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# Bismuth trihalide based coordination polymers with the N-donor cyanopyridine as source for charge transfer based luminescence

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Dedicated to Prof. Dr. Michael Ruck on the Occasion of his 60<sup>th</sup> Birthday

Two one-dimensional bismuth trihalide coordination polymers (CPs)  ${}^{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$  and  ${}^{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$  were obtained by the solvent free melt approach in molten 4-cyanopyridine under inert conditions and reduced pressure. The bismuth ions are surrounded by four halide atoms and two nitrogen atoms of the pyridyl ring of 4-cypy in *trans*-mode. The polymeric linkage of both CPs is achieved by halide-bismuth interactions while the 4-cyanopyridine ligands show  $\pi$ -stacking interactions of

their aromatic backbone. Both of compounds possess sufficiently intensive luminescence in the blue-green region of the visible spectra upon cooling to 77 K following the trend of halide anion influence on the position of the emission band. Emission of these CPs arises from the contribution of two energy transfer mechanisms, MLCT from  $\text{Bi}^{3+}$  to ligand and LMCT from ligand to  $\text{Bi}^{3+}$ , respectively.

## Introduction

Bi(III) coordination polymers (CPs) and inorganic-organic hybrid materials are considered as luminescence materials,<sup>[1–10]</sup> even reporting the possibility of achieving white light emission.<sup>[6]</sup> They are also discussed for perspective applications as host lattices for lanthanide ions<sup>[11–13]</sup> and as topological insulators with noble metals such as rhodium.<sup>[14,15]</sup>

Given that the luminescence spectra of bismuth compounds are characterized by broad bands, their nature is usually

described by various possible mechanisms, such as LMCT (ligand-to-metal charge transfer) or MLCT (metal-to-ligand charge transfer),<sup>[2–4,6–8,13]</sup> and in some cases, when several different Bi-centers are presented, IVCT (intervalence charge transfer).<sup>[3,16,17]</sup> However, a precise assignment of optical spectra of  $\text{Bi}^{3+}$  compounds is a problematic task, even if supported by additional DFT-calculations.<sup>[2,5,8,13,18]</sup>

A significant part of luminescent Bi(III) compounds are coordination polymers of halidobismutates ( $\text{BiX}_3$ , X = Cl, Br) with N-donor ligands, for example, pyridine-containing ligands.<sup>[1–3,5,6,8]</sup> It is worth noting that the halide nature plays a significant role in charge transfer processes and can affect the optical properties of compounds, i.e. intensity or position of bands.<sup>[2,13]</sup>

One promising ligand for pyridine-containing coordination polymers is 4-cyanopyridine (4-cypy), as it also contains a cyano group and thereby has two different N-donor atoms and the possibility to act as interlinking ligand. Therefore, bismuth halides with this ligand can be considered for a further improvement in the understanding of the interaction of bismuth(III) with the donors and the formation of N-donor based coordination polymers, their structural chemistry and photophysical properties. In this paper, we describe the crystal structure and luminescence properties of the two  $\text{Bi}^{3+}$  coordination polymers with different halides,  ${}^{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$  and  ${}^{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$ .

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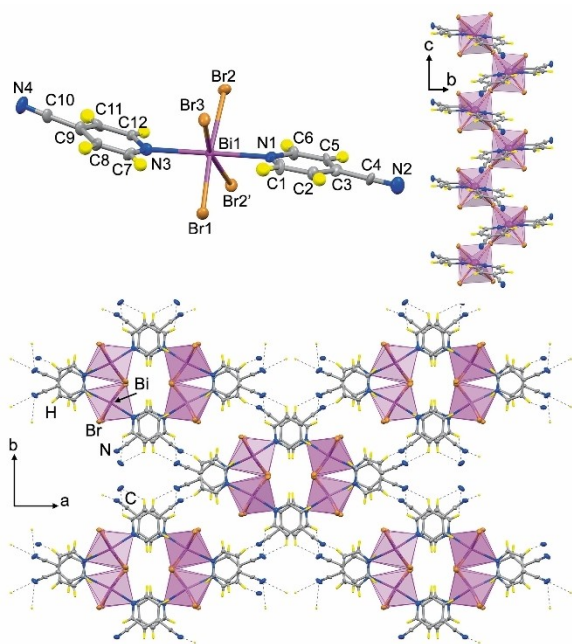
## Results and Discussion

### Crystal structures

The two coordination compounds  ${}^{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$  and  ${}^{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$  are isostructural, although they are not isotopic. The chloride CP crystallizes in the triclinic crystal

system in the space group  $P\bar{1}$ , while the respective bromide compound crystallizes in the space group  $C2/c$  in the monoclinic crystal system. Both compounds are 1D coordination polymers, for which the linkage to polymeric structures occurs exclusively through the halides and not through the organic ligands. While this linkage type is common for anionic halobismutates,<sup>[19–22]</sup> it is unusual for neutral coordination polymers. In the crystal structure of  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$ , two crystallographically independent chains are present which differ only by small (non-principal) differences in interatomic distances and angles. Both chains are parallel to the *a*-axis.

The bismuth atoms in  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$  and  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$  are located in a distorted octahedral coordination environment, formed by four halide atoms (two of which are bridging) and two N-atoms from 4-cypy ligands coordinated in *trans*-mode (Figures 1 and S1, ESI). The organic ligands in these coordination compounds act as mono-coordinating ligands connected



**Figure 1.** Top left: extended coordination of the Bi atoms of  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$ ; top right: detailed view of a zigzag chain with corner-sharing  $[\text{BiBr}_4\text{N}_2]$  octahedra depicted along  $[-100]$ ; Bottom: Crystal structure of  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$  with attractive N–H interactions (dashed lines) viewed along  $[00\bar{1}]$ . The vibrational ellipsoids represent a probability of 50% of the atoms.

**Table 1.** Comparison of the interatomic Bi–N, Bi– $X_{\text{term}}$ , and Bi– $X_{\text{brid}}$  distances in  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$  and  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$ .

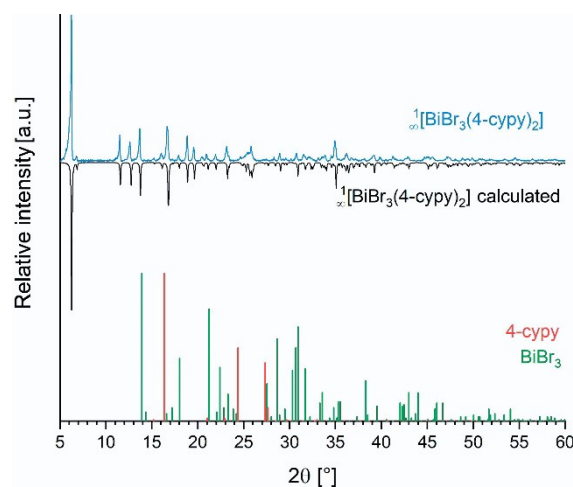
A–B, pm	${}^1_{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$ <sup>[a]</sup>	${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$
Bi–N	246.0(8), 261.7(9)	249(2), 256(2)
Bi– $X_{\text{term}}$	254.7(3), 255.2(3)	269.7(2), 272.3(2)
Bi– $X_{\text{brid}}$	287.4(3), 290.9(3)	299.9(2), 303.5(2)

<sup>[a]</sup> For comparison of the halide influence, for  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$  the average values of the corresponding interatomic distances of four Bi sites are given.

only through the pyridyl moiety, while the nitrile group is unbound, corresponding to its lower N-donor/basic character. Around  $\text{Bi}^{3+}$ ,  $\{\text{BiX}_4\text{N}_2\}$  ( $X = \text{Cl}, \text{Br}$ ) octahedra are bridged by two halide ligands via one corner each to neighboring octahedra, resulting in the formation of polymeric  $\{\text{BiX}_4\text{N}_2\}_n$  zigzag chains. The bridging results in an increase of the interatomic Bi– $X_{\text{brid}}$  distances compared to the interatomic Bi– $X_{\text{term}}$  distances (see Table 1).

The  $\{\text{BiX}_4\text{N}_2\}$  octahedra align within the zigzag chains, while the 4-cypy ligands stick out orthogonally to the chain direction. Between the 4-cypy ligands,  $\pi$ -stacking interactions are observed. The average distance between two pyridyl rings of 4-cypy ligands within a chain is 363.7 pm for  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$  and 373.8 pm for  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$ . The remaining 4-cypy ligands of two adjacent chains interlock like the links of a zipper, connecting two zigzag chains into pairs. The average distance between two pyridyl rings of 4-cypy ligands from different chains is 379.0 pm for  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$  and 390.5 pm for  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$ , which are slightly larger than the distances of two pyridyl fragments of 4-cypy ligands within a chain. The pairs of chains are connected to each other through N–H hydrogen bonding interactions between the nitrogen atoms of the free nitrile groups and hydrogen atoms of the pyridyl rings (Figure 1, dashed lines), being lower than the van-der-Waals radii (255.0(1) and 258.7(1) pm for the chloride CP, 244 and 270 pm for the bromide CP). Furthermore, both products can be obtained as crystalline bulk products with no observable side phases and no remaining reagents after reaction (see Figures 2 and S2, ESI).

The two coordination polymers  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$  and  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$  were also studied by simultaneous differential thermal analysis (DTA) and thermogravimetry (TG). The compounds show multistep thermal processes (Figures S3–S4, ESI), which start at comparably mild temperatures of 100 °C ( ${}^1_{\infty}[\text{BiCl}_3(4\text{-cypy})_2]_n$ ) and 145 °C ( ${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$ ), respectively,



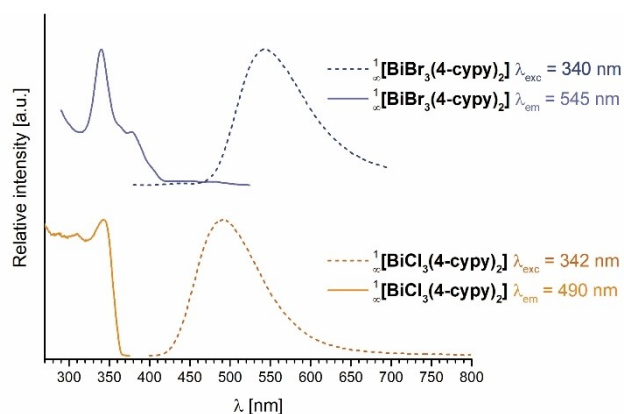
**Figure 2.** Comparison of the powder diffraction patterns of  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cypy})_2]_n$  (blue) with a simulated pattern from single-crystal structure data (black) and the reflection positions and intensities of the reagents ( $\text{BiBr}_3$ , green; 4-cypy, orange-red).

and end at about 500 °C. The low decomposition temperatures indicate a rather low stability of the halide bridges and weak bonding of the N-donors. TG data indicate a two-step mass loss with the second step starting around 300 °C. In the first step, the mass losses are 35% for  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cpy})_2]_n$  and 25% for  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$ , which can be addressed to the release of most of the organic ligands (calculated mass losses: 40% and 32%, respectively). Complete decomposition of  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cpy})_2]_n$  leads to a residual mass of 36%, while for  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$  a residual mass of only 10% is observed.

### Luminescence properties

Both compounds show luminescence upon excitation with UV light. The luminescence intensities of both,  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cpy})_2]_n$  and  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$  are low at room temperature (RT), as they show considerable thermal quenching already below RT. Therefore excitation and emission spectra were recorded at reduced temperature upon cooling with liquid nitrogen to 77 K. On cooling, thermal quenching due to molecular vibrations is greatly reduced, which results in more intense emission. However, the emission intensity of both compounds was insufficient to determine quantum yields (RT required) as well as trustworthy emission lifetimes. Therefore, despite the fact that the emission process is very likely to be phosphorescence, we cannot unambiguously state so.

Both, excitation and emission spectra of the two CPs show broad bands (see Figure 3). The maximum in the excitation spectrum of  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cpy})_2]_n$  is located at 342 nm (29,239  $\text{cm}^{-1}$ ), however the spectrum of  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$  has two maxima at 340 nm (29,411  $\text{cm}^{-1}$ ) and 378 nm (26,455  $\text{cm}^{-1}$ ). The positions of the maxima at 342 nm for  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cpy})_2]_n$  and 340 nm for  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$  are similar for both compounds studied, while they differ significantly from the absorption spectrum of 4-cpy that has one broad band located in higher energy region (218–315 nm, 31,746–45,871  $\text{cm}^{-1}$ ) (Figure S5, ESI). Several processes can be taken into account and assigned to these observations, such as metal-



**Figure 3.** Excitation (solid lines) and emission spectra (dotted lines) at 77 K of solid samples of  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cpy})_2]_n$  and  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$ .

to-ligand charge transfer (MLCT) and ligand-to-metal charge-transfer (LMCT).<sup>[2,3]</sup> Additional bands to a direct ligand excitation can be assigned to MLCT in the excitation spectra that can occur because of electron transfer to 4-cyanopyridine being a proper charge acceptor. The charge transfer (CT) in this case is attributed to the transitions from the electronic ground state being  $\text{Bi}^{3+}$ -centered and the  $\pi^*$ -centered orbitals of organic ligands. An intervalence charge transfer (IVCT) mechanism between  $\text{Bi}^{3+}/\text{Bi}^{3+}$  pairs is also possible,<sup>[16,17]</sup> but less likely in these compounds, as the  $\text{Bi}^{3+}$ -ions do not form pairs in the crystal structures. This also agrees with previous observations for the chemically related coordination polymers  ${}^1_{\infty}[\text{Bi}_2\text{X}_6(\text{L})_2]_n$  ( $\text{X} = \text{Cl}, \text{Br}; \text{L} = 1,2\text{-bis}(4\text{-pyridyl})\text{ethane}, 1,2\text{-bis}(4\text{-pyridyl})\text{ethane}, 4,4'\text{-bipyridine}$ ).<sup>[3]</sup>

Emission arises mainly because of LMCT, which is based on the delocalization of the excited state within the organic ligands and commences to the ground state being again  $\text{Bi}^{3+}$ -centered. The emission spectra of  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cpy})_2]_n$  and  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$  show only one broad emission band with its maximum at 490 nm (20,408  $\text{cm}^{-1}$ ) for  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cpy})_2]_n$  and at 545 nm (18,349  $\text{cm}^{-1}$ ) for  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$  (Figure 3). Thus, there is a remarkable energy difference between the maxima, and a shift of the emission band of about 2,060  $\text{cm}^{-1}$  accompanied by a color change of the emission from turquoise to yellow-green for the two compounds. Due to the close structural and chemical relationship between  ${}^1_{\infty}[\text{BiCl}_3(4\text{-cpy})_2]_n$  and  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$ , the differences in the excitation and emission spectra between the two compounds can be attributed to the influence of the halide anions, i.e.  $\text{Cl}^-$  and  $\text{Br}^-$ . Based on DFT-calculations for  $\alpha\text{-}{}^1_{\infty}[\text{Bi}_2\text{Cl}_6(4,4'\text{-bipy})_2]_n$ <sup>[2]</sup> a participation of the electronic states of the halide-ligands can be involved in the radiative processes. Thus, the ground state is more likely to be extended via several  $\text{Bi}^{3+}$ -ions and halide anions than to derive just from isolated  $\text{Bi}^{3+}$ -cations, influencing e.g., the excitation via MLCT processes involving the  $\pi^*$ -orbitals of the 4-cpy ligands. In addition, it can be assumed that the electronic state, from which emission occurs, can delocalized over a larger segment of the chain being responsible for the emissive ligand-to-metal charge-transfer (LMCT) processes. In contrast, calculations on  $\alpha\text{-}{}^1_{\infty}[\text{Bi}_2\text{Cl}_6(4,4'\text{-bipy})_2]_n$ <sup>[2]</sup> involve delocalized parts including several organic ligands acting as linkers. Therefore, the direction of the energetic shift may also be different, being hypochromic or bathochromic. Also, the significant difference of the halides concerning the position of luminescence band may be further explained by the more diffuse character of the heavier and larger  $\text{Br}^-$  anion compared to  $\text{Cl}^-$ . However, the origin of the additional excitation at 378 nm for  ${}^1_{\infty}[\text{BiBr}_3(4\text{-cpy})_2]_n$  remains elusive and cannot be explained by structural differences.

### Conclusions

In summary, two new luminescent 1D coordination polymers of bismuth(III) together with the potentially ambidentate pyridyl-nitrile N-donor 4-cpy were prepared from anhydrous  $\text{BiCl}_3$  and  $\text{BiBr}_3$ . The polymers were synthesized as crystalline bulk materials and as single crystals from a melt of the ligand 4-cpy.

The obtained compounds are isostructural, their polymeric chains being connected only through halide-bridges, as the donor strength of the cyano group is too weak to interlink the Bi-centers. Both studied CPs possess broad band luminescence properties caused mainly by LMCT (emission) and MLCT bands (excitation). This indicates an influence of the halide anions in the ground state, which is more significant for Br<sup>-</sup> than for Cl<sup>-</sup> and leads to a shift of the emission band to lower energy for the Br<sup>-</sup>-containing CP compared to Cl<sup>-</sup>-containing CP resulting in a color change (Cl to Br) of the emission from turquoise to yellow-green.

## Experimental Section

All experimental syntheses were carried out under inert conditions in an Ar atmosphere.

The starting materials BiCl<sub>3</sub> (ABCR, 98%, Merck, 98+%) and BiBr<sub>3</sub> (obtained by conventional method,<sup>[23]</sup> or Merck, 98+%) were purified immediately before syntheses by sublimation. Commercially available 4-cyanopyridine (*4-cppy*, Alfa Aesar, 98%) was used without further purification.

Elemental analysis was done on a fully automated elementary analyzer Vario Micro Cube and Vario EL (Elementar Analyzer Systems GmbH).

Infra-Red spectra were recorded using an attenuated total reflection (ATR) unit on a Nicolet 380 FT-IR spectrometer (Thermo). The evaluation of data was carried out using the software OMNIC 32 (V7.3.1.109, Thermo) and OriginPro 2019b (V9.6.5, OriginLab Corporation).

Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out simultaneously on a NETZSCH STA-409c in a mixed flow of Ar/N<sub>2</sub> at a heating rate of 10 K/min or 3 K/min for  $[\infty[\text{BiBr}_3(4\text{-cppy})_2]_n]$  and  $[\infty[\text{BiCl}_3(4\text{-cppy})_2]_n]$ , respectively. The software OriginPro 2019b (V9.6.5, OriginLab Corporation) was used for data analysis.

The photoluminescence properties of the compounds discussed in this work were examined on a Fluorolog 3 (Horiba Jobin Yvon GmbH) luminescence spectrometer. A 450 W xenon lamp was used as the light source. The energy of the incident radiation (excitation wavelength  $\lambda_{\text{exc}}$ ) and the energy of the detected radiation (emission wavelength  $\lambda_{\text{exc}}$ ) were varied using a double monochromator. Furthermore, the detected radiation is amplified by a photo-multiplier tube of type R928P (Horiba). All measurements were carried out using the device-specific FluorEssence software (Horiba, latest version 3.8.0.60).

Absorption spectra of 4-cyanopyridine were recorded on Cary 5000 Series UV-VIS-NIR Spectrophotometer (Agilent Technologies) equipped with the Praying Mantis (Harrick Scientific Products) diffuse reflectance accessory. The source changeover was set at 380 nm. The sample was prepared in a glovebox under Ar atmosphere and measured in an ambient chamber. A background correction was performed prior to the sample measurement. A spectrum with uncorrected absorbance was recorded with the absorbance set to 100% at 800 nm. The sample spectrum was corrected with the instrument software (Cary WinUV) by the mathematical operation  $\%R_{\text{corr}}^{\text{sample}} = \%R^{\text{sample}} / \%R^{\text{reference}}$ .

**X-ray Crystallography:** For single crystal X-Ray diffraction studies, a single crystal diffractometer AXS APEX II (Bruker) with Helios mirror and MoK $\alpha$  radiation was used. The implementation and evaluation of the data was carried out with the software AXS Apex3 Suite

(V2016.9, Bruker), while for data processing the XPREP (2014/2, Bruker) software was used. The structures were solved using the programs SHELXT.<sup>[24]</sup> SHELXT<sup>[24]</sup> was also used for the structure refinement together with the least squares method. The structures were solved and refined within the graphical user interface ShelXle.<sup>[25]</sup> Hydrogen atoms were fixed at geometrically optimized positions by using a riding model with their U<sub>iso</sub> values constrained to 1.2U<sub>eq</sub> of their pivot atoms. All other atoms were refined anisotropically. Pictures of the crystal structures were created using DIAMOND.<sup>[26]</sup> Generally, interatomic distances are of expected values.

Crystallographic data for the structures in this paper were deposited in Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2289231 ( $[\infty[\text{BiCl}_3(4\text{-cppy})_2]_n]$ ) and CCDC-2289232 ( $[\infty[\text{BiBr}_3(4\text{-cppy})_2]_n]$ ) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

**Crystal Data for  $[\infty[\text{BiCl}_3(4\text{-cppy})_2]_n]$ :** BiCl<sub>3</sub>C<sub>12</sub>H<sub>8</sub>N<sub>4</sub> (M = 523.55 g·mol<sup>-1</sup>, colorless): triclinic, space group P $\bar{1}$  (no. 2), *a* = 765.1(2) pm, *b* = 1554.3(3) pm, *c* = 2818.8(6) pm,  $\alpha$  = 74.67(3)°,  $\beta$  = 87.74(3)°,  $\gamma$  = 88.32(3)°, *V* = 3229.8(12) Å<sup>3</sup>, *Z* = 8,  $\rho_{\text{calcd.}}$  = 2.153 g·cm<sup>-3</sup>, *F*(000) = 1936.0, size of single crystal: 0.301×0.117×0.052 mm<sup>3</sup>, *T* = 100 K,  $\mu(\text{Mo-K}\alpha)$  = 11.408 mm<sup>-1</sup>. 40720 reflections observed ( $3.432^\circ \leq 2\theta \leq 52.744^\circ$ ), 13219 unique reflections ( $R_{\text{int}} = 0.0782$ ,  $R_{\text{sigma}} = 0.0968$ ), which were used in all calculations. GOF: 1.017.  $R_1 = 0.0490$  [ $I > 2\sigma_{(I)}$ ],  $wR_2 = 0.0902$  [ $I > 2\sigma_{(I)}$ ],  $R_1 = 0.0808$  (all data),  $wR_2 = 0.0994$  (all data), *S* = 0.995.

**Crystal Data for  $[\infty[\text{BiBr}_3(4\text{-cppy})_2]_n]$ :** BiBr<sub>3</sub>C<sub>12</sub>H<sub>8</sub>N<sub>4</sub> (M = 656.93 g·mol<sup>-1</sup>, light yellow): monoclinic, space group C2/c (no. 15), *a* = 2573.7(5) pm, *b* = 1682.8(3) pm, *c* = 795.9 (2) Å,  $\beta$  = 90.38(3)°, *V* = 3447.3(12) Å<sup>3</sup>, *Z* = 8,  $\rho_{\text{calcd.}}$  = 2.532 g·cm<sup>-3</sup>, *F*(000) = 2368.0, size of single crystal: 0.259×0.081×0.05 mm<sup>3</sup>, *T* = 100 K,  $\mu(\text{Mo-K}\alpha)$  = 17.178 mm<sup>-1</sup>. 12649 reflections observed ( $2.892^\circ \leq 2\theta \leq 57.148^\circ$ ), 4244 unique reflections ( $R_{\text{int}} = 0.1014$ ,  $R_{\text{sigma}} = 0.1319$ ), which were used in all calculations. GOF: 0.955.  $R_1 = 0.0526$  [ $I > 2\sigma_{(I)}$ ],  $wR_2 = 0.1012$  [ $I > 2\sigma_{(I)}$ ],  $R_1 = 0.1093$  (all data),  $wR_2 = 0.1221$  (all data), *S* = 0.955.

Powder diffraction patterns were obtained on a D8 Discover powder diffractometer with DaVinci design (Bruker), equipped with a linear Lynxx-Eye detector and a focusing Göbel mirror. The measurements were carried out in transmission geometry. CuK $\alpha$ 1 radiation was used. The software Diffrac Suite, AXS 2010–2014 (Bruker) and OriginPro 2019b (V9.6.5, OriginLab Corporation) were used to evaluate the data (Figures 2 and S4, ESI).

**Synthesis:** The two coordination polymers  $[\infty[\text{BiCl}_3(4\text{-cppy})_2]_n]$  and  $[\infty[\text{BiBr}_3(4\text{-cppy})_2]_n]$  were obtained by reactions of BiCl<sub>3</sub> or BiBr<sub>3</sub> with molten 4-cyanopyridine (*4-cppy*). For this purpose, BiCl<sub>3</sub> (197.3 mg, 625  $\mu\text{mol}$ ) or BiBr<sub>3</sub> (280.5 mg, 625  $\mu\text{mol}$ ) and *4-cppy* (195.3 mg, 1875  $\mu\text{mol}$ ) were sealed in a Duran glass ampoule and heated (rate 10 K·h<sup>-1</sup>) in a corundum resistance furnace under reduced pressure ( $p = 1.0 \cdot 10^{-3}$  mbar). Due to the low melting point of the organic ligand (79 °C),<sup>[27]</sup> the reactions can be carried out at moderate temperatures (100 °C). This temperature was maintained for 72 h before cooling to room temperature (rate 10 K·h<sup>-1</sup>). The reaction products were then transferred to double-chamber ampoule and an excess of the ligand was sublimed off at 70 °C during 48 h.  $[\infty[\text{BiCl}_3(4\text{-cppy})_2]_n]$  and  $[\infty[\text{BiBr}_3(4\text{-cppy})_2]_n]$  were formed as very fine colorless blocks and light yellow crystalline needles, respectively, which were suitable for X-ray single-crystal diffraction structure analysis. High completeness of the reaction of the Bi(III) halides to  $[\infty[\text{BiCl}_3(4\text{-cppy})_2]_n]$  and  $[\infty[\text{BiBr}_3(4\text{-cppy})_2]_n]$  and the absence of observable impurities of the starting compounds were confirmed by the

absence of reflections of the starting compounds (4-cypy, BiCl<sub>3</sub> or BiBr<sub>3</sub>) in the powder diffraction patterns (Figures 2 and S4, ESI) and by elemental analysis. Respective IR-spectra for both compounds containing all major IR active vibration bands of 4-cypy are given in (Figure S6, ESI).

$^1\infty\text{BiCl}_3(4\text{-cypy})_2\text{]}_n$ . BiCl<sub>3</sub>C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>: calcd. C 27.53, H 1.54, N 10.70%; found C 27.33, H 1.52, N 9.86%. FTIR (ATR): 3151 (w), 3095 (m), 3045 (m), 2999 (w), 2241 (w), 1604 (s), 1545 (w), 1491 (w), 1473 (w), 1456 (w), 1436 (w), 1414 (s), 1373 (w), 1361 (w), 1223 (m), 1194 (w), 1117 (w), 1059 (s), 1009 (s), 970 (w), 941 (w), 827 (s), 787 (m) cm<sup>-1</sup>.

$^1\infty\text{BiBr}_3(4\text{-cypy})_2\text{]}_n$ . BiBr<sub>3</sub>C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>: calcd. C 21.94, H 1.23, N 8.53%; found C 21.85, H 1.14, N 8.41%. FTIR (ATR): 3151 (w), 3114 (w), 3093 (m), 3041 (m), 2997 (w), 2243 (w), 1603 (s), 1547 (w), 1493 (w), 1473 (w), 1458 (w), 1437 (w), 1412 (s), 1257 (w), 1219 (m), 1194 (w), 1117 (w), 1093 (w), 1057 (s), 1007 (s), 982 (w), 966 (w), 941 (w), 872 (w), 827 (s), 787 (m) cm<sup>-1</sup>.

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## Conflict of Interest

There are no conflicts to declare.

## Data Availability Statement

The data that support the findings of this study are openly available in CCDC at <http://www.ccdc.cam.ac.uk>, reference number 2289231.

**Keywords:** Bismuth · halides · coordination polymers · luminescence · charge transfer

- [1] J.-C. Jin, Y.-P. Lin, L.-F. Lin, C. Xiao, Y. Song, N.-N. Shen, L.-K. Gong, Z.-Z. Zhang, K.-Z. Du, X.-Y. Huang, *CrystEngComm* **2021**, *23*, 3744–3752.
- [2] J. R. Sorg, T. Wehner, P. R. Matthes, R. Sure, S. Grimme, J. Heine, K. Müller-Buschbaum, *Dalton Trans.* **2018**, *47*, 7669–7681.

- [3] J. R. Sorg, T. Schneider, L. Wohlfarth, T. C. Schäfer, A. Sedykh, K. Müller-Buschbaum, *Dalton Trans.* **2020**, *49*, 4904–4913.
- [4] J. R. Sorg, K. C. Oberst, K. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **2018**, *644*, 1293–1296.
- [5] Z. Qi, H. Gao, X. Zhu, Z. Lu, X.-M. Zhang, *Inorg. Chem.* **2022**, *61*, 19483–19491.
- [6] A. C. Wibowo, S. A. Vaughn, M. D. Smith, H.-C. Zur Loye, *Inorg. Chem.* **2010**, *49*, 11001–11008.
- [7] A. K. Adcock, R. L. Ayscue, L. M. Breuer, C. P. Verwiel, A. C. Marwitz, J. A. Bertke, V. Vallet, F. Réal, K. E. Knope, *Dalton Trans.* **2020**, *49*, 11756–11771.
- [8] J.-C. Jin, Y.-P. Lin, Y.-H. Wu, L.-K. Gong, N.-N. Shen, Y. Song, W. Ma, Z.-Z. Zhang, K.-Z. Du, X.-Y. Huang, *J. Mater. Chem. C* **2021**, *9*, 1814–1821.
- [9] J.-C. Jin, N.-N. Shen, Y.-P. Lin, L.-K. Gong, H.-Y. Tong, K.-Z. Du, X.-Y. Huang, *Inorg. Chem.* **2020**, *59*, 13465–13472.
- [10] B. Wagner, N. Dehnhardt, M. Schmid, B. P. Klein, L. Ruppenthal, P. Müller, M. Zugermeier, J. M. Gottfried, S. Lippert, M.-U. Halbich, A. Rahimi-Iman, J. Heine, *J. Phys. Chem. C* **2016**, *120*, 28363–28373.
- [11] J. Heine, T. Wehner, R. Bertermann, A. Steffen, K. Müller-Buschbaum, *Inorg. Chem.* **2014**, *53*, 7197–7203.
- [12] A. K. Adcock, A. C. Marwitz, L. A. Sanz, R. Lee Ayscue, J. A. Bertke, K. E. Knope, *CrystEngComm* **2021**, *23*, 8183–8197.
- [13] R. L. Ayscue, V. Vallet, J. A. Bertke, F. Réal, K. E. Knope, *Inorg. Chem.* **2021**, *60*, 9727–9744.
- [14] M. Lê Anh, M. Kaiser, M. P. Ghimire, M. Richter, K. Koepf, M. Gruschwitz, C. Tegenkamp, T. Doert, M. Ruck, *Chem. Eur. J.* **2020**, *26*, 15549–15557.
- [15] M. Lê Anh, P. Potapov, D. Wolf, A. Lubk, B. Glatz, A. Fery, T. Doert, M. Ruck, *Chem. Eur. J.* **2021**, *27*, 794–801.
- [16] R. H. P. Awater, P. Dorenbos, *J. Lumin.* **2017**, *188*, 487–489.
- [17] P. Boutinaud, *J. Lumin.* **2018**, *197*, 228–232.
- [18] N. Dehnhardt, J.-N. Luy, M. Szabo, M. Wende, R. Tonner, J. Heine, *Chem. Commun.* **2019**, *55*, 14725–14728.
- [19] A. F. Holleman, E. Wiberg, N. Wiberg, G. Fischer, *Lehrbuch der anorganischen Chemie*, Walter De Gruyter, Berlin New York, **2007**.
- [20] L. D. Freedman, G. O. Doak, G. G. Long, T. Mahmood, C. B. Lindhal, in *Kirk-Othmer Encyclopedia of Chemical Technology* (Ed.: John Wiley & Sons, Inc), Wiley, **2003**.
- [21] S. A. Adonin, M. N. Sokolov, V. P. Fedin, *Coord. Chem. Rev.* **2016**, *312*, 1–21.
- [22] A. M. Goforth, M. A. Tershansy, M. D. Smith, L. Peterson, J. G. Kelley, W. J. I. DeBenedetti, H.-C. zur Loye, *J. Am. Chem. Soc.* **2011**, *133*, 603–612.
- [23] V. Meyer, *Justus Liebig's Ann. Chem.* **1891**, *264*, 116–129.
- [24] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.
- [25] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
- [26] W. T. Pennington, *J. Appl. Crystallogr.* **1999**, *32*, 1028–1029.
- [27] W. E. Feely, E. M. Beavers, *J. Am. Chem. Soc.* **1959**, *81*, 4004–4007.

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