Solvothermal syntheses, structures, and physical properties of four new coordination compounds constructed from a bent dicarboxylate ligand[†]

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Four new coordination compounds, namely $\{[Cd_3(L)_2(\mu_3-OH)_2(H_2O)] \cdot H_2O\}_n$ (1), $\{Ni(L)(bipy)\}_n$ (2), $\{Cu_3(L)_2(bipy)(\mu_2-OH)_2(DMF)_2\}_n$ (3), and $\{Co_2L_2(H_2L)(H_2O)\}_n$ (4), have been synthesized by the solvothermal reaction of 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H₂L) with different transition metal ions in the presence of co-ligand 4,4'-bipyridine (bipy). Compound 1 displays a three-dimensional (3D) framework containing infinite bands constructed of heptanuclear cadmium clusters. In compound 2, $[Ni_2C_2O_4]$ secondary building units (SBUs) are linked by L²⁻ ligands into a 1D ribbon, which are further assembled into a two-dimensional (2D) non-interpenetrated structure with $\{4^4 \cdot 6^2\}$ topology. Compound 3 possesses a 3D framework with a new topology of $\{4^3\}_2\{4^6 \cdot 6^{14} \cdot 8^8\}$ net, while the structure of 4 is a duplicate interpenetrated 3D framework with $\{4^{12} \cdot 6^3\}$ net. Temperature-dependent magnetic studies reveal that 3 exhibits ferromagnetic coupling between adjacent Cu(II) ions. The photoluminescent property of 1 has been studied in the solid state at room temperature.

Introduction

Metal-organic frameworks (MOFs) are crystalline materials with high porosities and good thermal stability composed of metal ions or metal ion clusters.¹ Some MOFs have been explored for applications such as gas storage,² catalysis,³ luminescence,⁴ magnetism⁵ and separations.⁶ Not only the aforementioned uses but also the new structures and topologies of MOFs have attracted more and more interest.⁷ The choice of metal ion and ligand can be judiciously selected to influence the overall chemical and physical properties of the MOFs. Accordingly, the most effective and facile method to design two-dimensional (2D) and three-dimensional (3D) metallosupramolecular species is to select appropriate organic ligands as building blocks with metal ions or metal clusters as nodes.⁸

4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H_2L) as semirigid dicarboxylate ligand has been investigated for its bent geometry which can induce porous framework with many characters such as selective adsorption, catalysis, magnetism, fluorescence and so on.⁹ 4,4'-bipyridine (bipy) and the other linear N-donor auxiliary co-ligands as bidentate pillar linkers have been used widely for the construction of supramolecular architectures. The research of compounds constructed by both H_2L and bipy have not been reported widely.¹⁰ It offered us an opportunity to find more diversity of both structures and topologies in the field. With the aim of understanding the coordination chemistry of the H₂L ligand and preparing new porous materials with not only interesting structures and topologies, but also good physical properties, especially the expected magnetic properties, we chose H₂L as the primary ligand and bipy as auxiliary co-ligand to react with the d-block metal ions, and successfully synthesized four compounds {[Cd₃(L)₂(μ_3 -OH)₂(H₂O)]·H₂O}_n (1), {Ni(L)(bipy)}_n (2), {Cu₃(L)₂(bipy)(μ_2 -OH)₂(DMF)₂}_n (3), and {Co₂L₂(H₂L)(H₂O)}_n (4). The details of their synthesis, structure, and physical properties are reported below.

Experimental

Materials and physical measurements

H₂L and bipy ligands were purchased and used as received. All other chemicals were of reagent grade quality from commercial sources and were used without further purification. The IR absorption spectra of the compounds were recorded in the range of 400-4000 cm⁻¹ by means of a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H, and N analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature (25 °C). Powder X-ray diffraction (PXRD) measurements were performed on a Philips X'pert MPD Pro Xray diffractometer using Cu-K α radiation ($\lambda = 0.15418$ nm), in which the X-ray tube was operated at 40 kV and 40 mA. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin-Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min⁻¹ under a N₂ atmosphere. Temperature dependent magnetic susceptibility data for polycrystalline compound 3 was obtained on a SQUID magnetometer under an applied field of 2000 Oe over the temperature range of 1.8-300 K. The output data was corrected for the experimentally determined diamagnetism of the sample holder

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and the diamagnetism of the sample calculated from Pascal's constants.

Synthesis of the compounds

Synthesis of {[Cd₃(L)₂(μ_3 -OH)₂(H₂O)]·H₂O}, (1). Cd(NO₃)₂· 4H₂O (30.84 mg, 0.1 mmol) was added to an aqueous solution of H₂L (12 mg, 0.03 mmol), which was adjusted to pH ≈ 8.0 with NaOH. The final mixture was sealed in a 15 mL PTFE-lined stainless-steel acid digestion bomb and heated at 170 °C for 96 h to give colorless needle-like crystals of 1 with large quantities of white powder. The pure crystals of 1 were isolated by filtration, washed with distilled water and dried in air. Yield of the reaction was *ca*. 40% based on H₂L. Anal. Calcd for C₃₄H₂₂O₁₂F₁₂Cd₃: C, 34.38%, H 1.87%; found C, 34.51%, H, 1.95%. IR(KBr,cm⁻¹): 3447(s), 1597(m), 1547(m), 1412(m), 1291(w), 1254(m), 1212(m), 1175(m), 1141(w), 1022(w), 971(w), 944(w), 930(w), 858(w), 782(w), 749(w), 726(m), 690(w).

Synthesis of $\{Ni(L)(bipy)\}_{\mu}$ (2). $Ni(NO_3)_2 \cdot 6H_2O$ (29.08 mg, 0.1 mmol) was added to an aqueous solution of H_2L (12 mg, 0.03 mmol) and bipy (5 mg, 0.03 mmol), which was adjusted to pH \approx 8.0 with NaOH. The final mixture was sealed in a 15 mL PTFE-lined stainless-steel acid digestion bomb and heated at 180 °C for 45 h to give green rhombohedra crystals of 2 with large quantities of white powder. The pure crystals of 2 were isolated by filtration, washed with copious quantities of ethanol and dried under ambient conditions. Yield of the reaction was *ca.* 67% based on H₂L. Anal. Calcd for $C_{27}H_{16}F_6O_4N_2Ni$: C, 53.59%, H, 2.67%, N, 4.63%; found C, 53.70%, H, 2.55%, N, 4.56%. IR (KBr, cm⁻¹): 3425(m), 1622(s), 1609(s), 1565(m), 538(m), 1488(w), 1428(s), 1414(s), 1401(s), 1319(w), 1292(m), 1244(s), 1216(s), 1178(s), 1140(m), 1068(w), 1046(w), 1023(w), 972(m), 932(m), 860(m), 843(w), 814(m), 782(m), 749(w), 726(m), 690(w), 635(m), 576(w), 544(w), 503(m).

Synthesis of $\{Cu_3(L)_2(bipy)(\mu_2-OH)_2(DMF)_2\}_n$ (3). A mixture of H_2L (12 mg, 0.03 mmol), bipy (5 mg, 0.03 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (24.16 mg, 0.1 mmol), and H_2O-DMF (1:4, v/v, 8 mL) was sealed in a 15 mL PTFE-lined stainless-steel acid digestion bomb and heated at 90 °C for 24 h and then was cooled to give large quantities of blue block crystals of 3 together with some unrecognized absinthe-green polycrystalline materials. The pure crystals of 3 were isolated by manual separation, washed with DMF and water and dried in air. Yield of the reaction was ca. 32% based on H₂L. Anal. Calcd for C₅₀H₄₀F₁₂O₁₂N₄Cu₃: C, 45.93%, H, 3.08%, N, 4.29%; found C, 45.41%, H, 3.38%, N, 4.12%. IR(KBr, cm⁻¹): 3415(m), 1671(s), 1610(s), 1558(m), 1549(m),1494(w), 1417(m),1387(s), 1324(w), 1291(m), 1252(s), 1240(m), 1224(m), 1207(m), 1172(s), 1143(m), 1133(m), 1096(m), 1078(m), 1047(w), 1019(w), 970(w), 942(w), 930(w), 859(w), 847(w), 827(w), 781(m), 748(m), 726(m), 687(w), 644(w), 542(w), 484(w), 458(m).

Synthesis of $\{Co_2L_2(H_2L)(H_2O)\}_n$ (4). A mixture of H_2L (12 mg, 0.03 mmol), $CoCl_2 \cdot 6H_2O$ (23.79 mg, 0.1 mmol), and H_2O -DMF (8 mL/1 drop) was sealed in a 15 mL PTFE-lined stainless-steel acid digestion bomb and heated at 160 °C for 48 h and then was cooled to give a little of purple needle-like crystals of 4, which were isolated by filtration, and air-dried after washed with DMF and water. Yield of the reaction could not be

calculated for the product was lack and unsuccessfully repeated. Anal. Calcd for $C_{51}H_{28}F_{18}O_{13}Co_2$: C, 46.81%, H, 2.16%; found C, 46.61%, H, 2.25%. IR(KBr, cm⁻¹): 3414(s), 1697(s), 1637(s), 1616(s), 1576(m), 1560(m), 1539 (m),1 504(w), 1427(m), 1387(s), 1329(w), 1289(m), 1254(s), 1209(s), 1176(s), 1141(m), 1021(w), 971(w), 945(w), 930(w), 861(w), 844(w), 827(w), 783(m), 747(m), 724(m), 690(w), 623(w), 559(w), 491 (w), 473(w).

X-Ray crystallography

Single crystals of 1–4 were prepared by the methods described in the synthetic procedure. X-ray crystallographic data of 1 was collected at 123 K, and 2–4 were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structures of 1–4 were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedures based on F^2 values.¹¹ The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The relevant crystallographic data are presented in Table 1, while the selected bond lengths and angles are given in Table S1, ESI.[†]

Results and discussion

Synthesis

The compounds were synthesized by the reaction of $M(NO_3)_2$ (M=Cd, Ni and Cu) or MCl₂ (M=Co) with H_2L and bipy. Solvothermal synthesis was applied to this system for multidimensional coordination compounds. The formation of products was not significantly affected by changes of the reaction mole ratio of the ligands and metal salts. Many parallel experiments proved that the quality of crystals depended on the pH, the solvent and the temperature. Usually high temperature will increase the dimensionality of connection and lead to polymeric compounds, but it will lead to impure products at the same time. We selected proper temperature and the other related factors by repeating parallel experiments. Compounds 1, 2, and 4 were obtained at high temperature above 160 °C for over 45 h, while 3 was obtained at lower temperature of 90 °C for only one day. In addition, the aqueous solution of H_2L in syntheses of compounds 1 and 2 were adjusted to pH \approx 8.0. The resultant crystals are stable in air and insoluble in water or common organic solvents.

Crystal structures

Structure of { $[Cd_3(L)_2(\mu_3-OH)_2(H_2O)]$, H_2O }, (1). The architecture of compound 1 is a three-dimensional open framework. Four crystallographically independent Cd(II) centers exist in an asymmetric unit, in which Cd2 and Cd4 are half occupancy but Cd1 and Cd3 are full occupancy. All the Cd(II) ions are hexacoordinated. As illustrated in Fig. 1a, the Cd1 center presents a slightly distorted octahedron, defined by six oxygen atoms from four different L^{2–} ligands, one μ_3 -OH and one coordinated water. The Cd–O bond distances vary in the range 2.223(4)–2.252(4) Å. Cd2 adopts a octahedral coordination environment, formed by four oxygen atoms from μ_3 -OH which located at an

Compound	1	2	3	4
Empirical formula	$C_{34}H_{22}O_{12}F_{12}Cd_3$	$C_{27}H_{16}F_6O_4N_2N_1$	$C_{50}H_{40}F_{12}O_{12}N_4Cu_3$	$C_{51}H_{28}F_{18}O_{13}Co_2$
Formula weight	1187.72	605.13	1307.48	1308.59
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	C2/c	P2/c
a/Å	7.5227(15)	8.2819(14)	25.003(3)	18.9503(19)
b/Å	14.626(2)	11.300(2)	8.107(2)	7.1992(7)
c/Å	18.9971(18)	14.848(3)	28.4059(19)	23.5351(17)
α (°)	102.432(2)	82.824(3)	90.00	90.00
β (°)	94.761(3)	74.649(4)	116.110(3)	123.836(5)
γ (°)	102.521(2)	71.770(4)	90.00	90.00
V/Å ³	1974.1(5)	1271.4(4)	5170.3(15)	2667.0(4)
Ζ	2	2	4	2
$D_{\rm c}/{\rm g~cm^{-3}}$	1.998	1.581	1.680	1.630
μ/mm^{-1}	1.717	0.845	1.333	0.748
F(000)	1148	612	2636	1308
$\theta \min - \max / \circ$	2.04, 26.00	1.90, 26.00	1.81, 26.00	1.74, 26.00
Tot., uniq. data	10708, 7575	6904, 4879	13420, 5054	13914, 5225
<i>R</i> (int)	0.025	0.0236	0.0362	0.0494
Observed data $[I > 2\sigma(I)]$	5653	3452	3657	3619
Nref, Npar	7575, 538	4879, 344	5054, 368	5225, 384
$R_1, WR_2 [I > 2\sigma(I)]$	0.0488, 0.1077	0.0593, 0.1190	0.0544, 0.0999	0.0636, 0.1339
GOF on F^2	1.079	1.009	1.012	1.002
Min. and max resd dens/e Å ⁻³	-1.14, 1.08	-0.31, 0.42	-0.52, 0.40	-0.39, 0.32

 Table 1
 Crystallographic data and structure refinement details for compounds 1–4

equatorial plane and two oxygen atoms from two L²⁻ ligands at the axial positions with the Cd-O distances ranging from 2.273(4) Å to 2.354(4) Å. It is obvious that the angles of O4#9-Cd2-O4#10, O9-Cd2-O9#11, O10-Cd2-O10#11 around the Cd2 center are all 180°. In contrast, Cd3 exhibits distorted octahedral geometry, which is coordinated by four oxygen atoms from three different L²⁻ ligands and two oxygen atoms from μ_3 -OH, and the distances of Cd-O ranges from 2.196(4) Å to 2.474(4) Å. Cd4 center displays an octahedral coordination environment similar to Cd2. Differently, the equatorial plane is constructed by four oxygen atoms belonging to four different L²⁻ ligands and the axial positions are occupied by two oxygen atoms from μ_3 -OH with the Cd–O distances ranging from 2.156(4) Å to 2.372(4) Å. And the angles of O1-Cd4-O1#2, O9-Cd4-O9#2, O3#6-Cd4-O3#10 are also 180°. A heptanuclear cadmium cluster is formed by seven cadmium atoms (two Cd1, two Cd2, two Cd3 and one Cd4 atoms) belonging to two asymmetric units through Cd-O bonds, which looks like a flower containing six petals.¹² The coordination illustration of the cluster with twelve L2- ligands is shown in Fig. 1a. Each heptanuclear cadmium cluster is connected to two adjacent clusters by two Cd2 atoms resulting in infinite bands constructed of cadmium clusters, which are further bridged by the L^{2-} ligands to complete the overall 3D network (Fig. 1b). The deprotonated carboxylate groups of the L²⁻ ligand adopt three coordination modes respectively (Scheme 1).¹³ The six ligands





along *b* axis use mode-I to coordinate to metal atoms, the other six ligands along *c* axis use both mode-II and III. Although related examples of metal–organic polymers constructed by cadmium clusters have been reported,¹⁴ but the band constructed by the heptanuclear cadmium clusters in compound **1** is unprecedented.

Structure of $\{Ni(L)(bipy)\}_n$ (2). X-Ray diffraction reveals that only one crystallographically independent Ni(II) center is contained in the fundamental asymmetric unit (Fig. 2a). The Ni(II) sites in "4+2" distorted octahedral geometry, defined by two nitrogen donors from two separate bipy ligands occupying the axial positions, and four oxygen atoms from three carboxylate groups of the acid ligands in the equatorial plane. The atoms in one ring of 4,4'pyridine (C23-C27 and N2) were disordered over two positions with occupancies of 0.48 and 0.52, respectively. The Ni-O distances are in the range 1.999(3)-2.121(3) Å, and Ni-N distances vary in the range 2.079(3)-2.15(2) Å, which are comparable to those values found in other reported similar complexes.¹⁵ As shown in Fig. 2b, the L^{2-} ligand acts as a μ_3 -bridge through one μ_2 -bridging carboxylate and two chelating oxygen atoms to link three nickel (II) atoms. The second building unit (SBU) is a dinickel carboxylate moiety ($[Ni_2C_2O_4]$), where two Ni atoms are bridged by two μ_2 -bridging carboxylate groups of two different L²⁻ ligands, with Ni \cdots Ni distance of 4.5058(9) Å. The [Ni₂C₂O₄] SBUs are linked by two L²⁻ ligands to result in a 1D ribbon of $[Ni_2(L)_2]_n$ with the two adjacent dinickel cores distance of 11.6874(24) Å. The two-dimensional (2D) double-layer network structure of **2** is achieved by the bipy ligands coordinating to Ni atoms in two adjacent 1D ribbons, whereas the Ni ··· Ni distance with the bipy bridge is 11.3000(21) Å (Fig. 2c). However, these layers are tightly stacked one by one along the crystallographic a axis (Fig. 2d). The structure of **2** can be simplified into a $\{4^4.6^2\}$ net.





Fig. 1 a View of the metal coordination sphere in compound 1 with 30% ellipsoid probability (Right: the ligands are omitted for clarity). b View of 3D framework of 1 containing the band of cadmium clusters along the *a* axis direction.

Structure of $\{Cu_3(L)_2(bipy)(\mu_2-OH)_2(DMF)_2\}_{\mu}$ (3). As shown in Fig. 3a, the asymmetric unit of 3 contains one and a half Cu(II) ions, one μ_2 -hydroxide, half a bipy ligand, and one L²⁻ ligand. The Cu1 ion sits on the bottom center in a distorted square pyramidal geometry, it is coordinated by two oxygen atoms from two L^{2-} ligands, one oxygen atom from μ_2 -OH and one nitrogen atom from bipy ligand on the basal plane, and the last one oxygen atom from another L^{2-} ligand at the apical position. The Cu-O distances in the square pyramid are in the range from 1.888(2) to 2.351(3) Å, and Cu-N distance is 2.053(3) Å, which are reasonably compared to those values of other reported similar compounds.¹⁶ Cu2 is located in a square environment by two oxygen atoms from two carboxylate groups and two oxygen atoms from μ_2 -OH with the Cu–O distances range from 1.810(2) to 1.945(2) Å, which are compared with those reported compounds.¹⁷ Interestingly, the Cu2 atom is bridged to neighboring two Cu1 atoms by both the μ_2 -OH and carboxyl groups from L²⁻ ligands. The adjacent "Cu1-Cu2-Cu1" units are linked by two carboxyl groups to come into being a zigzag chain of Cu atoms, and the distances of Cu1-Cu2, Cu1-Cu1 are 3.3262(8) and 4.3599(9) Å, respectively (Fig. 3b, left). And the continuous zigzag chains are connected by bipy and L²⁻ ligands in different directions to form the 3D porous framework as exhibited in Fig. 3b (right). With the topological viewpoint, the Cu(II) centers can be viewed as 8connecting nodes, and all crystallographically independent L²⁻ ligands act as 3-connecting nodes, the whole structure can be represented as a new $\{4^3\}_2\{4^6.6^{14}.8^8\}$ net, as displayed in Fig. 3c.

Structure of $\{Co_2(L)_2(H_2L)(H_2O)\}_n$ (4). The structure of 4 is isomorphous with that of the previously reported $[Cu(hfipbb)(H_2hfipbb)_{0.5}]$.¹⁸ The network of compound 4 is a 3D open framework containing only one crystallographically independent Co(II) center in the fundamental asymmetric unit. Each cobalt center has a square pyramidal coordination environment formed by four oxygen atoms from four separate L²⁻ ligands occupying the equatorial plane, and one oxygen atom from one carboxylate group of the protonated H₂L ligand in the axial positions. It is a different coordination mode compared with those of compounds 1–3. Four carboxylate groups of the four L²⁻ ligands, two oxygen atoms of the H₂L ligands, and two Co atoms constructed a paddle-wheel with the Co–Co distance of



Fig. 2 a View of the coordination sphere in compound **2** with 30% ellipsoid probability (the H atoms are omitted for clarity). $\mathbf{b} > A$ 1D ribbon of $[Ni_2(L)_2]_n$ along *c* axis in **2** (the H atoms and bipy ligands are omitted for clarity). **c** View of 2D crystalline framework of **2** (the H atoms are omitted for clarity). **d** Schematic representations of interdigitation between layers in compound **2** (the H atoms and bipy ligands are omitted for clarity).

2.9073(10) Å as shown in Fig. 4a. Each paddle-wheel unit binds to four adjacent paddle-wheel units through the four remaining carboxylate groups of L^{2-} to form an undulating 2D network. A layered structure is formed by two such identical networks consisting of micro channels, as shown in Fig. 4b. The adjacent layers are further interconnected by monodentate carboxylate groups of H₂L ligands in the axial position to generate a 3D duplicate interpenetrated network (Fig. 4c). A better insight into the nature of **4** can be achieved by regarding paddle-wheel unit as a six-connected node and the L²⁻ ligand as a linear linker to reduce multidimensional structures to simple node-and-linker nets. The simplified structure of **4** is a duplicate interpenetrated {4¹².6³} net topology (Fig. 4d).

Magnetic properties

To investigate the magnetic properties of **3**, the temperature dependence of the magnetic susceptibility was investigated by applying a magnetic field of 2000 Oe in the temperature range 1.8–300 K. $\chi_M T$ and χ_M versus T data for **3** are shown in Fig. 5. The $\chi_M T$ product of **3** at 300 K is 1.41 cm³ mol⁻¹ K, slightly above the value expected for three non-interacting S = 1/2 copper(II) ions (1.36 cm³ mol⁻¹ K for g = 2.2). This, along with the increase of $\chi_M T$ upon cooling to a maximum of 1.91 cm³ mol⁻¹ K at 14 K, indicates the interplay of ferromagnetic interactions. Upon further cooling, the $\chi_M T$ product drops abruptly to a value of 1.26 cm³ mol⁻¹ K at 1.8 K, suggesting the effect of antiferromagnetic interactions

Fig. 3 a View of the coordination sphere in compound **3** with 30% ellipsoid probability (the H atoms are omitted for clarity). **b** View of 3D framework of **3** (right) containing the zigzag chain (left) of Cu atoms along the *b* axis direction. (H atoms are omitted for clarity). **c** Topological illustration for the 3,8-connected network of **3**. Blue nodes represent Cu atoms and yellow nodes represent L^{2-} ligands.

and/or zero-field splitting at low temperatures. Since compound **3** has a trinuclear structure in which the Cu(II) ions are bridged by both carboxylate oxygen atoms and μ_2 -O atoms, the magnetic susceptibility data can be analyzed by the following expression based on a Heisenberg Hamiltonian $H = -2J(S_1S_2+S_1S_3) - 2J'S_2S_3$:¹⁹

$$\chi_{\rm M} = \frac{Ng^2\beta^2}{4kT} \times \frac{1 + e^{2J - 2J'/kT} + 10e^{3J/kT}}{1 + e^{2J - 2J'/kT} + 2e^{3J/kT}}$$

Where J and J' are the coupling constants, N, g, β , and k have their usual meanings. The best fit shown as the solid line in Fig. 7,

results in parameters g = 2.16, J = 29.73 cm⁻¹, and J' = 6.54 cm⁻¹ with $R = [(\chi_M T)_{calcd} - (\chi_M T)_{obsd}]^2 / (\chi_M T)_{obsd}^2 = 2 \times 10^{-5}$.

Photoluminescent properties

The photoluminescent properties of the Compounds 1–4 were studied in the solid state at room temperature, but only 1 is observed to have a fluorescence at room temperature (Fig. S1, ESI†). 1 showed a broad, weak violet photoluminescence around 425 nm upon excitation at 340 nm in the solid state, which suggest that the fluorescence of 1 is caused by the ligand. There is no obvious emission obtained for the free H_2L ligand under the same

Fig. 4 a View of the coordination sphere in compound **4** with 30% ellipsoid probability (H atoms and labels of C atoms in ph are omitted for clarity). **b** The illustration of interpenetration in **4** by two 2D nets, identical in structure (shown in solid and translucent). **c** View of 3D crystalline framework of **4** (the duplicate interpenetrations are shown in green and red, respectively). **d** the AB packing mode of the 6-connected layers.

Fig. 5 Plot of $\chi_M T$ and $\chi_M vs T$ for **3**. The solid line represent the best simulations obtained with the models described in the text.

experimental conditions. Therefore, the visible light emission of 1 can be assigned to the decrease of non-radiative vibrational transitions in the L unit, which arises from the coordination to Cd(II) centers.²⁰

Conclusions

In this work, four new compounds have been successfully synthesized under solvothermal conditions. The results proved that the alliance of H_2L and bipy ligands is good for diversity of the possible compound structures. Magnetic studies indicate that compound **3** exhibits ferromagnetic coupling between adjacent Cu(II) ions. The results reveal that the coordination mode of the H_2L ligand and the introduction of an auxiliary bipy ligand are important in the formation of coordination frameworks and would enrich the diversity of structures and topologies. Subsequent works will be focused on the structures and properties of a series of coordination compounds constructed by different linear assistant bipy ligands and H_2L ligand.

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References

- (a) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460–1494;
 (b) M. Eddaoudi, H. L. Li and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 1391–1397;
 (c) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–714.
- 2 (a) M. Eddaoudi, J. Kim, N. L. Rosi, D. T. Vodak, J. Wachter, M. O' Keeffe and O. M. Yaghi, Science, 2002, 295, 469–472; (b) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, Nature, 2005, 436, 238–241; (c) Y. Q. Li, L. Xie, Y. Liu, R. Yang and X. G. Li, Inorg. Chem., 2008, 47, 10372–10377; (d) P. D. C. Dietzel, R. E. Johnsen, H. Fjellvag, S. Bordiga, E. Groppo, S. Chavanc and R. Blom, Chem. Commun., 2008, 5125–5127; (e) H. P. Chun and H. J. Jung, Inorg. Chem., 2009, 48, 417–419.
- (a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982–986; (b) Y. Cui, O. R. Evans, H. L. Ngo, P. S. White and W. Lin, *Angew. Chem., Int. Ed.*, 2002, **41**, 1159–1162; (c) C. D. Wu, A. G. Hu, L. Zhang and W. B. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940–8941; (d) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastre, *J. Mater. Chem.*, 2006, **16**, 626–636; (e) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. B. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459.
- 4 (a) J. Pang, E. J. P. Marcotte, C. Seward, R. S. Brown and S. Wang, Angew. Chem., Int. Ed., 2001, 40, 4042–4045; (b) S. L. Zheng, J. H. Yang, X. L. Yu, X. M. Chen and W. T. Wong, Inorg. Chem., 2004, 43, 830–838; (c) Y. Q. Huang, B. Ding, H. B. Song, B. Zhao, P. Ren, P. Cheng, H. G. Wang, D. Z. Liao and S. P. Yan, Chem. Commun., 2006, 4906–4908; (d) C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons and M. D. Allendorf, J. Am. Chem. Soc., 2007, 129, 7136–7144; (e) Z. Chang, A. S. Zhang, T. L. Hu and Xian-He Bu, Cryst. Growth Des., 2009, 9, 4840–4846.
- (a) R. Clerac, H. Miyasaka, M. Yamashita and C. Coulon, J. Am. Chem. Soc., 2002, 124, 12837–12844; (b) L. K. Thompson, Ed. Special issue on MagnetismsMolecular and Supramolecular Perspectives, Coord. Chem. Rev., 2005, 249, 2549–2730; (c) C. S. Liu, J. J. Wang, L. F. Yan, Z. Chang, X. H. Bu, E. C. Sañudo and J. Ribas, Inorg. Chem., 2007, 46, 6299– 6310; (d) S. L. Veber, M. V. Fedin, A. I. Potapov, K. Y. Maryunina, G. V. Ronko, R. Z. Sagdeev, V. I. Ovcharenko, D. Goldfarb and E. G. Bagryanskaya, J. Am. Chem. Soc., 2008, 130, 2444–2445; (e) Z. R. Pan, H. G. Zheng, T. W. Wang, Y. Song, Y. Z. Li, Z. J. Guo and S. R. Batten, Inorg. Chem., 2008, 47, 9528–9536; (f) C. G. Carson, K. Hardcastle, J. Schwartz, X. T. Liu, C. Hoffmann, R. A. Gerhardt and R. Tannenbaum, Eur. J. Inorg. Chem., 2009, 2338–2343; (g) J. P. Zhao, B. W. Hu, Q. Yang, X. F. Zhang, T. L. Hu and X. H. Bu, Dalton Trans., 2010, 39, 56–58.
- 6 (a) D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim and K. Kim, J. Am. Chem. Soc., 2004, 126, 32–33; (b) M. Dinca and J. R. Long, J. Am. Chem. Soc., 2005, 127, 9376–9377; (c) B. L. Chen, S. Q. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky and H. C. Zhou, Inorg. Chem., 2007, 46, 1233–1236; (d) D. Dubbeldam, C. J. Galvin, K. S. Walton, D. E. Ellis and R. Q. Snurr, J. Am. Chem. Soc., 2008, 130, 10884–10885; (e) J. R. Li, R. J. Kuppler and H. C. Zhou, Chem. Soc. Rev., 2009, 38, 1477–1504.

- 7 (a) O. M. Yaghi, H. L. Li, C. Davis, D. Richardson and T. L. Groy, Acc. Chem. Res., 1998, 31, 474–484; (b) H. Chun, D. Kim, D. N. Dybtsev and K. Kim, Angew. Chem., Int. Ed., 2004, 43, 971–971; (c) C. Livage, P. M. Forster, N. Guillou, M. M. Tafoya, A. K. Cheetham and G. Ferey, Angew. Chem., Int. Ed., 2007, 46, 5877–5879; (d) F. Luo, Y. X. Che and J. M. Zheng, Cryst. Growth Des., 2009, 9, 1066–1071; (e) J. Xu, Z. R. Pan, T. W. Wang, Y. Z. Li, Z. J. Guo, S. R. Batten and H. G. Zheng, CrystEngComm, 2010, 12, 612–619.
- 8 (a) B. F. Hoskins and R. Robson, J. Am. Chem. Soc., 1990, 112, 1546–1554; (b) R. Robson, J. Chem. Soc., Dalton Trans., 2000, 3735–3744; (c) M. Eddaoudi, D. B. Moler, H. L. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, Acc. Chem. Res., 2001, 34, 319–330.
- 9 (a) A. Monge, N. Snejko, E. Gutiérrez-Puebla, M. Medina, C. Cascales, C. R. Valero, M. Iglesias and B. Gómez-Lor, *Chem. Commun.*, 2005, 1291–1293; (b) J. Y. Lee, J. Li and J. Jagiello, *J. Solid State Chem.*, 2005, **178**, 2527–2532; (c) F. Gándara, A. D. Andrés, B. Gómez-Lor, E. Gutiérrez-Puebla, M. Iglesias, M. A. Monge, D. M. Proserpio and N. Snejko, *Cryst. Growth Des.*, 2008, **8**, 378–380; (d) B. V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J. L. Jord, H. Garca, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem., Int. Ed.*, 2008, **47**, 1080–1083.
- 10 (a) W. B. Yang, X. Lin, A. J. Blake, C. Wilson, P. Hubberstey, N. R. Champness and Martin Schröder, *Inorg. Chem.*, 2009, **48**, 11067–11078; (b) F. Gándara, M. E. Medina, N. Snejko, E. Gutiérrez-Puebla, D. M. Proserpioc and M. A. Monge, *CrystEngComm*, 2010, **12**, 711–719; (c) P. Pachfule, C. Dey, T. Panda, K. Vanka and Rahul Banerjee, *Cryst. Growth Des.*, 2010, **10**, 1351–1363.
- 11 Bruker 2000, SMART (Version 5.0), SAINT-plus (Version 6), SHELXTL (Version 6.1), and SADABS (Version 2.03), Bruker AXS Inc., Madison, WI.
- 12 S Park, S. Y. Lee, M. Jo, J. Y. Lee and S. S. Lee, *CrystEngComm*, 2009, 11, 43–46.
- 13 N. L. Rosi, J. Kim, M. Eddaoudi, B. L. Chen, M. O'Keeffe and O. M. Yaghi, J. Am. Chem. Soc., 2005, 127, 1504–1518.
- 14 (a) J. Forniés, J. Gómez, E. Lalinde and M. T. Moreno, *Inorg. Chem.*, 2001, 40, 5415–5419; (b) Q. R. Fang, G. S. Zhu, Z. Jin, M. Xue, X. Wei, D. J. Wang and S. L. Qiu, *Angew. Chem.*, *Int. Ed.*, 2006, 45, 6126–6130; (c) Z. Li, M. Li, X. P. Zhou, T. Wu, D. Li and S. W. Ng, *Cryst. Growth Des.*, 2007, 7, 1992–1998; (d) V. Chandrasekhar, P. Sasikumar and R. Boomishankar, *Dalton Trans.*, 2008, 5189–5196.
- 15 G. Aromi, P. Gamez, O. Roubeau, P. Carrero-Berzal, H. Kooijman, A. A. L. Spek, W. L. Driessen and J. Reedijk, *Eur. J. Inorg. Chem.*, 2002, 1046–1048.
- 16 M. Ahlgren, U. Turpeinen and K. Smolander, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1980, 36, 1091–1095.
- 17 E. Yang, F. F. Yang and S. Y. Chen, Acta Crystallogr., Sect. E: Struct. Rep. Online, 2006, 62, m1586.
- 18 (a) L. Pan, M. B. Sander, X. Y. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath and J. K. Johnson, *J. Am. Chem. Soc.*, 2004, **126**, 1308–1309; (b) L. Pan, D. H. Olson, L. R. Ciemnolonski, R. Heddy and J. Li, *Angew. Chem., Int. Ed.*, 2006, **45**, 616–619.
- 19 O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, 1993.
- 20 L. Zhang, Z. J. Li, Q. P. Lin, J. Zhang, P. X. Yin, Y. Y. Qin, J. K. Cheng and Y. G. Yao, *CrystEngComm*, 2009, **11**, 1934–1939.