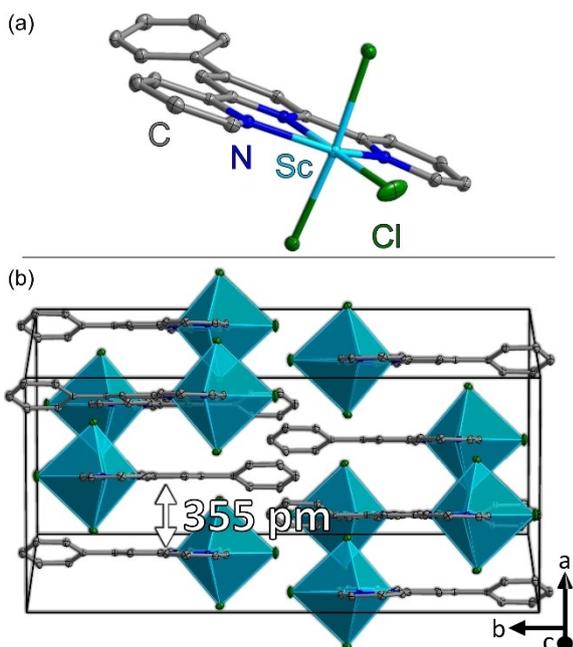


Figure 1. X-ray crystal structure of a complex unit (a) and a unit cell (b) of $[\text{ScCl}_3(\text{pty})]$. Thermal ellipsoids depict a 50% probability level of the atoms (Sc light blue, Cl green, C grey, N blue, hydrogen atoms are omitted).

being the additional phenyl ring in pty.^[32] Due to the small ionic radius of trivalent scandium, no additional molecules, such as solvent molecules, are coordinated to the metal center in the resulting $[\text{ScCl}_3(\text{pty})]$ complex, unlike with trivalent lanthanides, which form complexes of general formula $[\text{LnCl}_3(\text{pty})(\text{py})]$, in which the metal ion coordination sphere forms a distorted pentagonal bipyramid.^[28] Interatomic distances in the crystal structure of the obtained product are 237.32(7) and 244.81(4) pm for Sc–Cl and 223.9(2) and 225.0(2) pm for Sc–N, which is in consistency with the literature data for related compounds (Sc–Cl 238.8–257.4 pm, Sc–N 222.9–228.4 pm), namely $\text{ScCl}_3(\text{terpy})$,^[32] $(\text{Pr-Pybox})\text{ScCl}_3$,^[30] and $[\text{Sc}_2\text{Cl}_4(\mu\text{-OH})_2(\text{py})_4] \cdot 4\text{py}$.^[43] In the crystal packing of $[\text{ScCl}_3(\text{pty})]$, terpyridine fragments from different molecules are infinitely stacked on one another with a distance between them of 355 pm and an overlap of $\approx 25\%$, which is considered an offset π - π stacking (Figure 1).^[44] Such stacking is not present in the crystal structure of pty itself: even though the distance between aromatic rings of different layers is 357 pm, there is no overlap between different layers (SI Figure S2),^[45] which indicates that the packing is determined by a C–H $\cdots\pi$ interaction (π - σ attraction).^[44] The Sc^{3+} complex obtained as a powder is phase pure and has a good crystallinity, which is confirmed by powder X-ray analysis (Figure 2).

In the crystalline powder form, $[\text{ScCl}_3(\text{pty})]$ shows a blue colored emission at both, room temperature and 77 K. At low temperatures, a green-colored afterglow is noticeable with the naked eye.

Excitation and emission spectra are presented in Figure 3a. The energy of the S_1 state is 26530 cm^{-1} and of the T_1 states are

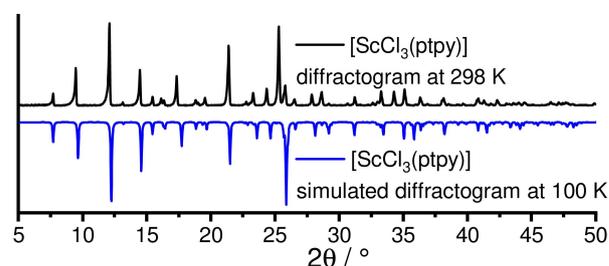


Figure 2. Comparison of experimental (top, black) and simulated (bottom, blue) powder X-ray diffractograms of $[\text{ScCl}_3(\text{pty})]$ indicating an excellent match with respect to the different measurement temperatures.

21050 cm^{-1} . The overall process decay time for the phosphorescence emission is $0.56(3) \text{ s}$ at 77 K. Even if the triplet state emission cannot be noticed in the emission spectrum immediately, with a gating (cutting off the singlet state emission), the phosphorescence emission can also be recorded (Figure 3a). Such photophysical behavior – a long afterglow effect upon cooling – is also observed for polycyclic aromatic compounds with heteroatoms such as terpyridines.^[37–42] Nonetheless, the new scandium complex is the only lanthanide and group 3 complex together with pty that shows this ligand specific afterglow in the crystalline form.^[28]

Dissolved in 2-MeTHF, the excitation and emission of $[\text{ScCl}_3(\text{pty})]$ are hypsochromically shifted in comparison to the crystalline powder form (see Figure 3b). The energy of the S_1 state is 29850 cm^{-1} and 22750 cm^{-1} of the T_1 , respectively. The afterglow is of cyan color and has a lifetime of $1.63(2) \text{ s}$ at 77 K. In the glass matrix, the triplet state emission has a higher relative intensity in comparison with the powder sample, and it can be observed in the emission spectra readily. Both, energy shift and increase of the afterglow lifetime are due to the increase of the intermolecular distances/absence of packing effects.

For comparison, the pure ligand pty as a powder shows similar photophysical properties to the obtained complex (Figure 3c), with the energies of the S_1 state being 27780 cm^{-1} and of the T_1 state 20660 cm^{-1} . The major difference between the complex and the free ligand as crystalline powder is that for pty the afterglow has a much lower intensity and cannot be observed by eye, even though it has a longer lifetime. In the crystalline powder form, the difference in the position of pty energy levels in $[\text{ScCl}_3(\text{pty})]$ and the pure ligand derives from its binding to Sc, which is strong a Lewis acid, and the different crystal packing, which is described above. Dissolved in 2-MeTHF, pty has the same energies of the S_1 and T_1 states as in the complexed form (Figure 3d). However, the relative intensity of transitions between ground and excited vibronic energy states differs, as can be seen from both, excitation and emission spectra (Figure 3c, d). The reason for this observation also derives from the coordination of the ligand to the Sc^{3+} ion and the change of the molecular geometry of pty. In the complex, nitrogen atoms of the side pyridyl terpyridine rings are in *cis*

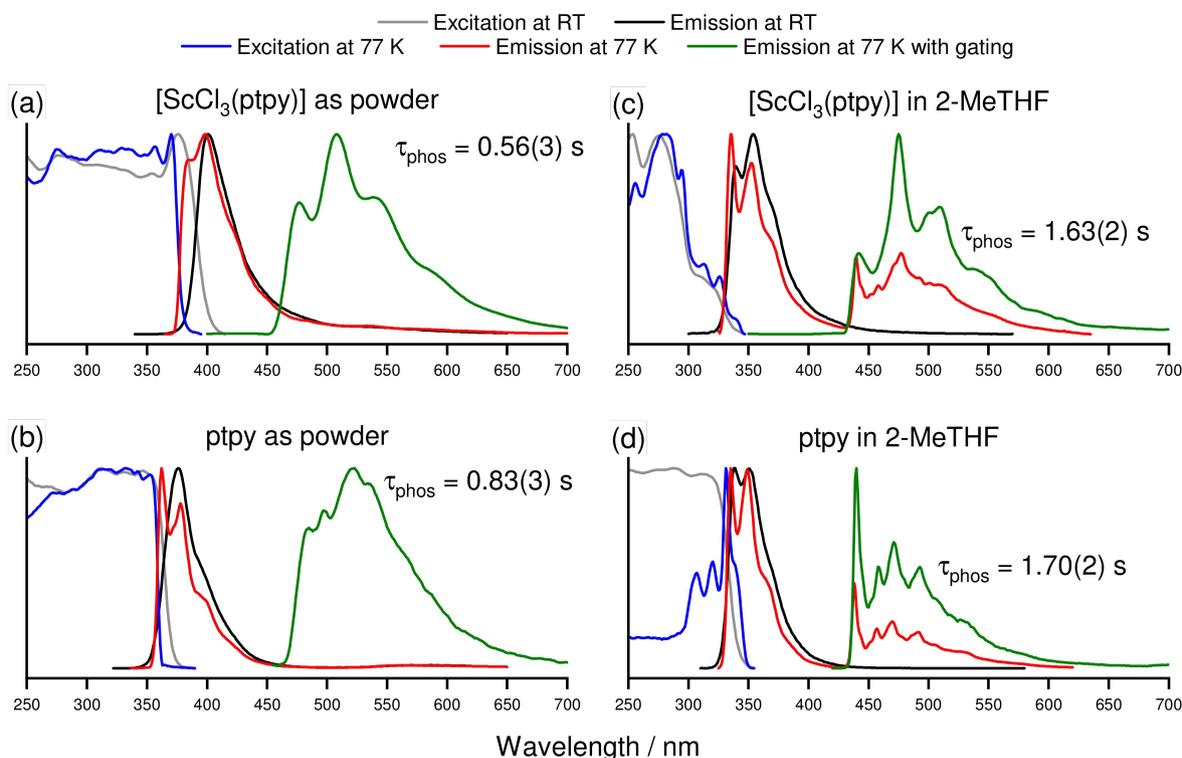


Figure 3. Normalized excitation (at RT – grey, at 77 K – blue) and emission (at RT – black, at 77 K – red, at 77 K with gating – green) spectra of pty and $[\text{ScCl}_3(\text{pty})]$ in the crystalline form and dissolved in 2-MeTHF (2 mM solutions).

positions to the central ring nitrogen atom, while in the non-coordinated ligand, they are typically rotated to *trans* positions.

Further differences in the photophysical properties between complexed and free pty are overall fluorescence decay times and quantum yields (Table 1). Overall, after complexation to trivalent scandium, the fluorescence lifetime shortens, but in solution/glass matrix, fluorescence lifetimes of both compounds are closer to one another as compared to those of the crystalline form. A difference of the fluorescence and phosphorescence lifetimes ratio between crystalline form and solution/

glass matrix indicates that the main influence of their shortening is the crystal packing and not the complexation itself.

For both compounds, the complex and the ligand, the efficiency of the photoluminescence process was determined for fluorescence, whereas this was not possible for the afterglow. The quantum yields for both are higher in the crystalline form, resulting in $\text{QY} = 0.18$ for pty and 0.11 for the complex. In 2-MeTHF, non-radiative energy transfer from the excited ligand states to states of the solvent molecules is possible, which reduces the quantum yield.

Table 1. Quantitative photophysical fluorescence and phosphorescence data of $[\text{ScCl}_3(\text{pty})]$ and pty in the crystalline form and the solution/glass matrix at room temperature and 77 K.

Compound	State	T	$\tau_{\text{fluor}}^{\text{[a]}}$	$\lambda_{\text{ex}}/\lambda_{\text{em}} \text{ (nm)}^{\text{[b]}}$	$\tau_{\text{phos}}^{\text{[c]}}$	$\lambda_{\text{ex}}/\lambda_{\text{em}} \text{ (nm)}^{\text{[d]}}$	$\Phi \text{ (\%)}^{\text{[e]}}$	$\lambda_{\text{ex}}/\lambda_{\text{em}} \text{ (nm)}^{\text{[f]}}$
$[\text{ScCl}_3(\text{pty})]$	Crystalline powder	RT	1.23(1) ns	290/400	–	–	10.8(2)	330/360–500
		77 K	1.47(1) ns	290/400	0.56(3) s	370/550	–	–
	2 mM in 2-MeTHF	RT	1.67(1) ns	290/354	–	–	4.8(1)	315/325–475
		77 K	2.87(1) ns	290/354	1.63(2) s	290/440	–	–
pty	Crystalline powder	RT	3.05(1) ns	290/376	–	–	18.2(2)	330/345–490
		77 K	3.38(1) ns	290/362	0.83(3) s	350/525	–	–
	2 mM in 2-MeTHF	RT	1.82(1) ns	290/354	–	–	10.4(1)	315/325–475
		77 K	3.17(1) ns	290/350	1.70(2) s	331/470	–	–

[a] Fluorescence emission lifetime. [b] Excitation and emission wavelengths of fluorescence emission lifetime measurement (a pulsed diode with a peak wavelength of 290 nm was used for excitation). [c] Phosphorescence emission lifetime. [d] Excitation and emission wavelengths of phosphorescence emission lifetime measurement. [e] Quantum yield. [f] Excitation wavelength and emission range of QY measurement.

In addition, the thermal stability of $[\text{ScCl}_3(\text{ptpy})]$ was investigated in the solid state (Figure 4a). The complex shows remarkable thermal stability, although it consists of monomeric units. At temperatures higher than 350°C , it becomes slightly volatile (mass loss 3.5% between 350 and 495°C). At higher temperatures (from 495°C on), it decomposes with overlapping heat flow signals in DTA and changes in the mass loss indicating several steps without a plateau in the investigation. No ScCl_3 (melting point of 960°C) is formed, as the m.p. of it was not detected by DTA. Moreover, the wt% of the final residual mass is 60%, whereas ScCl_3 unit in $[\text{ScCl}_3(\text{ptpy})]$ gives a theoretical residual mass of 32.8%, which means, that approximately half of the organic ligand amount is still present in the final sample indicating carbonization. The mass release does not reach a closing up to 1000°C , and therefore the composition of the final decomposition product cannot be determined unambiguously. The free ligand starts to melt at 205°C (lit.: 208°C)^[46] and becomes volatile at about 250°C (Figure 3b), combined to a very broad endothermic signal indicating completion of this process at the peak maximum at 370°C (afterwards, the DTA signal returns to the baseline). For comparison, Eu^{3+} complexes with ptpy $[\text{EuCl}_3(\text{ptpy})(\text{L})]$ (L = pyridine, acetamide) and $[\text{Eu}_2\text{Cl}_6(\text{ptpy})_2(4,4'\text{-bipy})]$ ·4,4'-bipy first release co-coordinated organic molecules (L or 4,4'-bipy) at $250\text{--}295^\circ\text{C}$, with the resulting residue $\text{EuCl}_3(\text{ptpy})$ being stable up to $435\text{--}445^\circ\text{C}$.^[47] In the another example, $[\text{Eu}_2\text{Cl}_4(\text{bc})_2(\text{ptpy})_2]$ is stable up to 395°C , where a carboxylate group is responsible for the start of the decomposition.^[48] As can be seen,

$[\text{ScCl}_3(\text{ptpy})]$ has a higher thermal stability than the Eu^{3+} complexes with ptpy.

Conclusions

The complex $[\text{ScCl}_3(\text{ptpy})]$ forms in a direct reaction between anhydrous scandium trichloride and 4'-phenyl-2,2':6',2''-terpyridine. Unlike all other lanthanide and group 3 metal ions, this complex shows a green colored (in the powder form) or cyan colored (in the glass matrix) afterglow of >1.5 s by ligand-based phosphorescence at 77 K. In addition, the typical fluorescence of ptpy is observed. Even though the ligand itself shows an afterglow at 77 K, too, only for the reported complex, the afterglow is so strong that it is noticeable with the naked eye in the crystalline form, resulting in a color change of the chromaticity during observation (between fluorescence and afterglow). The complex is thermally stable up to 495°C in the solid state. The photophysical and thermal properties of the complex obtained are compared with the free ligand. Obtaining this scandium complex completes the row of coordination compounds of trivalent rare earth metal chlorides with this ligand indicating remarkable photoluminescence properties.

Experimental Section

Experimental Details. 4'-phenyl-2,2':6',2''-terpyridine was synthesized from benzaldehyde and 2-acetylpyridine as described in the literature.^[49] ScCl_3 (99.99%, Strem Chemicals) was used as received. Pyridine and toluene were dried using standard techniques and stored in flasks with J. Young valve with molecular sieves. Anhydrous 2-methyltetrahydrofuran ($\geq 99\%$, inhibitor-free, Sigma-Aldrich) was degassed before use.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2027759. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Synthesis of $[\text{ScCl}_3(\text{ptpy})]$. ScCl_3 (60.5 mg, 0.4 mmol) and ptpy (125.3 mg, 0.405 mmol) were mixed in a Duran® culture tube with a screw cap with a hole and a septum inside the glovebox (Innovative Technology PureLab). To this mixture, a magnetic stir bar and 1 mL of dry pyridine were added. The reaction mixture was stirred for 30 min at 150°C . Afterward, the following procedure was repeated twice: the tube was centrifuged and the solvent was removed through the septum; a portion of dry toluene (1.5 mL) was added, also through the septum, and the reaction mixture was stirred. The tube was centrifuged again, and toluene was removed through the septum. Lastly, the tube was placed in a special quick-fit, which allows connecting the tube to the heating of the vacuum line, and the product was dried *in vacuo* at 100°C for 30 min. The isolated product was a white powder with blue luminescence, yield 158.1 mg (86%). Elemental analysis calculated (%) for $\text{ScCl}_3\text{C}_{21}\text{H}_{15}\text{N}_3$: C 54.75, H 3.28, N 9.12; found: C 54.55, H 3.27, N 9.19. ATR-MIR: $\tilde{\nu}_{\text{max}} = 3109$ w, 3087 w, 3060 m, 3032 w, 3012 w, 1624 w, 1601 s, 1568 m, 1556 w, 1545 m, 1533 m, 1518 w, 1508 m, 1496 w, 1481 s, 1466 w, 1458 m, 1448 w, 1437 m, 1429 w, 1412 s, 1398 m, 1387 w, 1375 w, 1361 m, 1338 m, 1306 m, 1266 w, 1250 s, 1242 s, 1211 w, 1198 w, 1186 w, 1159 m, 1132 w, 1116 w, 1105 w, 1093 m, 1070 m,

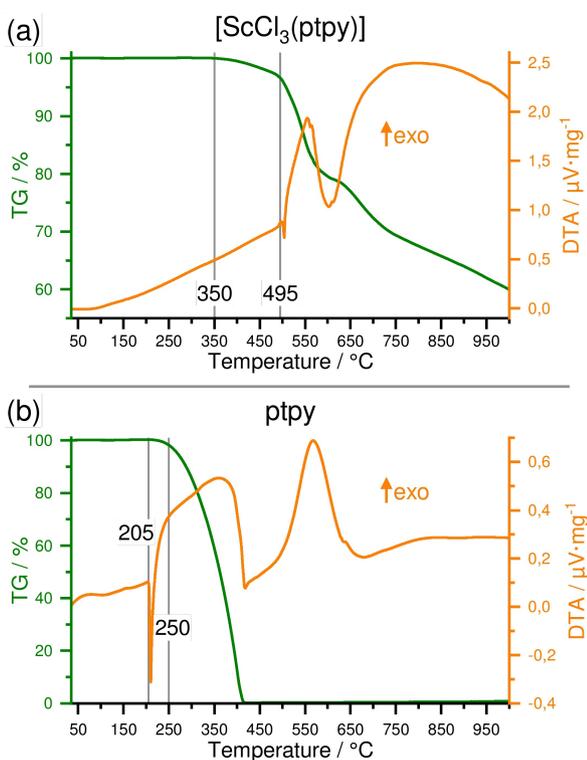


Figure 4. Thermal analysis of $[\text{ScCl}_3(\text{ptpy})]$ (a) and ptpy (b) by simultaneous DTA/TG with the heat-flow depicted in yellow-orange and the mass loss in green

1059 m, 1024 s, 1011 s, 982 m, 960 w, 945 w, 937 w, 930 w, 908 w, 893 m, 877 w, 866 w, 847 w, 843 w, 827 m, 810 w, 796 s, 762 s, 732 s, 708 w cm⁻¹.

Synthesis of Single Crystals. 1.5 mg (0.01 mmol) of ScCl₃ and 3.1 mg (0.01 mmol) of ptpy were mortared together and sealed with 0.5 mL of dry pyridine in a self-made Duran® glass ampoule under inert conditions. The ampoule was placed in the resistance heating oven with thermal control (Eurotherm 2416), heated to 200 °C within 1 hour, then the temperature was held for 24 hours, and finally, the oven was cooled down to room temperature. Resulting crystals were washed two times with toluene and dried under vacuum.

Single Crystal X-Ray Diffraction: A single of crystal [ScCl₃(ptpy)] was mounted on a goniometer head using a perfluorinated ether (viscosity 1800 cSt, 99.9%, ABCR). Data collection was performed using Mo-K_{α1} X-ray radiation with a BRUKER AXS Apex II diffractometer at 100 K with a Graphite monochromator using the BRUKER AXS Apex software package.^[50] Data processing was accomplished with XPREP.^[51] A structure solution was carried out with direct methods using SHELXT^[52] and the obtained crystal structure was refined with least square techniques using SHELXL^[53] on the graphical platform shelXle.^[54]

Powder X-Ray Diffraction. A sample for powder diffraction was ground in a mortar and filled in a soda-lime glass mark tube (Ø 0.3 mm, Hilgenberg GmbH), which was cut and sealed with picein wax. Diffraction data were collected with a powder X-ray diffractometer BRUKER AXS D8 Discover equipped with an LYNXEYE detector in transmission geometry. X-ray radiation (Cu-K_{α1}) was focused with a Goebel mirror; Cu-K_{α2} was eliminated by Ni absorber. Collection and analysis of data were performed using the BRUKER AXS Diffrac.Suite™ software.

Simultaneous Thermal Analysis. Simultaneous differential thermal analysis/thermogravimetry analysis was performed using a NETZSCH STA-409-PC instrument. [ScCl₃(ptpy)] (36.5 mg) as well as ptpy (33.9 mg) each were heated in a gas flow of argon (50 mL · min⁻¹) with a rate of 5 °C · min⁻¹ up to 1000 °C.

Photoluminescence Spectroscopy. Samples for PL spectroscopy were filled in spectroscopically pure quartz glass cuvettes under inert gas atmosphere and examined at 77 K using special liquid nitrogen-filled Dewar assembly (FL-1013, HORIBA) or at room temperature. For the measurement in the solution/glass matrix, 2 mM solution of [ScCl₃(ptpy)] and 2 mM solution of ptpy in 2-MeTHF were prepared. Excitation and emission spectra were recorded with a HORIBA Jobin Yvon Spex Fluorolog 3 spectrometer equipped with a dual lamp housing (FL-1040 A), a 450 W xenon 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 using a FluoroEssence™ software. Both, excitation and emission spectra were corrected for the spectral response of the monochromators and the detector using spectral corrections provided by the manufacturer. Additionally, excitation spectra were corrected for the spectral distribution of the lamp intensity by the use of a photodiode reference detector. Emission spectra with gating were recorded using a xenon flashlamp with a pulse every 41 ms, the first 2 ms were not recorded, and the sample window set to 5 ms. Phosphorescence lifetimes were determined by monitoring the emission intensity of the phosphorescence band with the integration time of 0.05 s, while the shutter was closed and opened 15 to 25 times; resulting decays were fitted with a single exponent decay and a lifetime value has been evaluated as an average (for details, see SI Figures S4 and S5). Overall fluorescence process decay times

were determined using a pulsed diode with a peak maximum at 290 nm (for details, see SI Figures S6 and S7).

For the photoluminescence quantum yield determination, a HORIBA Quanta-φ Integrating Sphere (F-3029) was used; the solid sample was filled into Starna Micro Cell cuvettes 18-F/ST/C/Q/10 (fluorescence with ST/C closed-cap, material UV quartz glass Spectrosil Q, pathlength 10 mm, matched); dry barium sulfate was used as reference material; the sample was measured several times and the quantum yield value with standard deviation was evaluated afterward. Quanta-φ Integrating Sphere was checked by measuring a standard (sodium salicylate as a powder, λ_{ex} = 340 nm, λ_{em} = 365–600 nm, measured QY = 52%, in the literature: 53%).^[55]

Elemental Analysis. For carbon, hydrogen, and nitrogen elemental analysis the compound was placed in a tin crucible with at least one mass equivalent of V₂O₅. The sample was stored under inert conditions before the measurements. The analysis was performed using a Vario Micro Cube (Elementar Analysensysteme GmbH).

Vibrational Spectroscopy. MIR spectrum was recorded under non-inert conditions from several milligrams of the compound with a Nicolet 380 FT-IR spectrometer equipped with an ATR module using OMNIC™ software. Description of the signals: w = weak, m = medium, s = strong.

Acknowledgments

Alexander E. Sedykh acknowledges the *Studienstiftung des deutschen Volkes* for a PhD scholarship. The authors acknowledge Stephanie Maaß (Lehrstuhl für Chemische Technologie der Materialsynthese, Julius-Maximilians-Universität Würzburg) for the synthesis of 4'-phenyl-2,2':6',2''-terpyridine. Open access funding enabled and organized by Projekt DEAL.

Keywords: Afterglow · Luminescence · N ligands · Phosphorescence · Scandium

- [1] L. R. Melby, N. J. Rose, E. Abramson, J. C. Caris, *J. Am. Chem. Soc.* **1964**, *86*, 5117–5125.
- [2] G. H. Frost, F. A. Hart, C. Heath, M. B. Hursthouse, *J. Chem. Soc. D* **1969**, 1421–1422.
- [3] D. A. Durham, G. H. Frost, F. A. Hart, *J. Inorg. Nucl. Chem.* **1969**, *31*, 833–838.
- [4] S. Petoud, J.-C. G. Bünzli, T. Glanzman, C. Piguet, Q. Xiang, R. P. Thummel, *J. Lumin.* **1999**, *82*, 69–79.
- [5] J. H. Ryu, Y. K. Eom, J.-C. G. Bünzli, H. K. Kim, *New J. Chem.* **2012**, *36*, 723.
- [6] H.-R. Mürner, E. Chassat, R. P. Thummel, J.-C. G. Bünzli, *J. Chem. Soc. Dalton Trans.* **2000**, 2809–2816.
- [7] Y. Suffren, B. Golesorkhi, D. Zare, L. Guénée, H. Nozary, S. V. Eliseeva, S. Petoud, A. Hauser, C. Piguet, *Inorg. Chem.* **2016**, *55*, 9964–9972.
- [8] G. Muller, J. C. G. Bünzli, K. J. Schenk, G. Piguet, C. Hopfgartner, *Inorg. Chem.* **2001**, *40*, 2642–2651.
- [9] R. F. Ziessel, G. Ulrich, L. Charbonnière, D. Imbert, R. Scopelliti, J. C. G. Bünzli, *Chem. Eur. J.* **2006**, *12*, 5060–5067.
- [10] K. P. Carter, K. E. Thomas, S. J. A. A. Pope, R. J. Holmberg, R. J. Butcher, M. Murugesu, C. L. Cahill, *Inorg. Chem.* **2016**, *55*, 6902–6915.
- [11] W. E. Silva, M. Freire Belian, R. O. Freire, G. F. de Sá, S. Alves Jr., *J. Phys. Chem. A* **2010**, *114*, 10066–10075.

- [12] C. Galaup, J. M. Couchet, S. Bedel, P. Tisnès, C. Picard, *J. Org. Chem.* **2005**, *70*, 2274–2284.
- [13] G. F. de Sá, F. R. G. e Silva, O. L. Malta, *J. Alloys Compd.* **1994**, *207–208*, 457–460.
- [14] E. S. Andreiadis, R. Demadrille, D. Imbert, J. Pécaut, M. Mazzanti, *Chem. Eur. J.* **2009**, *15*, 9458–9476.
- [15] K. P. Carter, S. J. A. Pope, C. L. Cahill, *CrystEngComm* **2014**, *16*, 1873–1884.
- [16] R. J. Batrice, R. L. Ayscue, A. K. Adcock, B. R. Sullivan, S. Y. Han, P. M. Piccoli, J. A. Bertke, K. E. Knope, *Chem. Eur. J.* **2018**, *24*, 5630–5636.
- [17] B. Golesorkhi, L. Guénee, H. Nozary, A. Fürstenberg, Y. Suffren, S. V. Eliseeva, S. Petoud, A. Hauser, C. Piguet, *Chem. Eur. J.* **2018**, *24*, 13158–13169.
- [18] J. August Ridenour, K. P. Carter, C. L. Cahill, *CrystEngComm* **2017**, *19*, 1190–1203.
- [19] R. J. Batrice, J. A. Ridenour, R. L. Ayscue III, J. A. Bertke, K. E. Knope, *CrystEngComm* **2017**, *19*, 5300–5312.
- [20] V.-M. Mikkala, M. Helenius, I. Hemmilä, J. Kankare, H. Takalo, *Helv. Chim. Acta* **1993**, *76*, 1361–1378.
- [21] A. Hussain, S. Gadadhar, T. K. Goswami, A. A. Karande, A. R. Chakravarty, *Eur. J. Med. Chem.* **2012**, *50*, 319–331.
- [22] A. Hussain, K. Somyajit, B. Banik, S. Banerjee, G. Nagaraju, A. R. Chakravarty, *Dalton Trans.* **2013**, 182–195.
- [23] R. T. Golkowski, N. S. Settineri, X. Zhao, D. R. McMillin, *J. Phys. Chem. A* **2015**, *119*, 11650–11658.
- [24] D. Wang, H. Liu, L. Fan, G. Yin, Y. Hu, J. Zheng, *Synth. Met.* **2015**, *209*, 267–272.
- [25] D. Wang, Z. Luo, Z. Liu, D. Wang, L. Fan, G. Yin, *Dyes Pigm.* **2016**, *132*, 398–404.
- [26] T. Sarkar, S. Banerjee, S. Mukherjee, A. Hussain, *Dalton Trans.* **2016**, *45*, 6424–6438.
- [27] L. L. Cai, Y. T. Hu, Y. Li, K. Wang, X. Q. Zhang, G. Muller, X. M. Li, G. X. Wang, *Inorg. Chim. Acta* **2019**, *489*, 85–92.
- [28] A. E. Sedykh, D. G. Kurth, K. Müller-Buschbaum, *Eur. J. Inorg. Chem.* **2019**, *2019*, 4564–4571.
- [29] M. G. B. Drew, M. J. Hudson, P. B. Iveson, C. Madic, M. L. Russell, *J. Chem. Soc. Dalton Trans.* **2000**, 2711–2720.
- [30] Y. Pan, T. Xu, S. Fu, G.-W. Yang, X.-B. Lu, *Macromolecules* **2013**, *46*, 8790–8796.
- [31] A. M. Arif, F. A. Hart, M. B. Hursthouse, M. Thornton-Pett, W. Zhu, *J. Chem. Soc. Dalton Trans.* **1984**, 2449–2454.
- [32] E. Curnock, W. Levason, M. E. Light, S. K. Luthra, G. McRobbie, F. M. Monzittu, G. Reid, R. N. Williams, *Dalton Trans.* **2018**, *47*, 6059–6068.
- [33] N. V. Hanhan, N. R. Ball-Jones, N. T. Tran, A. K. Franz, *Angew. Chem. Int. Ed.* **2012**, *51*, 989–992; *Angew. Chem.* **2012**, *124*, 1013–1016.
- [34] A. Perrier, M. Keller, A. M. Caminade, J. P. Majoral, A. Ouali, *Green Chem.* **2013**, *15*, 2075–2080.
- [35] J. Yuasa, S. Fukuzumi, *J. Am. Chem. Soc.* **2006**, *128*, 15976–15977.
- [36] J. Yuasa, S. Fukuzumi, *J. Am. Chem. Soc.* **2008**, *130*, 566–575.
- [37] A. Sarkar, S. Chakravorti, *J. Lumin.* **1995**, *63*, 143–148.
- [38] A. Credi, V. Balzani, S. Campagna, G. S. Hanan, C. R. Arana, J. M. Lehn, *Chem. Phys. Lett.* **1995**, *243*, 102–107.
- [39] A. Auffrant, A. Barbieri, F. Barigelletti, J. P. Collin, L. Flamigni, C. Sabatini, J. P. Sauvage, *Inorg. Chem.* **2006**, *45*, 10990–10997.
- [40] H. Isla, M. Srebro-Hooper, M. Jean, N. Vanthuyne, T. Roisnel, J. L. Lunkley, G. Muller, J. A. G. Williams, J. Autschbach, J. Crassous, *Chem. Commun.* **2016**, *52*, 5932–5935.
- [41] Q. Sun, L. Tang, Z. Zhang, K. Zhang, Z. Xie, Z. Chi, H. Zhang, W. Yang, *Chem. Commun.* **2017**, *54*, 94–97.
- [42] F. Ni, Z. Zhu, X. Tong, M. Xie, Q. Zhao, C. Zhong, Y. Zou, C. Yang, *Chem. Sci.* **2018**, *9*, 6150–6155.
- [43] W. Massa, S. Agarwal, N. Grabe, K. Dehnicke, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1910–1914.
- [44] C. Janiak, *J. Chem. Soc. Dalton Trans.* **2000**, 3885–3896.
- [45] E. C. Constable, J. Lewis, M. C. Liptrot, P. R. Raithby, *Inorg. Chim. Acta* **1990**, *178*, 47–54.
- [46] R. L. Frank, E. F. Riener, *J. Am. Chem. Soc.* **1950**, *72*, 4182–4183.
- [47] A. E. Sedykh, R. Bissert, D. G. Kurth, K. Müller-Buschbaum, *Z. Kristallogr. – Cryst. Mater.* **2020**, *235*, 353–363.
- [48] A. E. Sedykh, S. A. Sotnik, D. G. Kurth, D. M. Volochnyuk, S. V. Kolotilov, K. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **2020**, *646*, 1710–1714.
- [49] J. Wang, G. Hanan, *Synlett* **2005**, *2005*, 1251–1254.
- [50] *Apex 2 Suite*, BRUKER AXS Inc., Madison, WI, USA, **2014**.
- [51] *XPRED (Version 2014/7)*, Program for Symmetry Analysis and Data Reduction of Diffraction Experiments, Bruker AXS Inc., Madison, WI, USA, **2014**.
- [52] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.
- [53] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122.
- [54] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
- [55] M. S. Wrighton, D. S. Ginley, D. L. Morse, *J. Phys. Chem.* **1974**, *78*, 2229–2233.

Manuscript received: September 21, 2020
 Revised manuscript received: November 10, 2020
 Accepted manuscript online: November 20, 2020