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A comparison of the coordination preference of Cd, Zn, Cu(II) with flexible homophthalic acid and rigid bipyridine ligands

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ABSTRACT

The mild hydrothermal reaction of Cd, Zn, or Cu(II) acetate salts with the deprotonated flexible linker homophthalic acid (H₂hmph) and the rigid molecule 4,4'-bipyridine (bpy) produced the following complexes, featured structurally by the assembly of various metal carboxylate subunits cohered further by the bpy ancillary ligand: {[Cd₂(hmph)₂(bpy)(H₂O)₂]·H₂O}_n (**1**) manifests cadmium carboxylate zigzag chain motifs, containing the alternation of a hmph-bridged Cd₂(hmph)₂ dimer and an edge-shared Cd₂N₄O₁₀ dimer, connected further by the bpy ligands to form a layered structure with a large 50-membered ring; [Zn(hmph)(bpy)]_n (**2**) processes hmph-bridged Cd₂(hmph)₂ dimer motifs inter-linked further by the bpy ligands to generate mutually embedded layered structures with square (4,4) grids; and {[Cu(hmph)(bpy)]·H₂O}_n (**3**) consists of copper carboxylate helix motifs, featuring hmph-bridged CN₂O₄ octahedra cross-linked further by the bpy ligands into a twofold-interpenetrating 3D chiral framework with a homochiral topology of a *quartz dual* net. This well-defined synthetic system was proposed to highlight the fact that organic linkers display markedly different coordination preferences at specific metal ions. In addition, the fluorescence properties of complexes **1** and **2** were rationalized in terms of the local ligand environments in the crystal structures, and magnetic properties of complex **3** are also given.

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1. Introduction

Coordination polymers have become universally popular and recognized as one of the most promising class of functional materials, the structure of which can be conceptually simplified in such a way that a metal-containing inorganic cluster acting as the nodes is linked throughout space by a polydentate organic ligand as the linker to form an organic-inorganic hybrid architecture [1]. The use of combinatorial chemistry and designed synthetic strategies can provide innovative coordination polymers materials for many advanced technological applications such as catalysis [2], hydrogen storage [3], ion exchange [4], molecular separations [5], non-linear optics [6] and photoactive materials [7]. Considering the fact that coordination polymers are built on the inherent strong coordination of the linker to a metal center, the preparation of such materials is strongly influenced by the nature of the organic ligands, which have different molecule sizes, backbone flexibility, conformational preferences, symmetry and substituent groups, and by the coordination preference of the central metal ions, in addition to some other factors such as the crystallization conditions, the metal/ligand ratio, the reaction solvent system, etc.

Rigid aromatic poly-carboxylates are among the most widely studied class of linkers in this chemistry due to their structural rigidity and multi-functional coordination capability, which leads to a rich structural diversity of coordination networks [8]. Recently. work was geared toward syntheses using flexible linkers with long-spanning carboxyl groups [9,10], whereas aromatic poly-carboxylate linkers combining rigid and flexible carboxyl groups remain somewhat of a mystery in this field [11]. Compared to rigid ligands, using flexible ones to construct coordination polymers is prone to promote the formation of some particular structures, for example, helical or looped structural motifs through which other organic linkers can penetrate, because flexible molecules can easily adjust their conformations to meet various coordination requirements of the metal ion by their "breathing" ability in the solid state and their adaptive recognition property for coexisting guests or counterions [9a]. Thus, developing systematic methodologies for synthesizing such materials by using flexible ligands can afford a good opportunity to further enrich the structures and properties of coordination polymers and to provide more understanding for the directional synthesis of target complexes. On the other hand, one of the more recent strategies is cooperatively coordinating to metal centers the combination of a carboxylate linker and a N-donor ancillary ligand, affording some novel frameworks with attractive features [12].





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Our recent work presented a well-defined synthetic system based on a homophthalic acid linker (H₂hmph) with rigid –COOH and flexible –CH₂COOH carboxyl groups to investigate the sensitivity of the structures and properties of the formed coordination polymers to various N-donor ancillary ligands with differing flexibility [13]. To extend the above study, the aim of the present paper turned to illustrate the effect of different metal centers on the reaction outcome. Our strategy is to perform a series of reactions under a similar conditions, with only the metal cations varied. Thus, the widely used organic molecule 4,4'-bipyridine (bpy) was adopted as an ancillary ligand for each synthesis, because this pillared molecule is known to be an ideal linker between metal atoms for the propagation of coordination networks, resulting in the formation of a variety of structural types.

In this contribution we present the preparation and structural characterization of $\{[Cd_2(hmph)_2(bpy)(H_2O)_2] \cdot H_2O\}_n$ (1), with a layered structure containing the larger 50 membered ring, $[Zn(hmph)(bpy)]_n$ (2), featuring a mutually embedded layered structure with square (4,4) grids, and $\{[Cu(hmph)(bpy)] \cdot H_2O\}_n$ (3), which reveals a twofold-interpenetrating 3D chiral framework with *quartz-dual* (*qzd*) topology. In addition to highlighting their crystal chemistry, we also provide some insight into the influence of the local ligand environments in the crystal structures upon the fluorescence properties of complexes 1 and 2, and magnetic properties of complex 3 are also given. It is shown that the structures and physical properties of all these complexes are strikingly sensitive to the nature of the metal center.

2. Experimental

2.1. Materials and physical measurements

All commercially available solvents and reagents for the syntheses were of reagent grade and were used without further purification. Elemental analysis for C, H and N were performed on a Vario EL III elemental analyzer. Infrared spectra (IR) were obtained from sample powders pelletized with KBr on an Avatar(tm) 360 E.S.P.IR spectrophotometer over the range 4000–400 cm⁻¹. The luminescent spectra were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer with a xenon arc lamp as the light source. Variable-temperature magnetic susceptibilities were measured using a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. Syntheses of the complexes

Complexes 1-3 were hydrothermally synthesized by the reaction of the metal (Cd, Zn or Cu) acetate, H₂hmph ligand and bpy molecule. Typically, the metal acetate hydrate (0.10 mmol, 0.0266 g for Cd(OAc)₂·2H₂O, 0.10 mmol, 0.0219 g for Zn(OAc)₂· $2H_2O$ or 0.10 mmol, 0.0199 g for $Cu(OAc)_2 \cdot H_2O$), H_2hmph (0.10 mmol, 0.0180 g) and bpy (0.10 mmol, 0.0156 g) were placed into deionized water (8 mL) in a 25 mL Teflon-lined stainless steel vessel. Subsequently, 0.5 M NaOH solution (0.15 mmol) was added while constantly stirring. The vessel was then sealed and heated at 120 °C for 4 days under autogenous pressure, whereupon it was cooled slowly to room temperature. The resulting crystals were isolated after washing with distilled water, ethanol and acetone, and were then allowed to dry in air. { $[Cd_2(hmph)_2(bpy)(H_2O)_2] \cdot H_2O_n$ (1): Yield (based on Cd): 45%. Anal. Calc. for C₂₈H₂₀Cd₂N₂O₁₁: C, 42.83; H, 2.57; N, 3.57. Found: C, 42.67; H, 2.69; N, 3.51%. Selected IR (KBr, cm⁻¹): 3413(s, br), 1602(vs), 1548(vs), 1532(vs), 1488(s), 1460(s), 1413(vs), 1384(vs), 1219(m), 1065(m), 813(m), 807(s), 733(s), 633(s), 507(w). $[Zn(hmph)(bpy)]_n$ (**2**): Yield (based on Zn):

63%. Anal. Calc. for $C_{19}H_{14}N_2O_4Zn: C, 57.38; H, 3.55; N, 7.04.$ Found: C, 57.33; H, 3.71; N, 7.09%. Selected IR (KBr, cm⁻¹): 3456(w, br), 1611(vs), 1603(vs), 1580(s), 1526(s), 1499(s), 1451(s), 1422(vs), 1378(vs), 1271(m), 1224(m), 1146(m), 1081(s), 1049(m), 827(s), 741(m), 714(m), 645(s), 558(m), 502(w). {[Cu(hmph)(bpy)]·H₂O}_n (**3**): Yield (based on Cu): 57%. Anal. Calc. for $C_{19}H_{16}CuN_2O_5$: C, 54.87; H, 3.88; N, 6.74. Found: C, 54.83; H, 3.94; N, 6.81%. Selected IR (KBr, cm⁻¹): 3402(s, br), 1605(vs), 1587(vs), 1526(vs), 1492(s), 1478(s), 1380(vs), 1172(m), 1016(s), 857(m), 760(s), 726(s), 701(s), 638(m), 620(m), 602(w).

2.3. X-ray crystallography

The crystallographic data collections for complexes 1-3 were carried out on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo K α radiation $(\lambda = 0.71073 \text{ Å})$ by using the ϕ/ω scan technique at room temperature. Absorption corrections were based on symmetry equivalent reflections using the sadabs program [14]. The structures were solved by direct methods followed by successive difference Fourier syntheses, and a full-matrix least-squares refinement on F^2 was carried out using the SHELX 97 program package [15] with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined isotropically with a riding model, except for those bound to water molecules of crystallization in 1 and 3 which were assigned using a Fourier map with common isotropic displacement factors and were included in the final refinement by use of geometrical restraints. Relevant crystallographic data for **1–3** are listed in Table 1.

3. Results and discussion

3.1. Synthesis and IR spectra

Complexes 1-3 were prepared by following almost uniform hydrothermal procedures, including various synthetic parameters, except using different metal (Cd, Zn or Cu(II)) acetate salts for each run. In each synthetic process, NaOH was added as a mineralizer. Since the only difference in these syntheses is that of different metal centers, it is clear that the nature of the metal plays a key role in controlling the assembly of the complexes. The IR spectral data show features attributable to the carboxylate stretching vibrations of the complexes. The asymmetric stretching and the symmetric stretching bands for the carboxyl groups are in the range 1488-1602 and 1384–1460 cm⁻¹ for **1**, 1526–1611 and 1377–1499 cm⁻¹ for **2**, and 1524–1605 and 1380–1492 cm^{-1} for **3**, respectively. The strong broad band at about 3400 cm⁻¹ corresponds to the vibration of water in the complexes 1 and 3. The absence of bands in the range 1760–1630 \mbox{cm}^{-1} indicates the complete deprotonation of the H₂hmph ligand, which is also evidenced by the results of the structure analyses. The various coordination modes of H₂hmph observed in complexes 1-3 are shown in Scheme 1.

3.2. Structural description of $\{ [Cd_2(hmph)_2(bpy)(H_2O)_2] \cdot H_2O \}_n$ (1)

Single-crystal X-ray analysis revealed a layered structure for **1** with a large 50 membered ring. The asymmetric unit contains two crystallographically distinct Cd(II) cations, two completely deprotonated hmph anions, one bpy molecule, two coordinated water molecules and one guest water molecule, as shown in Fig. 1a.

The two Cd centers display a relatively rare combination of coordination geometries: the Cd1 atom is heptacoordinated with a distorted CdN_2O_5 pentagonal bipyramidal coordination sphere, which is defined by two oxygen atoms from the $-COO^-$ and

Table 1		
Crystal and structu	re refinement data	for complexes 1-3.

	1	2	3
Empirical formula	$C_{28}H_{20}Cd_2N_2O_{11}$	$C_{19}H_{14}N_2O_4Zn$	$C_{19}H_{16}CuN_2O_5$
Formula weight	785.26	399.69	415.88
Crystal system	monoclinic	monoclinic	hexagonal
Space group	C2/c	P2 ₁ /c	P61
a (Å)	28.054(2)	8.419(5)	11.1755(8)
b (Å)	11.8098(10)	20.234(11)	11.1755(8)
<i>c</i> (Å)	16.9995(14)	10.666(6)	24.825(3)
α (°)	90	90	90
β (°)	96.1840(10)	103.340(7)	90
γ (°)	90	90	120
$V(Å^3)$	5599.3(8)	1767.9(17)	2685.1(4)
Ζ	8	4	6
$D_{\text{calc}} (\text{g cm}^{-3})$	1.863	1.502	1.543
$\mu (\mathrm{mm}^{-1})$	1.585	1.416	1.254
F(0 0 0)	3088	816	1278
Crystal size (mm)	$0.42\times0.35\times0.31$	$0.47 \times 0.15 \times 0.10$	$0.33 \times 0.19 \times 0.08$
θ Range (°)	2.41-25.49	2.21-25.50	2.26-25.49
Reflections collected/unique	17933/5205, [<i>R</i> _{int} = 0.0130]	$13145/3292 [R_{int} = 0.1106]$	13489/2992 [R _{int} = 0.0686]
Completeness	99.7%	99.9%	99.9%
Data/restraints/parameters	5205/0/388	3292/0/235	3891/3/245
Goodness-of-fit	1.065	0.992	1.016
Absolute structure parameter	none	none	0.185(18)
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0200, wR_2 = 0.0577$	$R_1 = 0.0631, wR_2 = 0.1232$	$R_1 = 0.0437$, $wR_2 = 0.0740$
R indices (all data)	$R_1 = 0.0217$, $wR_2 = 0.0587$	$R_1 = 0.1381, wR_2 = 0.1454$	$R_1 = 0.0776$, $wR_2 = 0.0842$
Largest differences in peak and hole (e $\mbox{\AA}^{-3})$	0.725 and -0.307	0.676 and -0.523	0.270 and -0.258

^A $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$; $wR_2 = \{\Sigma[w(|F_0|^2 - |F_c|^2)^2]/\Sigma[w(|F_0|^2)^2]\}^{12}$.



Scheme 1. Coordination modes of H₂hmph observed in complexes 1-3.

 $-CH_2COO^-$ groups of one hmph anion, two oxygen atoms belonging to one chelating didentate $-CH_2COO^-$ group of the symmetryrelated hmph moiety and one water molecule coordinate to the cadmium center in the equatorial plane, with two nitrogen atoms from two bpy ligands located at the axial positions of the coordination sphere; while the Cd2 atom is octahedrally coordinated by four oxygen atoms belonging to chelating didentate $-COO^-$ and $-CH_2COO^-$ groups of two symmetry-related hmph moieties, and the remaining two oxygen atoms belonging to the $-COO^-$ group of another hmph anion and a coordinated water molecule. The Cd–O distances range from 2.1836(19) to 2.4946(18) Å, and the Cd–N distances are 2.3428(18) and 2.3448(18) Å.

Two categories of cadmium-based dimers as the fundamental building motifs are observed in complex **1**. One dimer is an edge-shared Cd(1)N₂O₅ pentagonal bipyramid. The Cd···Cd separation of 4.0795(4) Å does not indicate any significant direct interaction between the metal atoms due to the coordination geometry of pen-

tagonal bipyramid with a larger size. Another dimer concerns two Cd(2)O₆ octahedra bridged by a pair of hmph anions via a μ_1 - η^1 : η^1 chelating coordination mode (Scheme 1a). The larger Cd...Cd separation of 5.8370(4) Å is constrained by the bridging geometry of the hmph groups. The two types of dimers are linked alternatively by another type of hmph anion to form cadmium carboxylate zigzag chains, wherein the rigid -COOH group of the hmph anion adopts a μ_2 - η^1 : η^1 bridging coordination mode to link the two different type of dimers, while the flexible –CH₂COO⁻ group grafts to the edge-shared dimer by a μ_2 - η^1 : η^2 coordination mode (Scheme 1b). The edge-shared dimers in adjacent zigzag chains are further linked by bpy ligands to form a layered structure with the large 50 membered ring, as shown in Fig. 1b. In each layer, there exists weaker π - π interactions between the phenyl ring and pyridine ring, with a centroid-centroid distance ranging from 4.104 to 4.564 Å, and a dihedral angle range from 10.113° to 34.663°; all the pyridine rings are almost paralleled to each other, with a dihedral angle range from 0.260° to 8.572°, and centroid-centroid distance range from 4.048 to 4.414 Å.

The adjacent layers are stacked in an –ABAB– sequence and are entirely cohered together by relatively weak van der Waals interactions to form a 3D supramolecular network (Fig. S1); no significant π – π interaction is observed between adjacent layers (phenyl–phenyl distance = 6.331 Å).

3.3. Structural description of $[Zn(hmph)(bpy)]_n$ (2)

Complex **2** contains mutually embedded layered structures. The asymmetric unit contains one crystallographically distinct Zn(II) cation, one completely deprotonated hmph anion and one bpy molecule, as shown in Fig. 2a. The Zn atom is tetrahedrally coordinated by two N atoms belonging to two symmetry related bpy molecules, with Zn–N bond lengths of 2.036(5) and 2.044(5) Å, and by two O atoms belonging respectively to the rigid –COOH group and flexible –CH₂COO⁻ group of two symmetry-related hmph anions, with a μ_1 - η^1 monodentate coordination mode (Scheme 1c). All the Zn–O bond separations are in the range 1.937(4)–1.945(4) Å.



Fig. 1. (a) ORTEP plot of the asymmetric unit showing the local coordination environments of the Cd atoms in complex 1, with the symmetry related part drawn as open circles. Thermal ellipsoids are given at 30% probability. All the H atoms and an isolated water molecule are omitted for clarity. Symmetry codes: A = 0.5 - x, -0.5 - y, 1 - z; B = -x, y, 0.5 - z; C = x, -1 + y, z. (b) View of a layer extended by the byp ligands. CdO₆, grey, octahedra; CdN₂O₅, white, pentagonal bipyramids.

The fundamental building unit of **2** can be considered as a hmph anion-bridged Zn dimer with a Zn \cdots Zn distance of 4.4001(20) Å. The adjacent dimers are inter-linked by bpy ligands along two different directions to generate a square (4,4) grid layer, with hmph anions above and below the layer as dangling lateral arms. Each layer contains a large 52 membered ring, as shown in Fig. 2b.

Individual layers stack together in an –ABCABC– motif, with the dangling lateral arms in each layer deeply penetrating into the 52 membered rings of two adjacent layers (i.e., the 52 membered ring pores visible in Fig. 2b are, in fact, entirely occupied by the dangling lateral arms of two additional adjacent layers), giving a dense structure without any significant overall porosity. As a result, each phenyl ring is almost parallel to a pyridine ring in the adjacent layer, with a dihedral angle of 15.018° and a centroid–centroid distance of 3.826 Å. Thus there exists strong π – π interactions between these phenyl and pyridine rings to stabilize the 3D supramolecular architecture of **2** (Fig. 2c).

3.4. Structural description of ${[Cu(hmph)(bpy)] \cdot H_2O_n(3)}$

Complex **3** crystallizes in the hexagonal chiral space group $P6_1$ and reveals a remarkable extended twofold-interpenetrating 3D chiral framework. The asymmetric unit contains one crystallographically distinct Cu(II) atom, one completely deprotonated



Fig. 2. (a) ORTEP plot of the asymmetric unit showing the local coordination environments of Zn atoms in complex **2**, with the symmetry related part drawn as open circles. Thermal ellipsoids are given at 30% probability. All the H atoms are omitted for clarity. Symmetry codes: A = -x, 1 - y, 2 - z; B = -1 + x, 0.5 - y, 0.5 + z. (b) View of the layered structure in **2**. ZnO₂N₂, grey, tetrahedra. (c) View of the 3D packing of layers showing three adjacent layers (grey, black and grey).

hmph anion, one bpy molecule and one coordination water, as shown in Fig. 3a. The Cu atom is six-coordinated with a distorted CuN₂O₄ octahedral coordination sphere, which is defined by two oxygen atoms belonging to one $\mu_1-\eta^1:\eta^1$ chelating didentate – COO⁻ group of one hmph anion (Scheme 1d), two oxygen atoms belonging to one $\mu_1-\eta^1$ monodentate –CH₂COO⁻ group of the symmetry-related hmph moiety and one water molecule in the equatorial plane, with two nitrogen atoms from two bpy ligands located at the axial positions of the coordination sphere. The Cu–N bond lengths are in the range 2.042(3)–2.045(3) Å, and the Cu–O bond distances are in the range 1.950(3)–2.510(3) Å.

The Cu atoms are connected by μ_2 -bridging hmph anions to generate some helixes with homochirality propagating along the *c*-direction (Fig. 3b). The homochiral helixes are further cross-linked by bpy molecules affording a 3D chiral network with large



Fig. 3. (a) ORTEP plot of the asymmetric unit showing the local coordination environments of the Cu cations in complex **3**, with the symmetry related part drawn as open circles. Thermal ellipsoids are given at 30% probability. All the H atoms are omitted for clarity. Symmetry codes: A = -y, -2 + x - y, 0.3333 + z; B = x, -1 + y, z. (b) View of a helix motif running along the [0 0 1] direction. CuN₂O₄, hatched octahedra. (c) View of one set of two interpenetrating networks showing large propeller-like channels. CuN₂O₄, hatched octahedra. (d) Description of the helical tube in detail. Light grey, deep grey and black representing the three strands of the chiral-stranded helix; black, bpy ligands. (e) View of the 3D packing structure, showing twofold-interpenetrating networks (grey and black).

propeller-like channel pores (Fig. 3c). In fact, each channel is enclosed by three homochiral helixes cohered together by bpy molecules between them to form a helical tubular (Fig. 3d). Unfortunately, these large channels allows each net to be penetrated by another independent net (Fig. 3e), resulting in a dense structure without any significant overall porosity, that is two interpenetrating chiral nets coexist within the 3D chiral framework. Topological analysis reveals that the framework of **3** represents a commonly observed uninodal 4-connected net with a quartz-dual (qzd) topology (Fig. S2), featuring two chiral interpenetrating nets of quartz topology, which can be characterized by a short vertex symbol (7⁵·9) with each hmph and bpy ligand as 2-connected nodes and each Cu center as a 4-connected node. Moreover, in the overall crystal structure, each pyridine ring in one *quartz* net is almost paralleled to a pyridine ring in another quartz net with a dihedral angle of 8.314° and a centroid-centroid distance range of 4.586-6.212 Å. Thus there exist significantly weak π - π interactions between adjacent pyridine rings belonging to the two interpenetrating quartz nets that stabilize the entire 3D supramolecular framework of 3.

From the above structural results, it is demonstrated that the structures of all these complexes are strongly dependent on the nature of metal cations. The Cd(II) atoms in **1** exhibit octahedral and pentagonal bipyramidal coordination environments affording a layered structure, which are consistent with the tendency of Cd(II) to have a high coordination number, the Zn(II) centers in **2** have common tetrahedral coordination geometries producing mutually embedded layered coordination networks, whereas the Cu(II) cations display octahedral configurations, forming a 3D chiral framework with a *quartz-dual (qzd)* topology in complex **3**.

3.5. Photoluminescent properties of 1 and 2

The solid-state electronic emission spectra of compounds **1** and **2** are shown in Fig. S3. It can be seen that complex **1** has a strong emission with a maximum at 430 nm ($\lambda_{ex} = 354$ nm), while **2** exhibits a rather weak emission with a maximum at 392 nm ($\lambda_{ex} = 342$ nm). To more thoroughly understand the nature of the emission band, we also investigated the luminescence of the free powdered H₂hmph and bpy ligands. The H₂hmph ligand displays a strong fluorescence emission with a maximum at 452 nm ($\lambda_{ex} = 390$ nm), and a very weak photoluminescence emission is observed for the bpy molecule (Fig. S3).

It is a great challenge to understand the luminescence spectra of the cooperatively coordinated complexes mixing two types of linkers due to their unpredictable luminescence features. Fluorescence emission of both complexes can be tentatively attributed to the intraligand π – π * or n– π * transition [16] originating from different chromophores in the crystal structures. The strong emission of complex **1** is assigned to the hmph-based intraligand fluorescence emission, since this ligand also has a similar emission characteristic, and the rather weak emission of **2** has a total spectrum characteristic similar to that of the free powdered bpy ligand.

We consider that the different fluorescence emissions between 1 and 2 are mainly associated with the interchromophore interactions observed in the crystal structures, in addition to a small contribution from other uncertain factors, such as deprotonation of the ligands, inorganic architecture influences and crystallite size effects, etc. The neighbor distances between ring centroids and the dihedral angle between ring planes are 4.104-4.564 Å, 10.113-34.663° (for 1, between a phenyl ring and a pyridine ring in an individual layer), 4.048-4.414 Å, 0.260-8.572° (for 1, between paired pyridine rings in an individual layer) and 3.826 Å. 15.018° (for **2**, between phenyl ring and pyridine ring in adjacent layers). The longer cofacial chromophore distances in 1 lead to its fluorescence being similar to the free H₂hmph ligand, but with stronger emission. The intense interchromophore interactions in 2 may result in the rearrangement of energy levels, thus making the highest occupied molecular orbitals (HOMOs) and the lower unoccupied molecular orbitals (LUMOs) probably associated with the π and

 π^* orbitals from the bpy molecules [17]. This may be the origin why the fluorescence spectrum of **2** is similar to that of the free bpy molecule, with a weak emission. Certainly, some theoretical calculations on the experimental geometries are expected to further support the assignment of these emissions. Furthermore, the enhanced rigidity on the ligand moieties upon metal coordination in both complexes is responsible for the strength in fluorescence emission intensity of the linker, resulting from the reduced efficiency of non-radiative pathways [18]. Thus, the high luminescence efficiency indicates that **1** is a good candidate for luminescent materials.

3.6. Magnetic properties of 3

The variable-temperature magnetic susceptibility of **3** has been measured from 2 to 300 K in a 2000 Oe applied field to investigate the spin communication between the Cu(II) cations. As illustrated in Fig. S4, the $\chi_m T$ value of 0.372 cm³ K mol⁻¹ at 300 K is basically in accordance with the spin-only value of 0.375 cm³ K mol⁻¹ expected for one uncoupled Cu(II) ion with S = 1/2. Upon cooling, the $\chi_m T$ product remains almost constant until 50 K, and subsequently decreases rapidly to 0.295 cm³ K mol⁻¹ at 2 K. Such behavior can be referred to the presence of an extremely weak antiferromagnetic exchange behavior between the neighboring Cu(II) ions, which allowed the magnetism to obey the Curie–Weiss law $\chi_m = C/(T - \theta)$ over the full temperature range, giving a Curie constant C = 0.37 cm³ K mol⁻¹ and a Weiss constant $\theta = -0.56$ K.

As is shown in the crystallographic part, the 3D framework of complex **3** is made up of isolated Cu(II) entities connected by the ligand hmph to afford carboxylate helix motifs, with the bpy molecules acting as bridges between the interchains. Until now, no appropriate theory model has been established to determine the magnetic coupling constant between metal ions for a 3D polymeric framework. In order to evaluate the magnetic interactions in **3**, we expect that the magnetic pathways between the neighboring Cu(II) ions are through an intrachain exchange mode. Thus, the magnetic susceptibility of the complex has been fitted by an isotropic antiferromagnetic chain model of S = 1/2 spin. The following Eq. (1) is induced from the Hamiltonian [19]

$$\begin{aligned} \hat{H} &= -J \sum_{i=1}^{i=n-1} S_i S_{i+1} \\ \chi'_m &= \frac{Ng^2 \beta^2}{kT} \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \\ x &= \frac{|J|}{kT} \end{aligned}$$
(1)

where *J* is the exchange coupling parameter describing the magnetic interaction between any two nearest neighbor S = 1/2 spins. Other parameters have their usual meaning.

Due to further assembly of the carboxylate chains into a 3D framework, the fit function can be modified to include interchain coupling. The magnetic interactions through the bpy molecules were treated as a molecular field approximation. The total magnetic susceptibility is:

$$\chi_m = \frac{\chi'_m}{1 - \frac{2zj'}{Ng^2 \beta^2} \chi'_m} \tag{2}$$

where zJ' is the interchain exchange coupling constant. The leastsquares analysis of the magnetic data gives the best fit values, listed as follows: $J = -0.62 \text{ cm}^{-1}$, g = 2.00, $zJ' = 4.75 \times 10^{-2}$ and $R = 3.13 \times 10^{-5}$ ($R = \Sigma[(\chi_m T)_{exp} - (\chi_m T)_{calc}]^2 / \Sigma[(\chi_m T)_{exp}]^2$). The Jparameter of the complex is rather low, further indicating a weakly antiferromagnetic exchange coupling. Obvious, this is due to the long Cu···Cu separation and the complicated magnetic pathway by the ligand hmph.

4. Conclusions

Similar mild hydrothermal methods produce three metal (II) complexes, cooperatively coordinated by the flexible hmph anion and rigid bpy molecule. In these polymers, the metal centers adopt various coordination geometries cohered by hmph anions to form diversified metal carboxylate motifs manifesting a marked structural dependence on the nature of the metal ion. Complex 1 contains a cadmium carboxylate zigzag chain featuring alternatively edge-shared Cd pentagonal bipyramids and hmph-bridged dinuclear Cd octahedra, complex 2 possesses hmph-bridged dinuclear Zn tetrahedra, and complex **3** is composed of a copper carboxylate helix featuring hmph-bridged mononuclear Cu octahedra. In addition, complexes 1 and 2 exhibit intraligand fluorescence emissions originating from different chromophores, which can be rationalized in terms of the local ligand environments in the crystal structures, and complex 3 displays an extremely weak antiferromagnetic interaction between the Cu(II) ions due to the long Cu ··· Cu separation in its structure. This work demonstrates the continued utility of the nature of metal ion in determining accessible coordination polymer structures, and will expand the coordination chemistry of benzene carboxylate ligands. Further systematic studies for the design and synthesis such crystalline materials with H₂hmph and other ancillary ligands are underway in our laboratory.

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Appendix A. Supplementary data

CCDC 804745, 804746 and 804747 contains the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2011.02.053.

References

- (a) A.F. Wells, Three Dimensional Nets and Polyhedra, Wiley, New York, 1977.;
 (b) J.J. Perry IV, J.A. Perman, M.J. Zaworotko, Chem. Soc. Rev. 38 (2009) 1400;
 - (c) B.F. Hoskins, R. Robson, J. Am. Chem. Soc. 111 (1989) 5962;
 - (d) S.R. Batten, R. Robson, Angew. Chem., Int. Ed. 37 (1998) 1460;
 - (e) B.F. Hoskins, R. Robson, J. Am. Chem. Soc. 112 (1990) 1546;
 - (f) R. Robson, J. Chem. Soc., Dalton Trans. (2000) 3735;
 - (g) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Science 295 (2002) 469;
- (h) O.M. Yaghi, M. O'Keeffe, M. Kanatzidis, J. Solid State Chem. 152 (2000) 1. [2] (a) S.J. Lee, W. Lin, Acc. Chem. Res. 41 (2008) 521;
 - (b) S. Horike, M. Dincă, K. Tamaki, J.R. Long, J. Am. Chem. Soc. 130 (2008) 5854;
 (c) C.D. Wu, W. Lin, Angew. Chem., Int. Ed. 46 (2007) 1075;
- (d) J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, Nature 404 (2000) 982;
 - (e) J.Y. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Chem. Soc. Rev. 38 (2009) 1450;
 - (f) L. Ma, C. Abney, W. Lin, Chem. Soc. Rev. 38 (2009) 1248;
 - (g) T. Uemara, N. Yanai, S. Kitagawa, Chem. Soc. Rev. 38 (2009) 1228.
- [3] (a) S.S. Han, J.L. Mendoza-Cortés, W.A. Goddard III, Chem. Soc. Rev. 38 (2009) 1460;
- (b) L.J. Murray, M. Dincă, J.R. Long, Chem. Soc. Rev. 38 (2009) 1294.
- [4] (a) O.M. Yaghi, H. Li, J. Am. Chem. Soc. 118 (1996) 295;
 (b) W.-G. Lu, L. Jiang, X.-L. Feng, T.-B. Lu, Inorg. Chem. 48 (2009) 6997;
 (c) Q.-R. Fang, G.-S. Zhu, M. Xue, J.-Y. Sun, F.-X. Sun, S.-L. Qiu, J. Chem. Soc., Dalton Trans. (2006) 2399;

(d) X.-M. Zhang, M.-L. Tong, H.K. Lee, X.-M. Chen, J. Solid State Chem. 160 (2001) 118;

- (e) O.M. Yaghi, H. Li, T.L. Groy, Inorg. Chem. 36 (1997) 4292.
- [5] (a) J.R. Li, R.J. Kuppler, H.C. Zhou, Chem. Soc. Rev. 38 (2009) 1477;

(b) J. Zhang, T. Wu, C. Zhou, S. Chen, P. Feng, X. Bu, Angew. Chem., Int. Ed. 48 (2009) 2542;

(c) M.H. Alkordi, J.A. Brant, L. Wojtas, V.Ch. Kravtsov, A.J. Cairns, M. Eddaoudi, J. Am. Chem. Soc. 131 (2009) 17753;

(d) K. Li, D.H. Olson, J. Seidel, T.J. Emge, H. Gong, H. Zeng, J. Li, J. Am. Chem. Soc. 131 (2009) 10368;

- (e) H. Tagami, S. Uchida, N. Mizuno, Angew. Chem., Int. Ed. 48 (2009) 6160.
 [6] (a) S.-Q. Zang, Y. Su, Y.-Z. Li, Z.-P. Ni, Q.-J. Meng, Inorg. Chem. 45 (2006) 174;
- (b) L. Wang, M. Yang, G. Li, Z. Shi, S. Feng, Inorg. Chem. 45 (2006) 2474;
 (c) S. Wang, Y. Hou, E. Wang, Y. Li, L. Xu, J. Peng, S. Liu, C. Hu, New J. Chem. 27 (2003) 1144.
- [7] (a) M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk, Chem. Soc. Rev. 38 (2009) 1330;

(b) X.L. Zheng, Y. Liu, M. Pan, X.Q. Lü, J.Y. Zhang, C.Y. Zhao, Y.X. Tong, C.Y. Su, Angew. Chem., Int. Ed. 46 (2007) 7399;

(c) C.A. Bauer, T.V. Timofeeva, T.B. Settersten, B.D. Patterson, V.H. Liu, B.A. Simmons, M.D. Allendorf, J. Am. Chem. Soc. 129 (2007) 7136.

[8] (a) J.J. Perry, J.A. Perman, M.J. Zaworotko, Chem. Soc. Rev. 38 (2009) 1353;
 (b) H. Li, C.E. Davis, T.L. Groy, D.G. Kelley, O.M. Yaghi, J. Am. Chem. Soc. 120 (1998) 2186:

(c) N. Rossi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi, Science 300 (2003) 1127;

(d) C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louer, G. Férey, J. Am. Chem. Soc. 124 (2002) 13519;

- (e) D.N. Dybtsev, H. Chun, K. Kim, Angew. Chem., Int. Ed. 43 (2004) 5033;
- (f) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Soc. 34 (2001) 319;
- (g) N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 38 (2005) 176;

(h) N.L. Rosi, J. Kim, M. Eddaoudi, B.L. Chen, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 127 (2005) 1504;

- (i) H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Nature 402 (1999) 276.
 [9] (a) T.F. Liu, J. Lü, R. Cao, Cryst. Eng. Commun. 12 (2010) 660;
- (a) 1.F. Lu, J. Lu, K. Cao, Cryst. Eng. Commun. 12 (2010) 660;
 (b) L. Pan, K.M. Adams, H.E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko, J. Am. Chem. Soc. 125 (2003) 3062;
- (c) L.K. Sposato, J.A. Nettleman, R.L. LaDuca, Cryst. Eng. Commun. 12 (2010) 2374;
- (d) M.A. Braverman, R.L. LaDuca, Cryst. Growth Des. 7 (2007) 2343;

(e) O. Fabelo, J. Pasan, L. Canadillas-Delgado, F.S. Delgado, F. Lloret, M. Julve, C. Ruiz-Perez, Inorg, Chem. 48 (2009) 6086;

- (f) M.-L. Zhang, D.-S. Li, J.-J. Wang, F. Fu, M. Du, K. Zou, X.-M. Gao, J. Chem. Soc., Dalton Trans. (2009) 5355;
- (g) T. Liu, J. Lu, L. Shi, Z. Guo, R. Cao, Cryst. Eng. Commun. 11 (2009) 583;
- (h) M.A. Braverman, R.J. Staples, R.M. Supkowski, R.L. LaDuca, Polyhedron 27 (2008) 2291;

(i) A.D. Burrows, R.W. Harrington, M.F. Mahon, S.J. Teat, Eur. J. Inorg. Chem. (2003) 766.

[10] (a) Z.H. Zhang, Z.L. Shen, T. Okamura, H.F. Zhu, W.Y. Sun, N. Ueyama, Cryst. Growth Des. 5 (2005) 1191;
(b) G.X. Liu, Y.Q. Huang, Q. Chu, T. Okamura, W.Y. Sun, H. Liang, N. Ueyama, Cryst. Growth Des. 8 (2008) 3233;
(c) H.F. Zhu, J. Fan, T. Okamura, Z.H. Zhang, G.X. Liu, K.B. Yu, W.Y. Sun, N. Ueyama, Inorg. Chem. 45 (2006) 3941;

(d) H.-F. Zhu, W.-Y. Sun, T. Okamura, N. Ueyama, Inorg. Chem. Commun. 6 (2003) 168.

- [11] E. Shyu, A.M. Braverman, R.M. Supkowski, R.L. LaDuca, Inorg. Chim. Acta 362 (2009) 2283.
- [12] (a) D. Bradshaw, T.J. Prior, E.J. Cussen, J.B. Claridge, M.J. Rosseinsky, J. Am. Chem. Soc. 126 (2004) 6106; (b) L4. Bool E.M. Andreas, C. Munor, M. Julia, T. Crapier, A. Bousselson, F.

(b) J.A. Real, E.M. Andres, C. Munoz, M. Julve, T. Granier, A. Bousseksou, F. Varret, Science 268 (1995) 265;

(c) J. Fan, C. Slebodnick, R. Angel, B.E. Hanson, Inorg. Chem. 44 (2005) 552;
 (d) Z.Z. Lin, F.L. Jiang, D.Q. Yuan, L. Chen, Y.F. Zhou, M.C. Hong, Eur. J. Inorg. Chem. (2005) 1927;

(e) J. Fan, G.T. Yee, G. Wang, B.E. Hanson, Inorg. Chem. 45 (2006) 599;

(f) Z.B. Han, X.N. Cheng, X.M. Chen, Cryst. Growth Des. 5 (2005) 695;

- (g) W.J. Zhuang, X.J. Žheng, L.C. Li, D.Z. Liao, H. Ma, L.P. Jin, Cryst. Eng. Commun. 9 (2007) 653;
- (h) L.F. Ma, L.Y. Wang, M. Du, S.R. Batten, Inorg. Chem. 49 (2010) 365;
- (i) L.F. Ma, B. Liu, L.Y. Wang, C.P. Li, M. Du, J. Chem. Soc., Dalton Trans. 39 (2010) 2301.
- [13] G.Z. Liu, L.Y. Xin, L.Y. Wang, Cryst. Eng. Commun. (2011), doi:10.1039/ COCE00873G.
- [14] G.M. Sheldrick, A program for the Siemens Area Detector Absorption correction, University of Gottingen, Göttingen, Germany, 1997.
- [15] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution and Refinement, University of Gottingen, Göttingen, Germany, 1997.
- [16] (a) R.B. Fu, S.C. Xiang, S.M. Hu, L.S. Wang, Y.M. Li, X.H. Huang, X.T. Wu, Chem. Commun. (2005) 5292;
 (b) X.D. Guo, G.S. Zhu, Q.R. Fang, M. Xue, G. Tian, J.Y. Sun, X.T. Li, S.L. Qiu, Inorg. Chem. 44 (2005) 3850;
 (c) J. Zhang, W. Lin, Z.F. Chen, R.G. Xiong, B.F. Abrahams, H.K. Fun, J. Chem. Soc., Dalton Trans. (2001) 1806;
 (d) C.D. Wu, U.L. Nizo, W. Lin, Chem. Commun. (2004) 1528.
- (d) C.D. Wu, H.L. Ngo, W. Lin, Chem. Commun. (2004) 1588.
- [17] Z. Lu, L. Wen, Z. Ni, Y. Li, H. Zhu, Q. Meng, Cryst. Growth Des. 7 (2007) 268.
- [18] (a) W.-G. Lu, L. Jiang, X.-L. Feng, T.-B. Lu, Cryst. Growth Des. 6 (2006) 564;
 (b) X.-L. Wang, Y.-F. Bi, H.-Y. Lin, G.-C. Liu, Cryst. Growth Des. 7 (2007) 1086;
 (c) X. Li, X.-W. Wang, Y.-H. Zhang, Inorg. Chem. Commun. 11 (2008) 832;
 (d) L. Wen, Y. Li, Z. Lu, J. Lin, C.D. Meng, Cryst. Growth Des. 6 (2006) 530;
 (e) X.L. Wang, Q. Chao, E.B. Wang, X. Lin, Z.M. Su, C.W. Hu, Angew. Chem., Int. Ed. 43 (2004) 5036;
 (f) H.C. Wu, P. Thanasekaran, C.H. Tsai, J.Y. Wu, S.M. Huang, Y.S. Wen, K.L. Lu,
- Inorg. Chem. 45 (2006) 295. [19] J.C. Bonner, M.E. Fisher, Phys. Rev. A 135 (1964) 640.