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Synthesis, structures and physical properties of mixed-ligand coordination polymers based on a V-shaped dicarboxylic ligand

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Four coordination polymers formulated as $[Ni_2(hfipbb)_2(2,2'\text{-bipy})_2(H_2O)_4]$ (**1**), $[Ni(4,4'\text{-bipy})(hfipbb)(H_2O)]\cdot 0.5DMF$ (**2**), $Ni_2(hfipbb)_2(BPE)_{1.5}(H_2O)(\mu_2\text{-}H_2O)]\cdot DMF\cdot 2H_2O$ (**3**) and $Zn(hfipbb)(2,2'\text{-bipy})\cdot 0.5DMF$ (**4**) ($H_2hfipbb$ = 4,4'-(hexafluoroisopropylidene)-bis(benzoic acid); 2,2'-bipy = 2,2'-bipyridine; 4,4'-bipy = 4,4-bipyridine; BPE = 1,2-di(4-pyridyl)ethane; DMF = *N*,*N*-dimethylformamide) have been synthesized under solvothermal conditions based on the V-shaped $H_2hfipbb$ ligand and different auxiliary linear N-containing ligands. Compound **1** exhibits a three dimensional (3D) supramolecular network built by 0D rings linked through hydrogen bonds and π - π packing interactions. Compound **2** displays a 3D 3-fold interpenetrating diamond network with point symbol of (6^6). Compound **3** gives a double layer structure with $(4^4\cdot 6^2)$-**sql** topology built by $\{Ni_2\}$ clusters bridged by BPE and $hfipbb^{2-}$ligands. Compound **4** is a 3D array formed by interdigitated 1D zig-zag $[Zn_2(hfipbb)_2]_n$ ribbons, in which the $Zn_2(COO)_4$ paddle-wheel SBUs are linked by two $hfipbb^{2-}$ ligands. Compounds **2**-**4** exhibit hydrophobic properties which may have potential applications in hydrophobic materials area. The temperature-dependent magnetic susceptibility study shows that compound **3** exhibits antiferromagnetism property. The photoluminescence for **4** was studied in the solid state at room temperature, and it shows a broad emission with a maximum peak at around 385 nm upon excitation at 335nm.

Introduction

Coordination polymers (CPs) have gained immense attention not only because of their interesting structures and intriguing topologies,[1-3] but also their applications in diverse areas, such as gas storage and separation,[4-8] luminescence,[9-12] magnetism,[13, 14] nonlinear optics,[15] catalysis,[16] proton conduction[17-19] *etc.* Chemists and material scientists have long been working on designing and synthesizing coordination polymers with novel and fascinating topology structures,[15, 20] as well as some functional properties. There are multiple factors affecting the topology structures of the CPs, such as the metal ions, the synthesis temperature, the solvent *etc.*[21] In particular, the framework structure is strongly relied on the organic ligands (as linkers) with metal ions or metal clusters (as nodes) chosen in the preparation process of the functional coordination polymers.[2, 22, 23]

Among various ligands, 4,4´-(hexafluoroisopropylidene)-bis(benzoic acid) ($H_2hfipbb$) as an semi-rigid dicarboxylate ligand has been investigated for its bent geometry and hydrophobic feature, which can produce diverse CPs with many characters such as selective adsorption, catalysis, magnetism, fluorescence and so on.[24-30] The $-CF_3$ terminated surface was reported to possess the low free energy and the best hydrophobicity,[31, 32] so CPs constructed by $H_2hfipbb$ ligand may have hydrophobicity feature[26], which can have potential applications in hydrophobic materials.

Recently, mixed-ligands have also been used in the construction of CPs (such as acid-acid, base-base, and acid-based mixed-ligand CPs).The mixed-ligand strategy endows CPs with more structural diversity and some remarkable physical properties compared to using one type of ligands.[33] In our previous study, we have synthesized a series of cobalt-cluster-based coordination polymers by manipulating the mixed-ligand system of size-matching V-shaped dicarboxylate $H_2hfipbb$ ligand and linear bipyridyl ligand (BPE).[34] Taking all the above discussion into account and in order to proceed with our work on the systematic synthesis of mixed-ligand CPs, herein, 2,2´-bipy, 4,4´-bipy and BPE are employed as the auxiliary co-ligands in the assembly of $H_2hfipbb$ and different metal ions under solvothermal conditions to prepare new CPs with interesting topology structures and some functional properties. Four CPs, namely, $[Ni_2(hfipbb)_2(2,2'\text{-bipy})_2(H_2O)_4]$

(**1**), [Ni(4,4´-bipy)(hfipbb)(H_2O)]·0.5DMF (**2**), Ni_2(hfipbb)$_2$(BPE)$_{1.5}$(H_2O)(μ_2-O)]·DMF·$2H_2O$ (**3**), and Zn(hfipbb)(2,2´-bipy)·0.5DMF (**4**) are successfully isolated. Structural studies found that compounds **1-4** show versatile 0D to 3D structures. Compound **3** shows antiferromagnetic coupling between 2K and 300 K. Compound **4** shows a broad emission with a maximum peak at around 385 nm when excited at 334 nm.

Experimental Section

Materials and General Methods

All reagents were purchased as reagent grade and used without further purification. Elemental analyses of C, H and N were carried out on a Vario MICRO EL Ⅲ elemental analyzer. Infrared (IR) spectra were recorded on PerkinElmer Spectrum in the range of 4000-400 cm^{-1} using KBr pellets. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 10 ℃min^{-1} using a SDT Q600 thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku MiniFlex2 diffractometer using Cu-K_α radiation (λ =1.54056Å) under ambient conditions. Contact angles were measured on OCA20 video contact angle measurement instrument. Three independent experiments were done to get the average value of contact angle for each compound. The solid–state photoluminescent spectra were measured on an Edinburgh FLS920 fluorescence spectrometer at room temperature. The instrument is equipped with an Edinburgh Xe900 xenon arc lamp as the exciting light source. In the testing process, the excitation slits width was 3mm wavelength resolution, the emission slits width was 0.13 mm wavelength resolution, the emission scan step was 0.2nm, the emission scan dwell time was 0.1s, and the focal length of the mono-chromator was 300 mm. The data acquiring technique was single photon counting mode. For calculation method refer to the article published by J.C. de Mello *et al.*[35]

Synthesis of the compounds 1-4

Synthesis of Ni_2(hfipbb)$_2$(2,2´-bipy)$_2$(H_2O)$_4$ (1)

A mixture of $Ni(NO_3)_2\cdot 6H_2O$ (22.8 mg,0.10mmol), H_2hfipbb (39.2 mg, 0.10mmol) and 2,2´-bipy (15.6 mg, 0.10mmol) was dissolved in water (10mL). The mixture was ultrasonic for 20 min and heated at 150 °C for 3 days, and then cooled to room temperature. Blue crystals were collected in 80% yield based on H_2hfipbb. Anal. Calcd for $C_{54}H_{40}N_4O_{12}F_{12}Ni_2$ (%): C, 50.58; H, 3.14; N, 4.37. Found: C, 50.44; H, 3.15; N, 4.33. IR (KBr, cm^{-1}): 3371 (s), 1612 (s), 1544 (s), 1475 (w), 1444 (w), 1407 (s), 1247 (s), 1199(m), 1159 (s), 1026 (w), 956 (w), 937 (w), 85 (m), 746 (m), 730 (m), 694 (w), 559 (w), 466 (w).

Synthesis of [Ni(4,4´-bipy)(hfipbb)(H_2O)]·0.5DMF (2)

A mixture of $Ni(NO_3)_2\cdot 6H_2O$ (22.8 mg,0.10mmol), H_2hfipbb (29.4mg, 0.075mmol) and 4,4´-bipy (15.6 mg, 0.10mmol) was dissolved in a mixed solvent of H_2O (5mL) and DMF (5mL). The mixture was ultrasonic for 20 min and heated at 90 °C for 3 days, then cooled to room temperature. Light green needle-like crystals were collected in 75% yield based on H_2hfipbb. Anal. Calcd for $C_{114}H_{86}O_{22}F_{24}N_{10}Ni_4$(%): C, 51.89; H, 3.28; N, 5.31. Found: C, 51.02; H, 3.41; N, 5.01. IR (KBr, cm^{-1}):3377 (s), 1668 (w), 1600 (s), 1527 (s), 1402(s), 1271 (w), 1247 (s), 1207 (s), 1168 (s), 1147 (m), 1080(w), 1029 (w), 947 (m), 858 (m), 812 (s), 806 (m), 788 (m), 719 (s), 628 (m), 551 (w), 491 (w), 464 (w).

Synthesis of [Ni_2(hfipbb)$_2$(BPE)$_{1.5}$(H_2O)(μ_2-H_2O)]·DMF·$2H_2O$ (3)

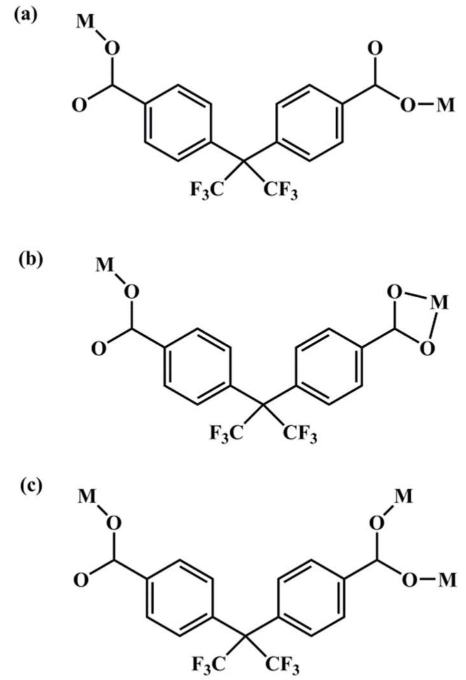
The same synthetic procedure as that for the compound **2** was used except that 4,4´-bipy was replaced by BPE (18.4 mg, 0.10mmol), producing light green block crystals of **3** in 70% yield based on H_2hfipbb. Anal. Calcd for $C_{55}H_{48}N_4O_{13}F_{12}Ni_2$ (%): C, 50.11; H, 3.67; N, 4.25. Found (%): C, 50.18; H, 3.65; N, 4.29. IR (KBr, cm^{-1}): 3437 (s), 2918 (w), 2848 (w), 2086 (w), 1633 (s), 1533 (m), 1388 (s), 1259 (s), 1215 (m), 1170 (s), 1128 (w), 1029 (m), 956 (m), 821 (m), 788 (m), 721 (m), 55 (m), 459 (m).

Synthesis of Zn(hfipbb)(2,2´-bipy)·0.5DMF (4)

A mixture of $Zn(NO_3)_2\cdot 6H_2O$(29.7 mg, 0.10mmol), H_2hfipbb (29.4 mg, 0.075mmol) and 2,2´-bipy(15.6 mg,0.10mmol) was dissolved in a mixed solvent of H_2O (5mL) and DMF (5mL). The mixture was ultrasonic for 20 min and heated at 90 °C for 3 days, then cooled to room temperature. Colorless needle-like crystals were collected in 78% yield based on H_2hfipbb. Anal. Calcd for (%): C, 52.79; H, 3.03; N, 5.40. Found(%): C, 52.68; H, 3.25; N, 5.26. IR (KBr, cm^{-1}): 3435(s), 3070 (w), 1593 (s), 1541 (s), 1496 (w), 1396 (s), 1286 (w), 1249 (s), 1218 (m), 1180 (s), 1145 (m), 1012 (m), 960 (m), 852 (m), 773 (s), 734 (s), 584 (w), 501 (w), 459 (w), 420 (w).

Single-Crystal X-ray Crystallography

Single-crystal X-ray diffraction data of compounds **1-4** were collected on SuperNova CCD-based diffractometer equipped with graphite-monochromated Cu-K_α radiation by ω-scan at 100K. All of the structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 with the SHELXTL-97 program. All non-hydrogen atoms except for some solvent molecules were refined with anisotropic thermal parameters. The hydrogen atoms attached to carbon atoms and nitrogen atoms were added theoretically.



Scheme 1 Coordination modes of hfipbb^{2-} ligands

Results and discussion

Description of the crystal structures

Crystal structure of $Ni_2(hfipbb)_2(2,2'\text{-}bipy)_2(H_2O)_4$ (1)

Single-crystal X-ray diffraction study shows that compound **1** crystallizes in the monoclinic system, space group $P2_1/c$. As shown in Fig. 1, the asymmetric unit of **1** contains one crystallographically independent nickel ion, one hfipbb^{2-} ligand, one 2,2´-bipy ligand and two coordinated water molecules. The central nickel ion is octahedrally surrounded by two nitrogen atoms (N1, N2) from the chelating 2,2´-bipy ligand, two oxygen atoms (O1A, O3) from two separate hfipbb^{2-} ligands and two oxygen atoms (O5w, O6w) from the two coordinated water molecules. The Ni-O distances range from 2.039 to 2.082 Å and Ni-N distances range from 2.051 to 2.068 Å. As shown in scheme 1a, the two carboxylic groups of the hfipbb^{2-} ligand adopt monodentate coordination mode. In this structure, two asymmetric units form a metal-organic ring by head-to-tail connection (Fig. 2). The rings are isolated, which can't be connected to each other through covalent bonds, suggesting that it is 0D structure. Alternately, the rings can be seen to connect each other by hydrogen bonds between O_4 and H5B (H5B means the hydrogen atom in the coordination water molecule around the central nickel atom, as seen in Figure 3) to give rise to a 1D chain along the crystallographic *a* axis(Fig. 3). At the same time, the separate rings can be joined each other by hydrogen bonds between O_2 and H5A (H5A means the hydrogen atom in the coordination water molecule around the central nickel atom, as seen in Figure S1) to result in planes paralleling to the crystallographic *ab* plane (Fig. S1). Moreover, there exists π-π packing interactions among the separate metal-organic rings, leading to planes almost paralleling to the crystallographic *ac* plane. (Fig. S2). These two types of planes are further cross-connected to each other, forming a 3D supramolecular network.

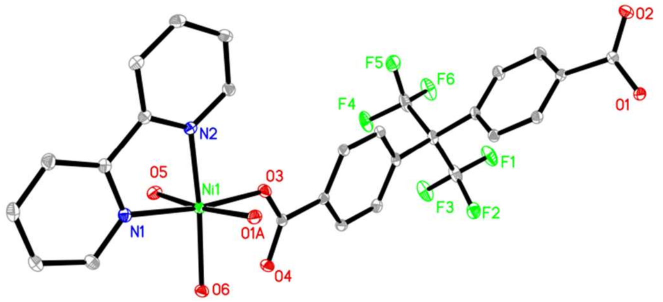


Fig. 1 The coordination environment of the central nickel (Ⅱ) ions in **1** with 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A, 1-*x*, 2-*y*, 1-*z*.

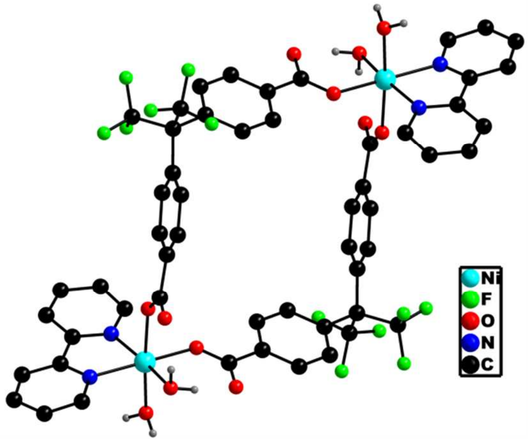


Fig. 2 The metal-organic rings formed by two asymmetric units in compound **1**.

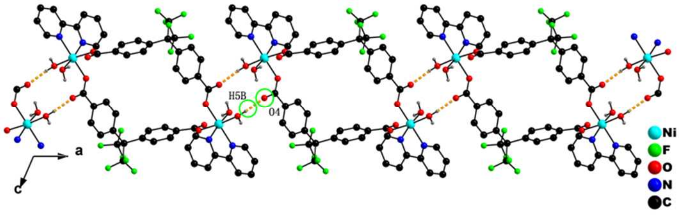


Fig. 3 The metal-organic rings link to each other to form 1D supramolecular chain by the hydrogen bonds between O4 and H5B. (H5B means the hydrogen atom in the coordination water molecule around the central nickel atom)

Crystal structure of $[Ni(4,4'\text{-}bipy)(hfipbb)(H_2O)]\cdot 0.5DMF$ (2)

The single crystal study indicates that compound **2** crystallizes in the monoclinic system, space group $C2/c$. There are one crystallographically independent nickel ion, one hfipbb^{2-} ligand, two half of 4, 4´-bipy molecules, one water molecule and half of the free DMF molecule in the asymmetric unit of **2**. The central nickel ion is six-coordinated, with an oxygen atom (O1) from one monodentate carboxyl group, two oxygen atoms (O4A, O5A) from a chelating carboxyl group, one oxygen atom (O3w) from a coordinated water molecule, and the remaining two atoms (N1,N2) from two separate 4,4´-bipy ligands (Fig. 4). The coordination mode of the carboxylic group of the hfipbb^{2-} ligand is shown in the Scheme 1b. The coordination environment of the central Ni (Ⅱ) ion is a distorted octahedral geometry with Ni-O bond lengths ranging from 2.035 to 2.151 Å and Ni-N distances ranging from 2.74 to 2.080 Å, which are comparable to those values of other reported similar compounds.[36, 37] Each Ni atom is connected to four adjacent Ni atoms through two hfipbb^{2-} ligands and two 4,4´-bipy ligands, generating the basic tetrahedral building block of **2** (Fig. 5), which further connects to each other to form an infinite 3D 3-fold interpenetrating diamond network with point symbol of (6^6) (Fig. 6). The diamond net has been introduced in many articles and in some review articles.[23] We have also reported one similar 4-connected topology network previously.[20] In the reported structure, another V-shaped ligand was also used, but the interesting **mok** net appeared instead of the **dia** net due to the presence of the self-catenation in the structure.

Table 1 Crystallographic data for **1-4**

Compound	1	2	3	4
Chemical formula	$C_{54}H_{40}N_4O_{12}F_{12}Ni_2$	$C_{114}H_{86}O_{22}F_{24}N_{10}Ni_4$	$C_{55}H_{46}N_4O_{13}F_{12}Ni_2$	$C_{57}H_{39}N_5O_9F_{12}Zn_2$
Formula Mass	1282.28	2638.69	1316.34	1296.68
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
a/Å	15.4570(4)	29.6835(10)	12.1471(4)	14.4565(4)
b/Å	13.4361(2)	22.6110(8)	14.5855(7)	38.2307(8)
c/Å	13.8616(3)	8.2315(2)	17.4940(7)	10.0080(2)
α(°)	90.00	90.00	111.295(4)	90.00
β(°)	113.356(3)	92.633(3)	90.612(3)	109.779(3)
γ(°)	90.00	90.00	91.087(3)	90.00
Unit cell volume/ Å^3	2642.91(10)	5518.9(3)	2886.8(2)	5204.9(2)
T/K	173(2)	173(2)	173(2)	173(2)
Space group	P21/c	C2/c	P -1	C2/c
Z	2	2	2	8
μ/mm^{-1}	1.870	1.781	1.740	1.030
Data measured	10394	10515	20676	10556
Unique data	5088	5371	11282	5085
R_{int}	0.0246	0.0351	0.0273	0.0280
R_1^a ($I>2\sigma(I)$)	0.0328	0.0515	0.0799	0.0389
$wR(F^2)^b$ ($I>2\sigma(I)$)	0.0805	0.1466	0.2110	0.0987
R_1^a(all data)	0.0428	0.0651	0.0900	0.0612
$wR(F^2)^b$ (all data)	0.0877	0.1561	0.2167	0.1091
Goodness of fit on F^2	1.036	1.071	1.187	0.949
CCDC number	1030450	1030451	1030452	1030453

$^aR_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. $^bwR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2/\Sigma[wFo^2]^2]\}^{1/2}$.

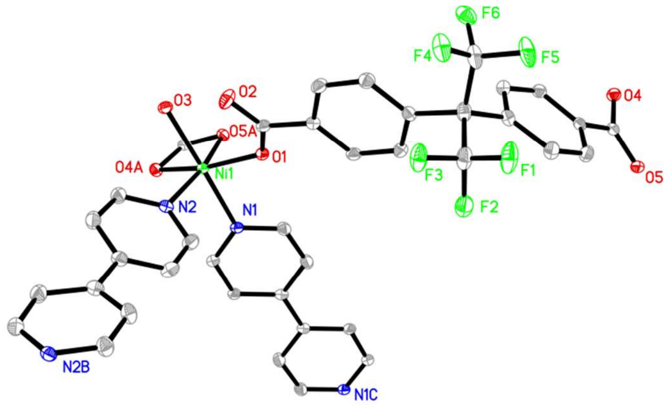


Fig. 4 The coordination environment of the central nickel (Ⅱ) ions in **2** with 30% probability of thermal ellipsoids. Hydrogen atoms and the free DMF molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A, 1/2-*x*, 1/2+*y*, 1/2-*z*.

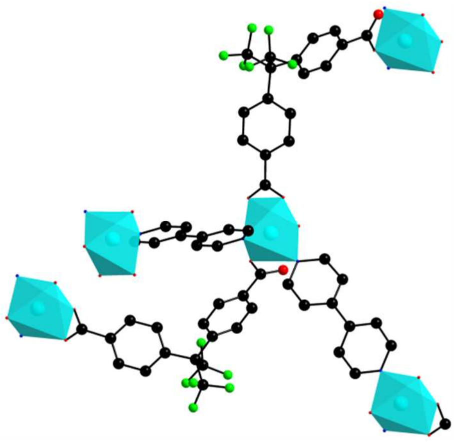


Fig. 5 View of the basic tetrahedral building block in the compound **2**.

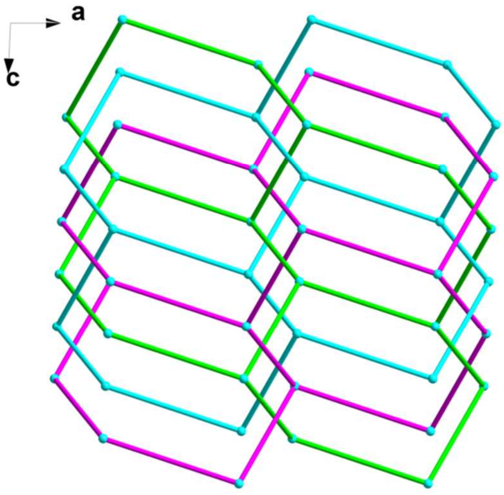


Fig. 6 3-fold interpenetrating **dia** network of compound **2**.

Crystal structure of $[Ni_2(hfipbb)_2(BPE)_{1.5}(H_2O)(\mu_2\text{-}H_2O)]\cdot DMF\cdot 2H_2O$ (3)

Compound **3** crystallizes in the triclinic system with space group *P*-1. The asymmetric unit of **3** contains two crystallographically independent nickel ions, two hfipbb^{2-} ligands, one and a half of BPE ligands, a μ_2-H_2O molecule and one uncoordinated DMF molecule (Fig. 7). In the structure, one of the crystallographically independent nickel ion (Ni1) is six coordinated, namely, two oxygen atoms from two separate bridging carboxyl group (O5, O4B), one oxygen atom from monodentate carboxyl group (O8C), one oxygen atom (O9) from coordinated water (O9) and two nitrogen atoms from two separate BPE ligands (N2, N3D). The other crystallographically independent nickel atom (Ni2) is also six coordinated, which are two oxygen atoms (O6, O3B) from two separate bridging carboxyl group，one oxygen atom from monodentate carboxyl group (O2), two oxygen atoms from two coordinated water molecules (O9, O10W), one nitrogen atom from one BPE ligand(N1). The coordination environments of the Ni1 and Ni2 ions can be seen as slightly distorted octahedral geometry. The carbon atoms (C41, C42, C44, C45) in one phenyl ring of BPE are distorted over two positions with occupancies of 0.51 and 0.48 respectively, whilst atoms (C49, C50, C51, C52) in the other phenyl ring of the BPE with occupancies of 0.50 and 0.50 respectively. Two adjacent nickel atoms are linked by bridging carboxyl group and μ_2-H_2O, resulting in a dinickel $\{Ni_2\}$ cluster. The Ni-O and Ni-N bond distances are in the range of 2.025-2.107 Å and 2.089-2.099 Å, respectively. The two carboxylate groups in hfipbb^{2-} ligand show either monodentate or bis-bridging coordination mode (Scheme 1C). In this structure, BPE ligands connect the $\{Ni_2\}$ clusters along the crystallographic-*a* axis, giving rise to a double layer structure with $(4^4\cdot 6^2)$-**sql** topology (Fig. 8). Compound **3** is similar to one structure previously reported by our group (compound **Co(BPE)(hfipbb) (1)** in that article) (Figure S3).[34] But there also exists difference between them. For compound **3**, there is a dihedral angle of 157° between neighboring planes formed by $\{Ni_2\}$ clusters and hfipbb^{2-} ligand, while in the reported one, the neighboring planes show a parallel orientation. Moreover, the BPE ligands connecting the $\{Ni_2\}$ clusters appear alternatively in the form of a single chain (with trans configuration) and double chain (both showing cis configuration), while in the reported compound (compound **Co(BPE)(hfipbb) (1)** in that article), the BPE ligands show parallel double chain (both with trans configuration) (BPE configuration seen in Figure S4). All this occurs because in compound **3** the slightly distorted octahedral coordination environments of Ni1 and Ni2 are defined by different atoms while in the reported compound, Co1 and Co2 are defined by the same atoms.

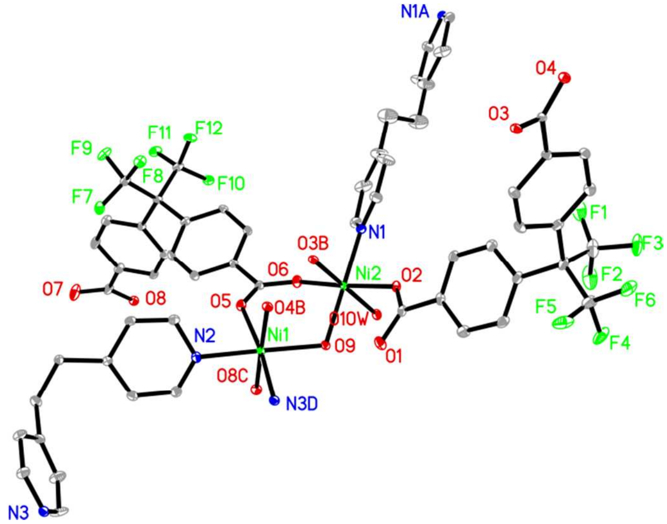


Fig. 7 The coordination environment of the central nickel (Ⅱ) ions in **3** with 30% probability of thermal ellipsoids. Hydrogen atoms, the free DMF and the free water molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A, 2-*x*, 2-*y*, 2-*z*; B, 1-*x*, 3-*y*, 2-*z*; C, 1-*x*, 1-*y*, 1-*z*; D, -*x*, 2-*y*, 1-*z*.

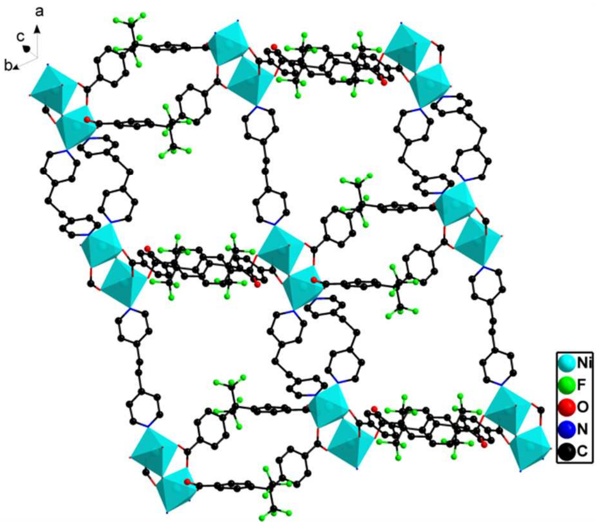


Fig. 8 A view of the double layer structure with $(4^4{\cdot}6^2)$-**sql** topology in compound **3**.

Crystal structure of Zn(hfipbb)(2,2´-bipy)·0.5DMF (4)

Compound **4** crystallizes in the monoclinic system, space group *C*2/*c*. The asymmetric unit of **4** contains one zinc atom, one hfipbb^{2-} ligand, one 2,2´-bipy and half of one DMF molecule (Fig. 9). The central zinc ion is five coordinated with three oxygen atoms from three separate hfipbb^{2-} ligands (O4, O1A, O2B) and two nitrogen atoms from a chelating 2,2´-bipy ligand (N1, N2), composing a trigonal bipyramidal geometry with Zn-O distances ranging from 1.950 to 2.099 Å and Zn-N distances ranging from 2.107 to 2.149 Å. Secondary building unit (SBU) is a dizinc carboxylate moiety $Zn_2(COO)_4$, where two zinc atoms are bridged by two μ_2-bridging carboxylate groups from two different hfipbb^{2-} ligands, with Zn···Zn distances of 4.015 Å. The coordination mode of the carboxylic group of the hfipbb^{2-} is the same as that in compound **3**. The paddle-wheel $Zn_2(COO)_4$ SBUs are linked by two hfipbb^{2-} ligands to generate a 1D zig-zag ribbon of $[Zn_2(hfipbb)_2]_n$ in the *ac* plane with the two adjacent dizinc cores distance of 12.356 Å which cannot be extended in other directions due to the restriction of the 2,2´-bipy ligand ($Zn_2(COO)_4$). These 1D zig-zag ribbons are further interdigitated each other by the 2, 2´-bipy and the hfipbb^{2-} ligands to form a 3D array (Fig. 11). The free solvent DMF molecules are dispersed among the 3D array.

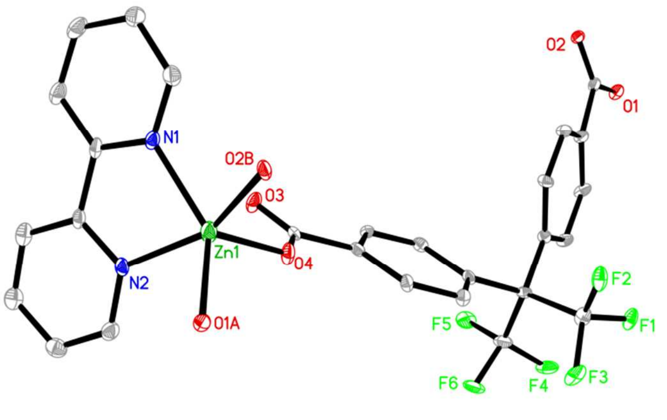


Fig. 9 The coordination environments of the central zinc (Ⅱ) ions in **4** with 30% probability of thermal ellipsoids. Hydrogen atoms and the free water molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A, 1+*x*, *y*, 1+*z*; B, -*x*, *y*, 1/2-*z*.

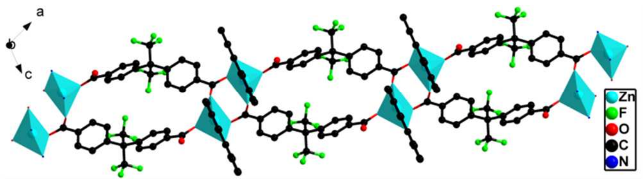


Fig. 10 1D zig-zag ribbon of $[Zn_2(hfipbb)_2]_n$ in the ac plane of compound **4**.

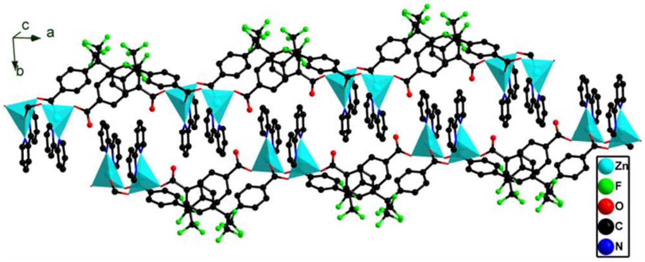


Fig. 11 the interdigitation between 1D zig-zag ribbons in compound **4**

Powder X-ray diffraction and thermal analysis

To check the purity and homogeneity of the bulk crystals of the compounds, the as-synthesized samples of **1**-**4** were measured by power X-ray diffraction (PXRD) at room temperature. As shown in Fig. S5-S8, the peak positions of the experimental patterns are in good agreement with those calculated from single-crystal X-ray diffraction data, which suggest the purity and homogeneity of the compounds. Thermogravimetric analyses (TGA) were carried out to examine the thermal stability. As shown in Fig. S9-S12, compound **1** loses coordinated water molecules from room temperature to 158°C (observed 5.5%, calculated 5.6%). For compound **2**, the weight loss of 8.36% (calculated 8.27%) occurs from room temperature to 182.7°C, corresponding to the release of free DMF and coordinated water molecules. For compound **3**, the continuous weight loss from room temperature to *ca*. 198°C corresponds to the loss of all solvent molecules (calculated: 8.29%; found, 8.78%), which is followed by the framework collapse with increasing temperature. Compound **4** loses the solvent DMF molecules from room temperature to *ca*. 141°C (calculated, 5.63%; found, 5.22%). With further heating, gradual weight loss occurs and the framework decomposes.

Structural analysis

In compound **1**, the nitrogen atoms in co-ligand 2,2´-bipy are chelated to the central Ni atom, giving rise to individual 0D metal-organic rings together with the semi-rigid V-shaped geometry of the H_2hfipbb ligand, which limits the extension of **1** into higher dimensional frameworks. Similarly, in compound **4**, the nitrogen atoms in 2,2´-bipy are also chelated to the central Zn atom, resulting in the 1D zig-zag ribbon in the *ac* plane, which also restrict the framework's extension. In the preparation of compounds **1** and **4**, with the same ligands, H_2hfipbb ligand and co-ligand 2,2´-bipy, but different solvent, temperature and metal salts, different structures are obtained. Since the nitrogen atoms in 2,2′-bipy are liable to chelate to the central metal atom, in order to avoid the chelation of the nitrogen atoms, the auxiliary ligands 4,4′-bipy and BPE are used instead of 2,2′-bipy in the construction of coordination polymers **2** and **3**. As expected, the extended 2D and 3D structures are successfully synthesized.

Wetting properties

The characterization of hydrophobic feature is usually performed by contact angle measurement with water. When the water contact angle is lower than 90°, the surface is hydrophilic; when it is higher than 90°, the surface is hydrophobic.[38, 39] In order to study the wetting properties of **1-4,** the water contact angles of **1-4** and the free H_2hfipbb ligand were measured at room temperature. As shown in Fig. 12, the contact angles of the free H_2hfipbb ligand and **1-4** are 99.2°, 36.2°, 111.6°, 121.5°, and 108.5° respectively. The free H_2hfipbb ligand and compounds **2-4** exhibit hydrophobic properties, however, differently, compound **1** shows hydrophilic property. The phenomenon may be related to the presence of H-bonding interactions[32] in **1** and varied structures or composition [40] of the coordination polymers surface. Thus compounds **2-4** may be potential hydrophobic materials.

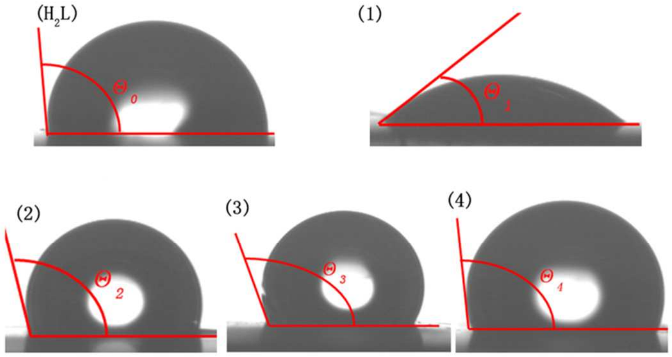


Fig. 12 Photographs of a drop of water on the surface of H2hfipbb ligand and compounds **1-4**. Lines have been drawn tangent to the surface of the liquid where it meets the solid. The angle between this line and the solid surface is *ϑ*.

Magnetic properties

To investigate the temperature dependence of the magnetic susceptibility, compound **3** was studied in the temperature range 2-300K under an applied magnetic field of 1000 Oe. The magnetic data of compound **3** is shown in Fig. 13, plotted as χ_m, χ_mT and χ_m^{-1} versus T. The χ_mT value of compound **3** at 300K is 2.46 $cm^3mol^{-1}K$. Upon cooling of the sample, the χ_mT value decreases to 1.69 cm^3 mol^{-1} K at 2K. The magnetic data of compound **3** follows the Curie-Weiss law in the temperature range of 2K to 300K, and the fit of the χ_m^{-1} versus T curve yields a Curie constant C= 2.44 cm^3 mol^{-1} K per Ni_2 cluster, *i.e.* ~1.22 cm^3 mol^{-1} K per Ni^{2+} ion. This value is larger than the spin-only value of 1.00 cm^3 mol^{-1} K expected for the S= 1 Ni^{2+} ion, suggesting orbital contribution to the total magnetic moment. The Weiss constant θ obtained from the fit of the χ_m^{-1} versus T curve is -0.12K, which indicates the presence of weak antiferromagnetic coupling between Ni(II) ions.[41]

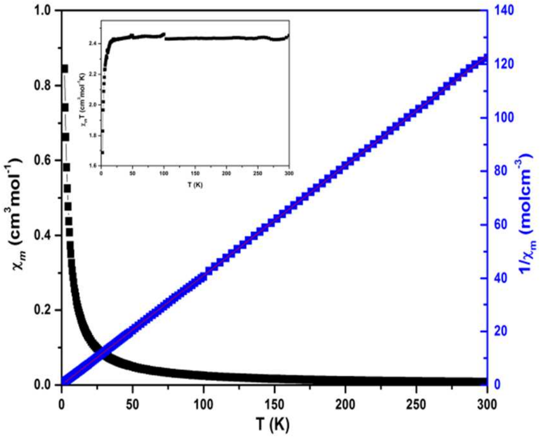


Fig. 13 Temperature dependence of the magnetic susceptibility of compound **3**. Inset: temperature dependence of $\chi_m T$ vs. *T*.

Photoluminescent properties

Presently, the organic-inorganic hybrid complexes are attracting great attention due to their various potential applications in light emitters, chemical sensors, electroluminescent (EL) displays, biomedicine and photochemistry.[42-45] Therefore, the photoluminescent property of **4** was studied in the solid state at room temperature. It shows photoluminescence at around 385 nm upon excitation at 335 nm. At the same time, when excited at 335 nm, the free H_2hfipbb ligand exhibits the photoluminescence at around 380 nm (Fig. 14). Due to the similarity in the photoluminescent spectra between compound **3** and the free H_2hfipbb ligand, the photoluminescence can be attributed to ligand-centered electronic excitations.[44, 46, 47]

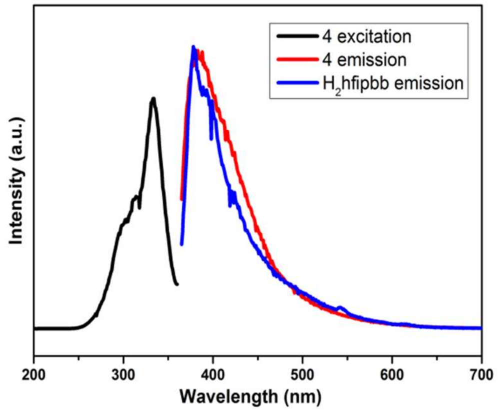


Fig. 14 The solid-state photoluminescent spectra of compound **4** and the free H_2hfipbb ligand.

Conclusions

In this work, four coordination polymers based on the V-shaped H_2hfipbb ligand and some auxiliary linear N-containing ligands have been successfully synthesized by the solvothermal method. The compounds show diverse structures from 0D to 3D network when synthesized under different temperature and solvent conditions. The results show that the auxiliary linear N-donor ligands play important roles in the construction of CPs. Moreover compounds **2-4** exhibit hydrophobic properties which may have potential applications in hydrophobic materials area. Compound **3** shows antiferromagnetic coupling between 2K and 300 K. And compound **4** shows photoluminescence at around 385nm which is mainly dominated by the ligand-based emission. Thus, compounds **3** and **4** can be potential magnetic and photoactive materials.

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Notes and references

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1. H.-L. Jiang, T. A. Makal and H.-C. Zhou, *Coordination Chemistry Reviews*, 2013, **257**, 2232-2249.
2. D. Zhao, D. J. Timmons, D. Yuan and H.-C. Zhou, *Accounts of Chemical Research*, 2010, **44**, 123-133.
3. W. Jia, J. Luo and M. Zhu, *Crystal Growth & Design*, 2011, **11**, 2386-2397.
4. D. Lässig, J. Lincke, J. Moellmer, C. Reichenbach, A. Moeller, R. Gläser, G. Kalies, K. A. Cychosz, M. Thommes, R. Staudt and H. Krautscheid, *Angewandte Chemie International Edition*, 2011, **50**, 10344-10348.
5. Z.-J. Lin, Y.-B. Huang, T.-F. Liu, X.-Y. Li and R. Cao, *Inorganic Chemistry*, 2013, **52**, 3127-3132.
6. Z.-J. Lin, T.-F. Liu, Y.-B. Huang, J. Lü and R. Cao, *Chemistry – A European Journal*, 2012, **18**, 7896-7902.
7. S. Ma and H.-C. Zhou, *Chemical Communications*, 2010, **46**, 44-53.
8. M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chemical reviews*, 2011, **112**, 782-835.
9. Z. Hu, B. J. Deibert and J. Li, *Chemical Society reviews*, 2014, **43**, 5815-5840.
10. C. A. Kent, D. Liu, T. J. Meyer and W. Lin, *Journal of the American Chemical Society*, 2012, **134**, 3991-3994.
11. X.-C. Shan, F.-L. Jiang, D.-Q. Yuan, M.-Y. Wu, S.-Q. Zhang and M.-C. Hong, *Dalton transactions*, 2012, **41**, 9411-9416.
12. X. Zhao, X. Wang, S. Wang, J. Dou, P. Cui, Z. Chen, D. Sun, X. Wang and D. Sun, *Crystal Growth & Design*, 2012, **12**, 2736-2739.
13. Z. Guo, R. Cao, X. Wang, H. Li, W. Yuan, G. Wang, H. Wu and J. Li, *Journal of the American Chemical Society*, 2009, **131**, 6894-6895.
14. W. Zhang and R.-G. Xiong, *Chemical reviews*, 2011, **112**, 1163-1195.
15. L. Meng, Q. Cheng, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Chen, M. J. Zaworotko, X. P. Zhang and S. Ma, *Angewandte Chemie International Edition*, 2012, **51**, 10082-10085.
16. J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chemical Society reviews*, 2014, **43**, 6011-6061.
17. P. Ramaswamy, N. E. Wong and G. K. H. Shimizu, *Chemical Society reviews*, 2014, **43**, 5913-5932.
18. T. Yamada, K. Otsubo, R. Makiura and H. Kitagawa, *Chemical Society reviews*, 2013, **42**, 6655-6669.
19. M. Yoon, K. Suh, S. Natarajan and K. Kim, *Angewandte Chemie International Edition*, 2013, **52**, 2688-2700.
20. Y. Gong, Y.-C. Zhou, T.-F. Liu, J. Lu, D. M. Proserpio and R. Cao, *Chemical Communications*, 2011, **47**, 5982-5984.
21. N. Stock and S. Biswas, *Chemical reviews*, 2011, **112**, 933-969.
22. D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe and O. M. Yaghi, *Chemical Society reviews*, 2009, **38**, 1257-1283.
23. O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705-714.
24. L. Pan, D. H. Olson, L. R. Ciemnolonski, R. Heddy and J. Li, *Angewandte Chemie International Edition*, 2006, **45**, 616-619.
25. F. Gándara, V. A. de la Peña-O'Shea, F. Illas, N. Snejko, D. M. Proserpio, E. Gutiérrez-Puebla and M. A. Monge, *Inorganic Chemistry*, 2009, **48**, 4707-4713.
26. B. V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J. L. Jordá, H. García, D. Ananias, L. D. Carlos and J. Rocha, *Angewandte Chemie International Edition*, 2008, **47**, 1080-1083.
27. C. Ji, L. Huang, J. Li, H. Zheng, Y. Li and Z. Guo, *Dalton transactions*, 2010, **39**, 8240-8247.
28. L. Qin, J. Hu, M. Zhang, Q. Yang, Y. Li and H. Zheng, *Crystal Growth & Design*, 2013, **13**, 2111-2117.
29. M. C. Bernini, A. E. Platero-Prats, N. Snejko, E. Gutierrez-Puebla, A. Labrador, R. Saez-Puche, J. Romero de Paz and M. A. Monge, *CrystEngComm*, 2012, **14**, 5493-5504.
30. A. Monge, N. Snejko, E. Gutierrez-Puebla, M. Medina, C. Cascales, C. Ruiz-Valero, M. Iglesias and B. Gomez-Lor, *Chemical Communications*, 2005, 1291-1293.
31. T. Nishino, M. Meguro, K. Nakamae, M. Matsushita and Y. Ueda, *Langmuir*, 1999, **15**, 4321-4323.
32. T. Sun, G. Qing, B. Su and L. Jiang, *Chemical Society reviews*, 2011, **40**, 2909-2921.
33. M. Du, C.-P. Li, C.-S. Liu and S.-M. Fang, *Coordination Chemistry Reviews*, 2013, **257**, 1282-1305.
34. L.-W. Han, J. Lu, Z.-J. Lin and R. Cao, *CrystEngComm*, 2014, **16**, 1749-1754.
35. J. C. de Mello, H. F. Wittmann and R. H. Friend, *Advanced Materials*, 1997, **9**, 230-232.
36. C. Ji, L. Huang, J. Li, H. Zheng, Y. Li and Z. Guo, *Dalton transactions*, 2010, **39**, 8240-8247.
37. G. Aromí, P. Gamez, O. Roubeau, P. Carrero-Berzal, H. Kooijman, Anthony L. Spek, Willem L. Driessen and J. Reedijk, *European Journal of Inorganic Chemistry*, 2002, **2002**, 1046-1048.
38. X. Zhang, F. Shi, J. Niu, Y. Jiang and Z. Wang, *Journal of Materials Chemistry*, 2008, **18**, 621-633.
39. S. Aguado, J. Canivet, Y. Schuurman and D. Farrusseng, *Journal of Catalysis*, 2011, **284**, 207-214.
40. R. Williams and A. M. Goodman, *Applied Physics Letters*, 1974, **25**, 531-532.
41. A. K. Ghosh, M. Pait, M. Shatruk, V. Bertolasi and D. Ray, *Dalton transactions*, 2014, **43**, 1970-1973.

42. B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian and E. B. Lobkovsky, *Advanced Materials*, 2007, **19**, 1693-1696.
43. M.-S. Wang, S.-P. Guo, Y. Li, L.-Z. Cai, J.-P. Zou, G. Xu, W.-W. Zhou, F.-K. Zheng and G.-C. Guo, *Journal of the American Chemical Society*, 2009, **131**, 13572-13573.
44. G.-Y. Wang, C. Song, D.-M. Kong, W.-J. Ruan, Z. Chang and Y. Li, *Journal of Materials Chemistry A*, 2014, **2**, 2213-2220.
45. Y. Cui, Y. Yue, G. Qian and B. Chen, *Chemical reviews*, 2011, **112**, 1126-1162.
46. H.-L. Jiang and Q. Xu, *CrystEngComm*, 2010, **12**, 3815-3819.
47. D. Tian, Y. Li, R.-Y. Chen, Z. Chang, G.-Y. Wang and X.-H. Bu, *Journal of Materials Chemistry A*, 2014, **2**, 1465-1470.

Synthesis, structures and physical properties of coordination polymers based on a V-shaped dicarboxylic ligand

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Four coordination polymers based on a V-shaped H_2hfipbb ligand, (H_2hfipbb = 4, 4′-(hexafluoroisopropylidene)-bis(benzoic acid), and different auxiliary linear N-donor ligands have been constructed under solvothermal conditions and structurally characterized. Single-crystal X-ray diffraction analysis reveals a significant structural diversity of the coordination polymers, such as 3D supramolecular network built by metal-organic rings linked through the hydrogen bonds and π-π packing interactions (**1**), 3-fold interpenetrating diamond network (**2**), double layer structure (**3**), and 3D array formed by interdigitated1D zig-zag ribbons (**4**). The wetting properties of compounds **1**-**4**, the magnetic property of compound **3** and luminescent property of compound **4** have also been investigated.