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ARTICLE

Coordination polymers constructed from a tripodal phosphoryl carboxylate ligand: synthesis, structures and physical properties

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By employment of a new tripodal phosphoryl carboxylate ligand, tris(p-carboxyl-biphenyl)phosphine oxide (H₃TBPPPO), four novel coordination polymers, namely, Zn₃(TBPPPO)₂ (**1**), Cd₃(TBPPPO)₂ (**2**), Co₃(TBPPPO)₂ (**3**) and In(TBPPPO) (**4**), have been synthesized and characterized. Complexes **1**, **2** and **3** are isostructural. The crystal structure analysis reveals that complexes **1-3** consist of trinuclear metal building units, which are further bridged by the tripodal phosphine oxide carboxylate ligands to give a (4,8)-connected 2-fold interpenetrating **flu** topological net with point symbol of (4¹²·6¹²·8⁴)(4⁶)², while complex **4** possesses a 3D 4-fold interpenetrating **dia** network with point symbol of (6⁶). Luminescence measurements indicate that complexes **1**, **2** and **4** all show strong emission bands at around 378 nm in the solid state at room temperature. Furthermore, the temperature-dependent magnetic susceptibility study shows that complex **3** exhibits antiferromagnetism property.

Introduction

Coordination polymers (CPs) have attracted enormous interest due to their intriguing structural topologies,^{1, 2} and potential applications in diverse areas, such as luminescence,³⁻⁵ gas adsorption and separation,⁶⁻⁸ nonlinear optics,⁹ catalysis,^{10, 11} drug delivery,^{12, 13} proton conduction¹⁴ *etc.* CPs are made up of metal ions or metal clusters (as nodes) and organic ligands (as spacers). The rational choice of ligands plays significant role in the final framework structure and properties.^{1, 15, 16}

Among various ligands, multifunctional carboxylate organic ligands have been utilized to construct CPs with novel structures and diverse applications as functional materials. Particularly, carboxylate ligands bearing high C₃ symmetry have been intensively studied,¹⁷⁻²³ which show great advantages over those ligands with low symmetry in constructing novel CPs.

As one type of C₃ symmetry ligand, tris(p-carboxylphenyl)phosphine oxide (TPO) has received increasing attention, because the ligand not only possess three C₃ symmetrical benzoates, but also has one more coordination atom O of the P=O, which can impose great influence on the synthesized material. Based on TPO ligand, some CPs with interesting properties such as gas separation, luminescence have been designed and constructed.²⁴⁻³⁷ Inspired by the fruitful research results concerning on H₃TPO, we extend the ligand H₃TPO to tris(p-carboxyl-biphenyl)phosphine oxide(H₃TBPPPO) ligand to elaborately build new CPs. Herein, four new CPs formulated as Zn₃(TBPPPO)₂ (**1**), Cd₃(TBPPPO)₂ (**2**), Co₃(TBPPPO)₂ (**3**) and In(TBPPPO) (**4**) have been successfully constructed. The synthesis, crystal structures and physical properties of these complexes are discussed.

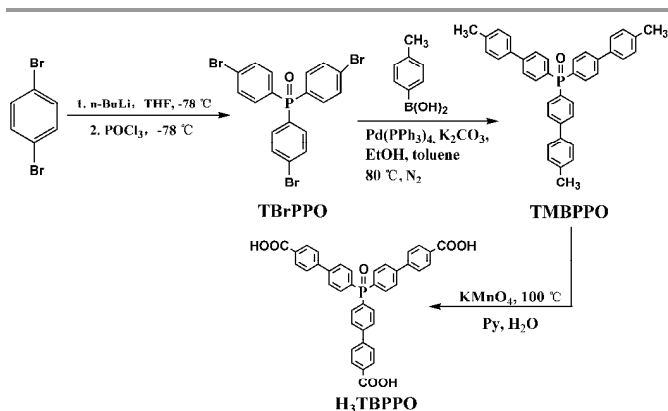
Experimental Section

Materials and General Methods

All commercially purchased chemicals are of reagent grade quality and used as received without further purification. C, H and N analyses were recorded with a Vario MICRO EL III elemental analyzer instrument. Infrared (IR) spectra were carried out on PerkinElmer Spectrum instrument with KBr pellets. Thermogravimetric analyses (TGA) were performed on an SDT Q600 thermogravimetric instrument with a heating rate of 10 °C min⁻¹ under a flowing nitrogen atmosphere. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex2 diffractometer with Cu-K_α radiation (λ = 1.54056 Å) at room temperature. The solid-state photoluminescent excitation and emission spectra were collected at room temperature on an Edinburgh FLS920 fluorescence spectrometer with an Edinburgh Xe900 xenon arc lamp as the light source. The absolute quantum yields for these samples were measured at room temperature. They were measured by using a barium sulfate coated integrating sphere (Edinburgh) as the sample chamber, which then was mounted on the fluorimeter (FLS920); at the same time, the entry and output port of the sphere were located at a 90° geometry from each other in the plane of the spectrometer. The magnetic measurement was performed with a Quantum Design SQUID MPMS-XL. The single crystal sample **3** was placed in a gel

capsule sample holder and then it was suspended in a plastic drinking straw. Magnetic susceptibility was measured at a temperature scan rate of 2 K min⁻¹ in the temperature range of 300K to 2 K at 1000 Oe.

Synthesis of H₃TBPPO ligands



Scheme 1 Strategy for the synthesis of H₃TBPPO ligand.

Synthesis of Tris(p-bromophenyl)phosphine oxide (TBrPPO)

A solution of *n*-BuLi (15% in hexane, 1.6 mol/L) (14.5 mL, 23.3 mmol) in freshly distilled THF (16 mL) was added dropwise to a solution of *p*-dibromobenzene (5g, 17.0 mmol) in freshly distilled THF (30 mL) at -78 °C. When the addition was completed, POCl₃ (0.6 mL, 7.1 mmol) in freshly distilled THF (30 mL) was charged into the mixture at -78 °C over a period of 3 h. The reaction mixture was allowed to warm to room temperature, and then stirring was continued for 12 h. Afterwards, the reaction mixture was extracted with a saturated aqueous solution of NH₄Cl (50 mL) and *n*-hexane (50 mL). The organic phase was collected and dried over Na₂SO₄ before evaporated in vacuo. The yellow residue was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (v/v = 1:6) to give compound TBrPPO as a white solid (2.2 g, 4.2 mmol, 60% yield based on POCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.65 (m, 6H), 7.50 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 133.40 (d), 132.12 (d), 131.17 (d), 130.08 (s), 127.84 (m); ³¹P NMR (162 MHz, CDCl₃) δ 27.46 (s). HR-MS (ESI): m/z calcd for TBrPPO [M + Na]⁺ 534.8068, found 534.8063. Elemental analysis (EA) for TBrPPO (%): Calcd: C, 41.98; H, 2.35. Found(%): C, 42.05; H, 2.40.

Synthesis of tris(p-methyl-biphenyl)phosphine oxide (TMBPPO)

TBrPPO (515.0 mg, 1 mmol), 4-methylbenzeneboronic acid (608.4 mg, 4.5 mmol), potassium carbonate (1658.5 mg, 12 mmol) and tetrakis(triphenylphosphine)palladium (57.8 mg, 0.05 mmol) were charged into a 250 mL schlenk flask protected by nitrogen gas. Then 20 mL degassed solvent ethanol and 20 mL degassed toluene were introduced into the system. The

mixture was allowed to reflux for 2 days at 80 °C under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was extracted with mixed solvent of water and ethyl acetate (3 × 10 mL) and the organic phase was dried with sodium sulfate. After removing the solvent using a rotary evaporator, the crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (v/v = 1:6) to give compound TMBPPO as a white solid (411.5mg, 0.75 mmol, 75% yield based on TBrPPO).

¹H NMR (400 MHz, CDCl₃) δ 7.82 (m, 6H), 7.72 (d, 6H), 7.54 (d, 6H), 7.29 (d, 9H), 2.43 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 144.68, 138.13, 137.06, 132.61, 130.37, 129.69, 127.12, 127.00, 21.15; ³¹P NMR (162 MHz, CDCl₃) δ 28.93 (s).

HR-MS (ESI): m/z calcd for TMBPPO [M + H]⁺ 549.2342, found 549.2346. Elemental analysis (EA) for TMBPPO (%): Calcd: C, 85.38; H, 6.06. Found (%): C, 86.03; H, 6.40.

Synthesis of tris(p-carboxyl-biphenyl)phosphine oxide (H₃TBPPO)

A mixture of TMBPPO (176.00 mg, 0.32 mmol), pyridine (150 mL) and H₂O (100 mL) was added to a 500 mL schlenk flask equipped with mechanical stirring device. The mixture was allowed to reflux for 2 days at 100 °C, to which potassium permanganate (330.00 mg, 2.08 mmol) was added in batches during the reflux process. After cooling to room temperature, the reaction mixture was filtered under vacuum, and then the filtrate was evaporated in vacuo. The residue was acidified with 6 M HCl to yield white precipitate of H₃TBPPO, which was filtered, washed with water, and dried under vacuum (178.8 mg, 0.28 mmol, 88% yield based on TMBPPO). ¹H NMR (400 MHz, DMSO) δ 13.09 (s, 3H), 8.06 (d, 6H), 7.96 (d, 6H), 7.88 (d, 6H), 7.82 (d, 6H); ¹³C NMR (101 MHz, DMSO) δ 167.48, 143.46, 143.03, 133.11, 132.79, 132.09, 130.92, 130.53, 127.91, 127.71; ³¹P NMR (162 MHz, DMSO) δ 25.02 (s).

HR-MS (ESI): m/z calcd for H₃TBPPO [M - H]⁻ 637.1422, found 637.1422. Elemental analysis (EA) for H₃TBPPO (%): Calcd: C, 73.35; H, 4.26. Found (%): C, 73.40; H, 4.32.

Synthesis of compounds 1-4

Synthesis of M₃(TBPPO)₂ [M=Zn (1), Cd (2) and Co (3)]

A mixture of nitrate salt [Zn(NO₃)₂·6H₂O (1), Cd(NO₃)₂·4H₂O (2), or Co(NO₃)₂·6H₂O (3)] (0.06 mmol), H₃TBPPO (6 mg, 0.01 mmol) and concentrated HNO₃ (150 μL) was added to a mixed solvent of DMA (1 mL) and distilled water (1 mL) in a 20 mL stainless glass vial. The mixture was ultrasonicated for 20 min and heated at 120 °C for 3 days, and then cooled to room temperature.

For 1: Colorless block-shaped large crystals were collected in 80% yield based on H₃TBPPO. Elemental analysis (EA) for C₇₈H₄₈O₁₄P₂Zn₃ (%): Calcd: C, 63.85; H, 3.30. Found: C, 64.20; H, 3.96. IR (KBr, cm⁻¹): 3436 (m), 3046 (m), 2774 (w), 2619 (w), 1923 (w), 1807 (w), 1706 (m), 1601 (s), 1544 (s), 1391 (s),

1275 (w), 1201 (s), 1115 (s), 991 (s), 960 (w), 839 (m), 765 (s), 698 (m), 638 (s), 571 (s), 452 (w), 360 (m).

For **2**: Colorless block-shaped crystals were collected in 70% yield based on H₃TBPPO. Elemental analysis (EA) for C₇₈H₄₈O₁₄P₂Cd₃ (%): Calcd: C, 58.25; H, 3.01. Found (%): C, 59.02; H, 3.45. IR (KBr, cm⁻¹): 3441 (w), 3031 (w), 2605 (w), 1920 (w), 1814 (w), 1705 (s), 1595 (s), 1536 (s), 1390 (s), 1267 (w), 1176 (m), 1112 (s), 1076 (w), 988 (m), 841 (m), 766 (s), 708 (m), 632 (w), 568 (s), 387 (w).

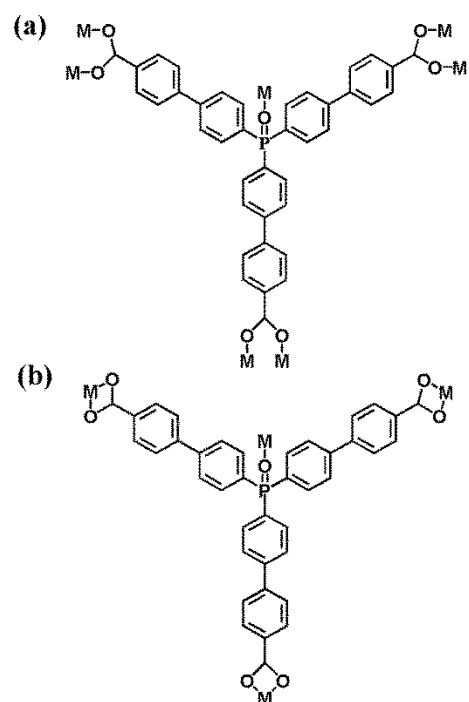
For **3**: Dark violet block crystals of **3** were collected in 70% yield based on H₃TBPPO. Elemental analysis (EA) for C₇₈H₄₈O₁₄P₂Co₃ (%): Calcd: C, 64.70; H, 3.34. Found (%): C, 63.93; H, 3.81. IR (KBr, cm⁻¹): 3437 (s), 3453 (w), 3030 (w), 1916 (w), 1797 (w), 1722 (m), 1584 (s), 1521 (s), 1404 (s), 1196 (m), 1112 (m), 986 (m), 839 (m), 762 (s), 691 (w), 566 (s), 449 (w), 419 (w), 359 (m).

Synthesis of In(TBPPO) (**4**)

A mixture of In(NO₃)₃ (18.0 mg, 0.06 mmol), H₃TBPPO (6 mg, 0.01 mmol), concentrated HNO₃ (200 μL), distilled water (1 mL) and DMA (1 mL) was sealed in a 20 mL stainless glass vial. The mixture was ultrasonicated for 20 min and heated at 100 °C for 3 days. After cooling to room temperature, colorless crystals of **4** were collected in 80% yield based on H₃TBPPO. Elemental analysis (EA) for C₃₀H₂₄O₇PIn (%): Calcd: C, 62.42; H, 3.22. Found: C, 62.41; H, 3.93. IR (KBr, cm⁻¹): 4073 (w), 3437 (w), 3052 (m), 2940 (w), 2790 (w), 2620 (w), 2488 (w), 1917 (m), 1820 (w), 1713 (s), 1605 (s), 1507 (s), 1404 (s), 1229 (s), 1162 (m), 1114 (m), 989 (s), 882 (s), 784 (w), 696 (w), 568 (s), 401 (w), 357 (m).

Single-Crystal X-ray Crystallography

Single-crystal X-ray diffraction data of compounds **1-4** were collected on a SuperNova CCD-based diffractometer equipped with graphite-monochromated Cu-K_α radiation by using the ω-scan at 100 K. All of the structures were solved by direct methods and refined on F² by full matrix least-squares using the SHELXL-97 program package. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to carbon atoms were added theoretically. Detailed final refinements and structure data of these compounds are presented in Table 1.



Scheme 2 Coordination modes of H₃TBPPO ligand.

Results and discussion

Description of the crystal structures

Crystal structures of M₃(TBPPO)₂ [M=Zn (**1**), Cd (**2**) and Co (**3**)]

Single-crystal X-ray diffraction studies reveal that complexes **1-3** are 3D frameworks, crystallizing in the cubic system, with the space group *Ia*-3. Because they are isostructural, herein, only the structure of **1** will be described in detail as a representative. Each asymmetric unit of **1** contains three crystallographically independent zinc ions and two TBPPO³⁻ ligands. The coordination mode of H₃TBPPO ligand is shown in Scheme 1a. In the structure, one of the crystallographically independent zinc ion (Zn1) is octahedrally coordinated by six oxygen atoms from six separate bridging carboxyl groups (O1, O1B, O1C, O1D, O1E, O1G); the other zinc ion (Zn2) is four coordinated by three separate bridging carboxyl groups (O2, O2B, O2D) and one oxygen atom (O3F) from the P=O of the fourth ligand (Figure 1). The three adjacent zinc centers are bridged by six carboxylate groups from six TBPPO³⁻ ligands, three between each pair, in bis-bridging fashion, leading to the construction of a trinuclear zinc cluster Zn₃(COO)₆. Considering the trinuclear Zn₃(COO)₆ building units as 8-connected nodes and the TBPPO³⁻ ligands as 4-connected nodes, the structure of **1** can be viewed as a 3D two-fold interpenetrating 4,8-connected binodal **flu** net with point symbol of (4¹².6¹².8⁴)(4⁶)² (Fig 2, Fig.3). The Zn-O bond lengths range from 1.895 to 2.075 Å, which are comparable with values of other reported zinc-oxygen donor complexes.

Table 1 Crystallographic data for 1-4

Compound	1	2	3	4
Chemical formula	C ₇₈ H ₄₈ O ₁₄ P ₂ Zn ₃	C ₇₈ H ₄₈ O ₁₄ P ₂ Cd ₃	C ₇₈ H ₄₈ O ₁₄ P ₂ Co ₃	C ₃₉ H ₂₄ O ₇ PIn
Formula Mass	1467.21	1608.30	1447.89	750.37
Crystal system	cubic	cubic	cubic	cubic
a/Å	23.3664(3)	23.7697(4)	23.3991(4)	23.5428(2)
b/Å	23.3664(3)	23.7697(4)	23.3991(4)	23.5428(2)
c/Å	23.3664(3)	23.7697(4)	23.3991(4)	23.5428(2)
α(°)	90.00	90.00	90.00	90.00
β(°)	90.00	90.00	90.00	90.00
γ(°)	90.00	90.00	90.00	90.00
Unit cell volume/ Å ³	12757.8(3)	13429.8(4)	12811.4(4)	13048.92(19)
T/K	173(2)	173(2)	173(2)	173(2)
Space group	<i>Ia</i> -3	<i>Ia</i> -3	<i>Ia</i> -3	<i>I</i> -43 <i>d</i>
Z	8	8	8	16
μ/mm ⁻¹	2.378	8.552	7.072	6.686
Data measured	5643	5746	5020	4856
Unique data	2085	2193	2093	1755
R _{int}	0.0206	0.0279	0.0487	0.0286
R ₁ ^a (I > 2σ(I))	0.0703	0.0967	0.0892	0.0578
wR(F ²) ^b (I > 2σ(I))	0.2264	0.2967	0.2700	0.1555
R ₁ ^a (all data)	0.0867	0.1314	0.1747	0.0668
wR(F ²) ^b (all data)	0.2576	0.3380	0.3250	0.1702
Goodness of fit on F ²	1.065	1.174	1.056	1.180
CCDC number	1046861	1046862	1046863	1046864

^aR₁ = Σ||F_o| - |F_c||/Σ|F_o|. ^bwR₂ = {Σ[w(F_o² - F_c²)/Σ[wF_o²]}^{1/2}.

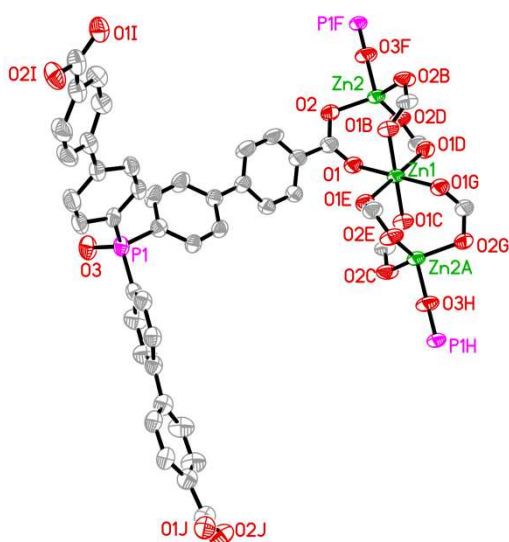


Fig. 1 The coordination environment of the central Zn (II) ions in **1** with 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry codes: A, $z - 1/2, 1 - x, y$; B, $1 - z, 1/2 + x, 3/2 - y$; C, $z - 1/2, 1 - x, y$; D, $y - 1/2, 3/2 - z, 1 - x$; E, $1 - y, z, 1/2 + x$; F, $1/2 - y, 1 - z, 1/2 + x$; G, $1/2 - x, 3/2 - y, 3/2 - z$; H, $y, 1/2 + z, 1 - x$; I, z, x, y ; J, y, z, x .

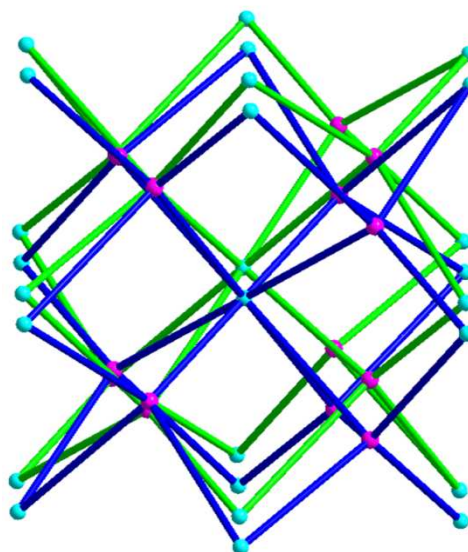


Figure 2 Two-fold interpenetrating flu net topology of **1**.

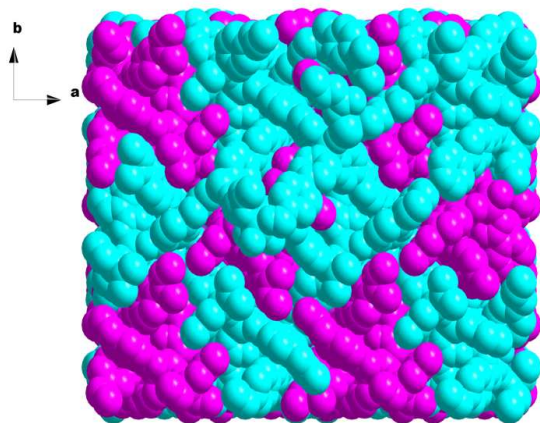


Figure 3 Two-fold interpenetrating framework of **1**.

Crystal structure of In(TBPPO) (**4**)

Single-crystal X-ray diffraction study showed that that complex **4** crystallizes in the cubic system, with the space group $I-43d$. As shown in Fig. 4, the central indium ion (In1) is coordinated by six oxygen atoms (O2, O2A, O2B, O3, O3A, O3B) from three carboxylate groups of three individual H₃TBPPO ligands, as well as one oxygen atom (O1) from the P=O of the fourth ligand, composing a monocapped octahedron geometry with In-O bond lengths ranging from 2.086 Å to 2.234 Å. The coordination mode of the carboxylic group of the H₃TBPPO ligand is shown in Scheme 1b. From the topological viewpoint, the metal centers and the ligands can both be seen as distorted tetrahedral 4-connected nodes. They connect to each other to produce an infinite 3D 4-fold interpenetrating **dia** network with point symbol of (6⁶) (Fig. 5, Fig. 6).

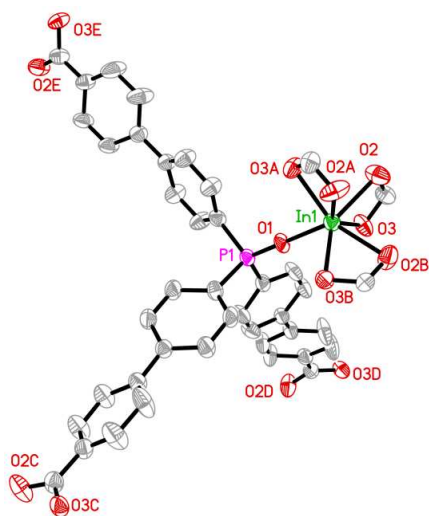


Fig. 4 The coordination environment of the central In(III) ion in **4** with 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry codes: A, z, x, y ; B, y, z, x ; C, $z - 1/2, 3/2 - x, 1 - y$; D, $1 - y, z - 1/2, 3/2 - x$; E, $3/2 - x, 1 - y, z - 1/2$.

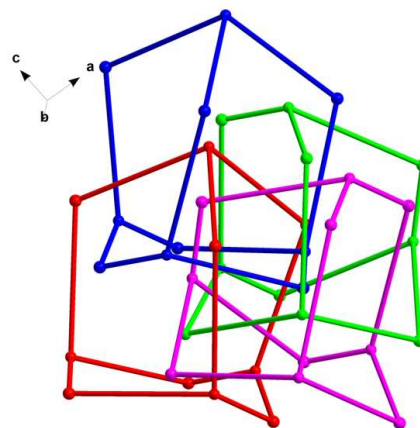


Fig. 5 4-fold interpenetrating **dia** net of **4**

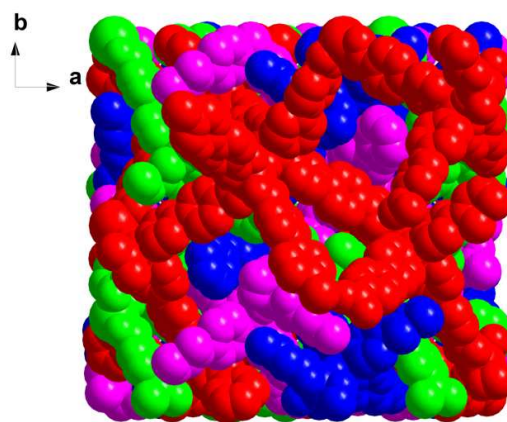


Fig. 6 4-fold interpenetrating framework of **4**

To investigate the purity and homogeneity of the bulk materials of compounds **1-4**, the as-synthesized samples of the four complexes were measured by power X-ray diffraction (PXRD) at room temperature. As shown in Fig. S8-S11, the peak positions of the experimental patterns are in good agreement with those calculated from single-crystal X-ray diffraction data, which obviously suggest the good purity and homogeneity of these samples. To explore their thermal stabilities, thermogravimetric analyses (TGA) were performed on a STQ 600 instrument. As shown in Fig. S12, compounds **1-4** show similar thermal stabilities. Because they contain no solvent molecules in the crystal lattice, significant weight losses are observed only after 400 °C, corresponding to the structural decomposition of the coordination polymers.

Photoluminescence properties

Luminescent properties of complexes constructed from d¹⁰ metal ions have gained immense attention due to their extensive applications in light-emitting devices, chemical sensors, photophysical devices, optoelectronic devices *etc.*^{38, 39} Therefore, the photoluminescence properties of complexes **1, 2** and **4** as well as the free ligand H₃TBPPO have been

investigated at room temperature in the solid state. As shown in Figure 7, the free H₃TBPPO ligand shows photoluminescence at *ca.* 398 nm when excited at 350 nm, which may be ascribed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electron transition.^{27, 40} Upon excitation at 345 nm, 340 nm, and 340 nm, the similar emission bands at *ca.* 378 nm were observed in complexes **1**, **2**, and **4**. Because the central metal ions Zn²⁺, Cd²⁺, and In³⁺ are not apt to be oxidized or reduced owing to their d¹⁰ configuration, the emissions of these complexes are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT), which can probably be attributed to the intraligand or ligand-to-ligand charge transfer.⁴¹⁻⁴⁵ Besides, compared with the free H₃TBPPO ligand, the enhancement of the emissions for **1**, **2** and **4** may be assigned to the increase of the ligand conformation rigidity owing to their coordination with metal ions, resulting in a decrease in the nonradiative decay of intraligand excited states.^{27, 46, 47} Furthermore, the small blue shift in the emission spectra maximum for compounds **1**, **2** and **4** may be associated with the perturbation caused by the metal coordination.⁴⁸ It is worthy to note that the luminescent quantum yield of compounds **1**, **2** and **4** is up to 53.31%, 49.02% and 57.31%, respectively, which is moderate compared to some reported CPs.^{28, 49} The photoluminescence properties of compounds **1**, **2** and **4** suggest that these complexes can be potential candidates for organic-inorganic hybrid luminescent materials.

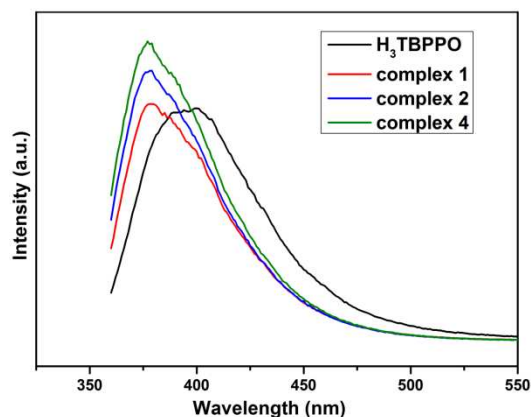


Fig. 7 The solid-state photoluminescence spectra for compounds **1**, **2**, **4** and the free H₃TBPPO ligand.

Magnetic properties

Temperature dependence of the magnetic susceptibility at 2–300 K in a field of 1000 Oe was investigated for magnetic ions containing compound **3**. The magnetic data are shown as χ_m , χ_m^{-1} , and $\chi_m T$ versus T plots in Figure 8. The experimental $\chi_m T$ product of **3** at 300 K is 8.53 cm³ mol⁻¹ K, it continuously decreases to 2.19 cm³ mol⁻¹ K as the temperature is lowered to 2 K. The temperature dependence of the reciprocal susceptibilities (χ_m^{-1}) of **3** follows the Curie-Weiss law above 50 K, giving a Weiss constant $\theta = -45.7$ K and a Curie constant $C = 9.67$ cm³ mol⁻¹ K, which indicates the presence of antiferromagnetic interactions between adjacent Co(II) ions.⁵⁰⁻⁵²

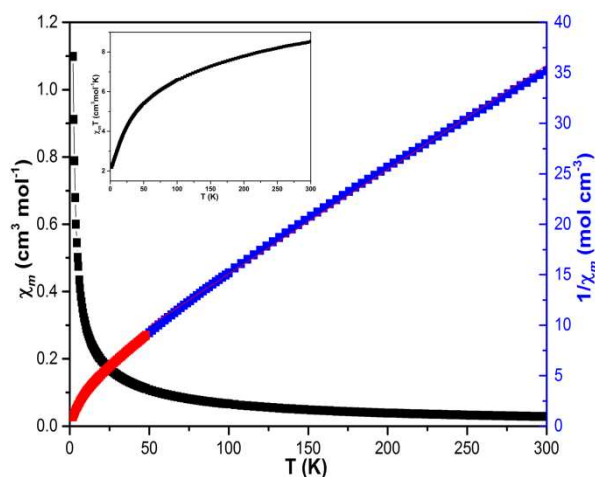


Fig. 8 Temperature dependence of the magnetic susceptibility of compound **3**. Inset: temperature dependence of $\chi_m T$ vs. T .

Conclusions

In this work, four coordination polymers formulated as Zn₃(TBPPO)₂ (**1**), Cd₃(TBPPO)₂ (**2**), Co₃(TBPPO)₂ (**3**) and In(TBPPO) (**4**) have been successfully synthesized under solvothermal conditions based on a new tripodal phosphoryl carboxylate H₃TBPPO ligand. Complexes **1**, **2** and **3** are isostructural, all of them consist of trinuclear metal building units, and show a (4, 8)-connected 2-fold interpenetrating **flu** topological net, while complex **4** possesses a 3D 4-fold interpenetrating **dia** network. Luminescence measurements indicate that complexes **1**, **2** and **4** all show strong emission bands at around 378 nm which are mainly dominated by the ligand. Remarkably, the luminescent quantum yield of compounds **1**, **2** and **4** is up to 53.31%, 49.02% and 57.31%, respectively. Besides, complex **3** exhibits antiferromagnetism property.

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Notes and references

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Coordination polymers constructed from a tripodal phosphoryl carboxylate ligand: synthesis, structures and physical properties

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Four coordination polymers based on a new tripodal phosphoryl carboxylate H₃TBPPO ligand have been constructed by solvothermal method and structurally characterized. Complexes **1**, **2** and **3** are isostructural, all of them consist of trinuclear metal building units, and show a (4, 8)-connected 2-fold interpenetrating **flu** topological net, while complex **4** possesses a 3D 4-fold interpenetrating **dia** network. The luminescent properties of complexes **1**, **2**, **4** and the magnetic property of complex **3** have been investigated. Remarkably, the luminescent quantum yield of complexes **1**, **2** and **4** is up to 53.31%, 49.02% and 57.31%, respectively.

