CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

Journal Name RSCPublishing

ARTICLE

Syntheses, structures, magnetic and luminescent properties of a series of coordination polymers constructed from 1,4-naphthalenedicarboxylic and N-donor ligands

aCite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Liu Yang, Chao Qin,* Bai-Qiao Song, Xiao Li, Chun-Gang Wang and Zhong-Min Su*

Five new coordination polymers constructed from 1,4-naphthalenedicarboxylic and N-donor ligands including $[Cd_2(1,4\text{-ndc})_2(bpy)_2]\cdot0.5H_2O$ (**1**), $[Cd(1,4\text{-ndc})(phen)]\cdot0.5H_2O$ (**2**), $[Cu_2(1,4\text{-ndc})_2(L1)]\cdot H_2O$ (**3**), $[Co_3(H_2O)_2(1,4\text{-ndc})_4(HL2)_2]$ (**4**), $[Cd_2(NO_3)_2(1,4\text{-ndc})(L3)_2]\cdot H_2O$ (**5**) have been synthesized under hydrothermal conditions and characterized by elemental analysis, infrared spectrometry, powder X-ray diffraction and single crystal X-ray diffraction. Compounds **1** and **2** are 2D layers with 4-connected $(4^4\cdot6^2)$ topology. Compound **3** is a 3D two-fold interpenetrating **pcu** network based on binuclear cluster. Compound **4** exhibits an eight-connected **bcu** network constructed by trinuclear cluster. Compound **5** is a 3D two-fold interpenetrating network with uninodal 4-connected CdS ($CdSO_4$) topology. Furthermore, magnetic properties of compounds **3** and **4** were investigated and photoluminescent properties of compounds **1**, **2** and **5** show that the three compounds have strong emissions under λ_{ex} = 320 nm at room temperature.

Introduction

In recent years, the preparation of new coordination polymers has been significantly provoked not only because of their aesthetically beautiful architectures and topologies but also their potential applications in diverse areas such as catalysis, lithium batteries, drug delivery, explosives detection, optoelectronics, supramolecular storage of molecules, molecular magnetism, gas storage, chemical separations, microeletronics, nonlinear optics.[1-8] Although the term coordination polymer was created in 1964, the principles of "crystal engineering" to design coordination polymers were not applied until 1995.[9] In crystal engineering, the final structures of coordination polymers rely upon a large amount of factors, such as flexibility, shape, symmetry, length and substituent groups. It means that the coordination geometry of the metal ions and the chemical nature of the organic ligands are of the importance, but it still remains a long-term challenge for crystal engineers to rationally design and construct the desired coordination polymers through controlling the factors that can affect their structures.[1-6] Generally, the nonrigid N-containing ligands are apt to be used in polymeric coordination networks, but it is not easy to predict the structures of coordination polymers constructed by nonrigid ligands since the nonrigid ligands can freely rotate and these ligands may potentially provide various coordination modes according to the coordination geometry of the metal ions.[5-8,10] As we known, an increasing number of networks incorporating carboxylate ligands and nonrigid N-containing ligands have been reported and we are interested in the coordination polymers containing such kinds of mixed ligands.

Recently, dicarboxylate ligands have been proven to be good candidates for the preparation of coordination polymers, because they can be regarded not only as hydrogen-bonding acceptors but also as hydrogen-bonding donors.[11] Herein, we chose 1,4-naphthalenedicarboxylic ($1,4\text{-}H_2ndc$) which can afford various coordination modes and influence the final structures of coordination polymers during the assembly and varied N-containing ligands to form a series of mixed-ligand compounds, namely $[Cd_2(1,4\text{-ndc})_2(bpy)_2]\cdot0.5H_2O$ (**1**), $[Cd(1,4\text{-ndc})(phen)]\cdot0.5H_2O$ (**2**), $[Cu_2(1,4\text{-ndc})_2(L1)]\cdot H_2O$ (**3**), $[Co_3(H_2O)_2(1,4\text{-ndc})_4(HL2)_2]$ (**4**), $[Cd_2(L3)_2(1,4\text{-}H_2ndc)]\cdot H_2O$ (**5**). (L1 = 1,3-bis(1,2,4-triazol-1-yl)propane, L2 = 1,6-bis(imidazol)hexane, L3 = 4,4'-di(1H-imidazol-1-yl)biphenyl, $1,4\text{-}H_2ndc$ = 1,4-naphthalenedicarboxylic). Meanwhile, some reported works on 1,4-naphthalenedicarboxylic and other N-donor ancillary ligands also support our works.[12] In this article, we report their syntheses, crystal structures, magnetic and photoluminescent properties.

Experimental

Materials and physical measurements

All reagents and solvents for syntheses were purchased from commercial sources and used as received without further purification. IR spectra were recorded in the range 4000-400 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 °C under nitrogen atmosphere at a rate of 10 °C min^{-1}. Fluorescence spectra for the compounds were recorded on an F-4600 FL Spectrophotometer equipped with a xenon lamp and quartz carrier at room temperature. PXRD patterns were recorded on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418Å) radiation in the range of 3-50° at 293 K. Variable-temperature magnetic susceptibility data were obtained in the temperature range of 2-300 K using a SQUID magnetometer (Quantum Design, MPMS-5) with an applied field of 1000 Oe.

Synthesis of [Cd_2(1,4-ndc)$_2$(bpy)$_2$]·0.5H_2O (1). A mixture of 1,4-H_2ndc (22 mg, 0.1 mmol), bpy (15.6 mg, 0.1mmol) and $Cd(NO_3)_2\cdot 4H_2O$ (30.8 mg, 0.1 mmol) in distilled water (8 mL) was stirred for 10 min at room temperature and then heated in a 23 mL Teflon-lined autoclave at 140 °C for 3 days. After being cooled to ambient temperature over a period of 24 h at a rate of 5 °C h^{-1}, colorless blocks of crystals of **1** were obtained, which were washed with water and dried in air. Yield: 26 mg (53% based on Cd). Anal. calcd for $C_{44}H_{29}Cd_2N_4O_{8.5}$: C 54.23; H 3.00; N 5.75. Found: C 54.15; H 3.08; N 5.69. IR (KBr, cm^{-1}): 3652m, 3060m, 1591s, 1554s, 1469m, 1405s, 1357s, 1251m, 1153m, 1055m, 870w, 835m, 790m, 765s, 734m, 647m, 623m, 585mm, 562s, 503m, 439s, 408s

Table 1. Crystal data and structure refinement for compounds 1-5.

Compound reference	1	2	3	4	5
Chemical formula	$C_{44}H_{29}Cd_2N_4O_{8.5}$	$C_{24}H_{15}CdN_2O_{4.5}$	$C_{31}H_{24}Cu_2N_6O_9$	$C_{72}H_{66}Co_3N_8O_{18}$	$C_{48}H_{36}Cd_2N_{10}O_{11}$
Formula weigh	974.51	515.78	751.64	1508.12	1153.67
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	11.057(5)	11.561(5)	15.0315(14)	15.481(5)	9.7473(19)
b (Å)	12.600(5)	14.705(5)	10.8209(10)	15.415(5)	15.238(3)
c (Å)	13.982(5)	11.867(5)	20.3310(19)	15.994(5)	30.160(6)
α (°)	82.660(5)	90.00	90.00	90.00	90.00
β (°)	84.841(5)	95.169(5)	106.002(2)	118.221(5)	93.463(3)
γ (°)	82.541(5)	90.00	90.00	90.00	90.00
V (Å^3)	1910.3(13)	2009.2(14)	3178.8(5)	3363.1(19)	4471.4(14)
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Z	2	4	4	2	4
D_{calcd} (g · cm^{-3})	1.694	1.705	1.571	1.489	1.714
GOF on F^2	1.029	1.027	1.023	1.020	1.018
R_1 [$I > 2\sigma(I)$]^a	0.0357	0.0294	0.0474	0.0439	0.0821
wR_2 [$I > 2\sigma(I)$]^b	0.0845	0.0660	0.0834	0.1071	0.2085
$R_1{}^a$ (all data)	0.0538	0.0447	0.0923	0.0630	0.1349
w$R_2{}^b$ (all data)	0.0930	0.0717	0.0925	0.1172	0.2446
R_{int}	0.0318	0.0407	0.0635	0.0393	0.0808

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o$. ^{b} w$R_2 = |\sum w(|F_o|^2 - |F_c|^2)|/\sum|w(F_o{}^2)^2|^{1/2}$

Synthesis of [Cd(1,4-ndc)(phen)]·0.5H$_2$O (2). **2** was isolated by using the similar method to that of **1**, where phen (19.8 mg, 0.1 mmol) was utilized in place of bpy. Colorless blocks of crystals products were obtained, which were washed with water and dried in air. Yield: 37 mg (71% based on Cd). Anal. calcd for $C_{24}H_{15}CdN_2O_{4.5}$: C 55.89; H 2.93; N 5.43. Found: C 55.78; H 3.04; N 5.39. IR (KBr, cm^{-1}): 3623m, 3065w, 1741w, 1699w, 1565m, 1539m, 1458m, 1405s, 1361s, 1260m, 1212m, 1143w, 1098w, 970w, 872m, 841m, 805m, 777s, 725m, 638w, 579m, 548w, 439w.

Synthesis of [Cu$_2$(1,4-ndc)$_2$(L1)]·H$_2$O (3). **3** was isolated by using the similar method to that of **1**, where L1 (17.8 mg, 0.1 mmol) and Cu(NO$_3$)$_2$·3H$_2$O (24.2 mg, 0.1 mmol) were utilized in place of bpy and Cd(NO$_3$)$_2$·4H$_2$O. Green blocks of crystals products were obtained, which were washed with water and dried in air. Yield: 17 mg (45% based on Cu). Anal. calcd for $C_{31}H_{24}Cu_2N_6O_9$: C 49.54; H 3.22; N 11.18. Found: C 49.23; H 3.34; N 11.09 IR (KBr, cm^{-1}): 3481m, 3139w, 1617s, 1525m, 1461m, 1416s, 1367s, 1264m, 1212m, 1158w, 1130m, 1038w, 991w, 890w, 860w, 832m, 798m, 785m, 749w, 679m, 653w, 595m, 529w, 471w, 421w.

Synthesis of [Co$_3$(H$_2$O)$_2$(1,4-ndc)$_4$(HL2)$_2$] (4). **4** was isolated by using the similar method to that of **1**, where L2 (21.8 mg, 0.1 mmol) and CoCl$_2$·6H$_2$O (23.8 mg, 0.1 mmol) were utilized in place of bpy and Cd(NO$_3$)$_2$·4H$_2$O. Colorless blocks of crystals were obtained, which were washed with water and dried in air. Yield: 23 mg (46% based on Co). Anal. calcd for $C_{72}H_{66}Co_3N_8O_{18}$: C 57.34; H 4.41; N 7.43. Found: C 57.21; H 4.19; N 7.61. IR (KBr, cm^{-1}): 3130m, 3064w, 1619s, 1564s, 1524m, 1511m, 1460m, 1410s, 1365s, 1281m, 1263m, 1207m, 1103m, 1089m, 1034m, 942w, 904w, 863m, 821m, 802m, 789s, 744m, 662m, 633m, 579w, 558w, 519w, 448m.

Synthesis of [Cd$_2$(NO$_3$)$_2$(1,4-ndc)(L3)$_2$]·H$_2$O (5). **5** was isolated by using the similar method to that of **1**, where L3 (28.6 mg, 0.1 mmol) was utilized in place of bpy. Colorless blocks of crystals products were obtained, which were washed with water and dried in air. Yield: 23 mg (40% based on Cd). Anal. calcd for $C_{48}H_{36}Cd_2N_{10}O_{11}$: C 49.97; H 3.15; N 12.14. Found: C 50.13; H 2.98; N 12.29. IR (KBr, cm^{-1}): 3627m, 3128m, 1554s, 1516s, 1458m, 1403m, 1358m, 1298s, 1258s, 1155w, 1068m, 1031m, 1004w, 961m, 841m, 816m, 802m, 686w, 650m, 621m, 582w, 560w, 519m, 437w.

Crystallographic data collection and refinement

Single-crystal X-ray diffraction data for **1**-**5** were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromator using Mo-Kα radiation (λ = 0.71073 Å) by using the Φ/ω scan technique at room temperature and there was no evidence of crystal decay during data collection. A multiscan technique was used to perform adsorption corrections. The crystal structures of **1**-**5** were solved using direct methods and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXL-97 program.[13] In the case of **3**, the rest solvents cannot be exactly assigned from the very weak refelctions. Thus, the SQUEEZE program was used to remove the contribution of these weak reflections. In the case of **4**, the carbon chain group was found to be disordered on two sites with an occupancy factor of 0.70/0.30 for C4/C4A and C7/C7A. In the case of **5**, the L3 ligands and one NO$_3^-$ anion were found to be disordered over two sites and the imidazole ring of the L3 was refined as a rigid group since the atoms are not planar. All non-hydrogen atoms refined anisotropically. The hydrogen atoms of the free water molecules could not be theoretically generated and they were also not added by difference Fourier maps due to the lack of large enough Q peaks around the water oxygen atoms. The hydrogen atoms of all the organic ligands were generated theoretically and refined with isotropic thermal parameters. Pertinent crystallographic data collection and structure refinement parameters for **1**-**5** are collated in Table 1. Selected bond lengths and angles for **1**-**5** were listed in Table S1 (ESI†).

Results and discussion

The five compounds are constructed from 1,4-naphthalenedicarboxylic and N-donor ancillary ligands. **1** and **2** are isostructural with 2D layers. **3**-**5** have 3D structures based on different flexible N-donor ancillary ligands and metal salts which lead to different coordination environments and different topologies. Detailed descriptions are listed.

Crystal structure of [Cd$_2$(1,4-ndc)$_2$(bpy)$_2$]·0.5H$_2$O (1) and [Cd(1,4-ndc)(phen)]·0.5H$_2$O (2).

1 and **2** crystallize in the triclinic space group $P\bar{1}$ and monoclinic space group $P2_1/c$. Single-crystal X-ray diffraction analyses revealed that **1** and **2** have similar structures and topologies. As a result, **1** is described in detail as a representative structure. As shown in Fig. 1a, there exist two Cd(II) ions, two 1,4-ndc ligands, two bpy ligands, and a half lattice water molecule in the asymmetric unit of **1**. Each Cd(II) ion has a distorted octahedral geometry which is surrounded by four O atoms from three different 1,4-ndc ligands, and two N atoms from one bpy ligand. The Cd-O bonds range from 2.232(3) Å to 2.410(3) Å and Cd-N distances are from 2.309(4) Å to 2.347(4) Å. While, the asymmetric unit of **2** contains one Cd(II) ion, one 1,4-ndc ligand, one phen ligand and a half lattice water molecule. The central Cd(II) ion is surrounded by five O atoms from three 1,4-ndc ligands, and two N atoms from one phen ligand (Fig. 1b). In **1** and **2**, The two neighboring Cd(II) ions are linked by two carboxylate groups to form a binuclear unit. Each adjacent binuclear unit is connected by two carboxylate groups to form a linear chain in one orientation (Fig. 1c). On the other orientation, each adjacent binuclear unit is connected by two bridging 1,4-ndc ligands to form a 2D layer with the linear chains (Fig. 1d). Topologically, if the centroids of two central Cd(II) ions are viewed as 4-connected nodes, respectively, the overall motif of **1** will be a 2D uninodal 4-connected network with a sql with point symbol ($4^4 \cdot 6^2$) topology (Fig. 1e). Some networks with sql topology have been reported.[14]

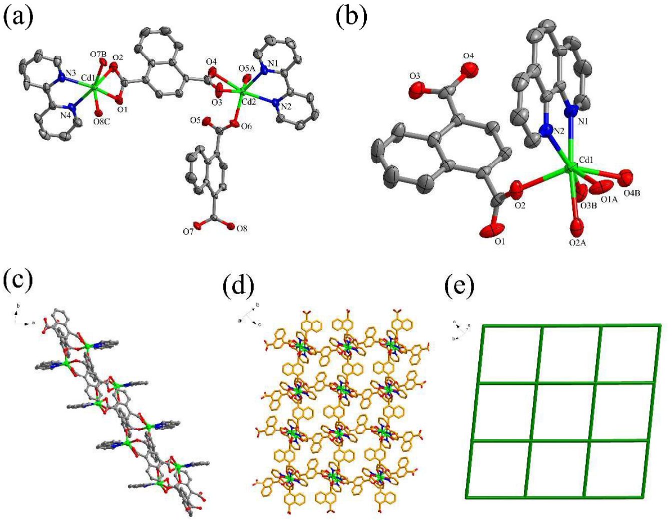

Fig. 1 (a) Cd(II) coordination environments of **1**. Symmetry codes: (A) −x, −y + 1, −z + 1; (B) x, y, z – 1; (C) −x + 1, −y, −z + 1. (b) Cd(II) coordination environments of **2**. Symmetry codes: (A) −x, −y + 1, −z; (B) x − 1/2, −y + 1/2, z − 1/2. (c) A linear chain in one orientation of **1**. (d) 2D layer of **1**. (e) 2D uninodal 4-connected network with a sql with point symbol $(4^4\cdot6^2)$ topology of **1**. All hydrogen atoms are omitted for clarity. The green, red and blue represent cadmium, oxygen and nitrogen atoms, respectively.

Crystal structure of $[Cu_2(1,4\text{-ndc})_2(L1)]\cdot H_2O$ (3).

3 crystallizes in the monoclinic space group $P2_1/n$. The independent unit of **3** is composed of two Cu(II) ions, two 1,4-ndc ligands, one L1 ligand and one lattice water molecule. Each central Cu(II) ion is five-coordinated with a square pyramidal geometry which is surrounded by four O atoms from four different 1,4-ndc ligands, and one N atom from one L1 ligand. The Cu-O distances are from 1.919(2) Å to 2.0552(19) Å. The Cu-N distances are from 2.115(3) Å to 2.145(3) Å (Fig. 2a). The two neighboring Cu(II) ions are linked by two carboxylate groups to form a binuclear {Cu2} unit and thus the {Cu2} units are connected by 1,4-ndc ligands to form a 2D $[Cu(1,4\text{-ndc})]_n$ layer parallel with the *bc* plane (Fig. 2b). Each of 2D net is further linked by 1,4-ndc ligands and L1 ligands along the *a* axis to form a 3D framework where each 1,4-ndc ligand connects four Cu(II) ions. The 3D framework is interpenetrated by a crystallographic equivalent net to form a two-fold interpenetrating 3D framework (Fig. 2c). Topologically, if the {Cu2} units are viewed as 6-connected nodes, respectively, the overall motif of **3** will be a 3D uninodal 6-connected network with a pcu with point symbol $(4^{12}\cdot6^3)$ topology (Fig. 2d). Some networks with pcu topology have been reported.[15]

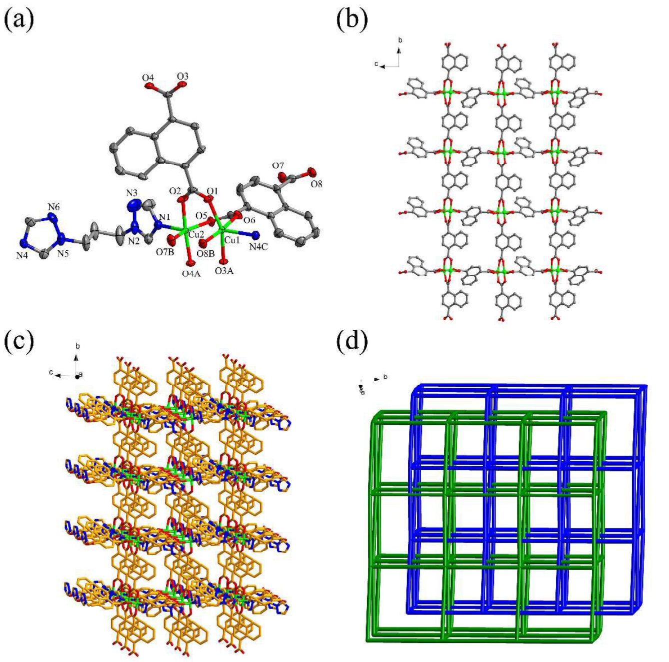

Fig. 2 (a) Cu(II) coordination environments of **3**. Symmetry codes: (A) x, y − 1, z; (B) x − 1/2, −y + 1/2, z − 1/2; (C) x − 1/2, −y + 1/2, z + 1/2. (b) View of the 2D $[Cu(1,4\text{-ndc})]_n$ net from the *bc* plane layer of **3**. (c) 3D framework of **3**. (d) 3D uninodal 6-connected network with a pcu with point symbol $(4^{12}\cdot6^3)$ topology of **3**. All hydrogen atoms are omitted for clarity. The green, red and blue represent copper, oxygen and nitrogen atoms, respectively.

Crystal structure of $[Co_3(H_2O)_2(1,4\text{-ndc})_4(HL2)_2]$ (4).

4 crystallizes in the monoclinic space group $P2_1/n$. There exist one and a half Co(II) ions, two 1,4-ndc ligands, one protonated L2 ligand and one coordination water molecule in the asymmetric unit. Although each of two Co(II) ions is six-coordinated with a distorted octahedral geometry, they adopt two different types of coordination modes where Co1 is surrounded by four O atoms from four different 1,4-ndc ligands and two bridging μ-O atoms from two water molecules and Co2 is surrounded by four O atoms from four different 1,4-ndc ligands, one O atom from one water molecule and one N atom from one L2 ligand. The Co-O distances are from 2.046(2) Å to 2.2103(19) Å. The Co-N distance is 2.108(2) Å (Fig. 3a). Each Co1 ion is linked by two Co2 ions to form a trinuclear {Co3} unit and Co1 ion is on an inversion centre (Fig. 3b). Each {Co3} unit is further bridged by eight 1,4-ndc anions in various orientations and thus afford a 3D framework where all of N4 atoms of L2 ligands are not coordinated (Fig. 3c). Topologically, if {Co3} clusters are viewed as 8-connected nodes, the overall structure of **4** can be simplified as a 3D uninodal 8-connected network with a bcu with point symbol $(4^{24}\cdot6^4)$ topology (Fig. 3d). Some networks with bcu topology have been reported.[16]

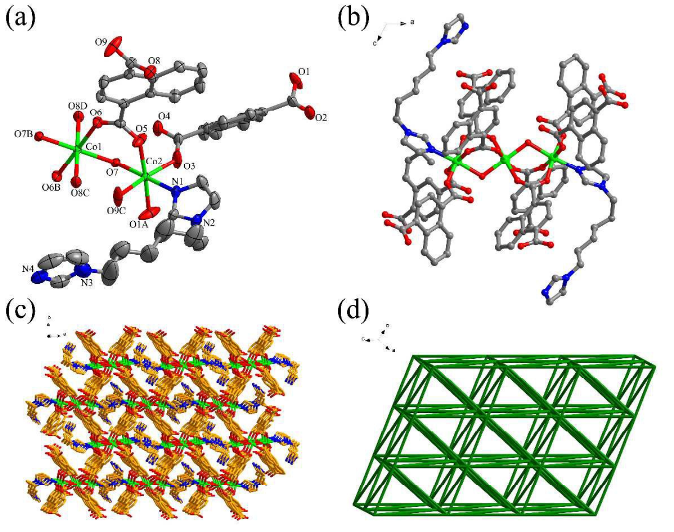

Fig. 3 (a) Co(II) coordination environments of **4**. Symmetry codes: (A) –x − 1/2, y − 1/2, −z + 1/2; (B) −x, −y, −z; (C) –x − 1/2, y − 1/2, −z − 1/2; (D) x + 1/2, −y + 1/2, z + 1/2. (b) $\{Co_3\}$ unit of **4**. (c) 3D framework of **4**. (d) 3D uninodal 8-connected network with a bcu with point symbol ($4^{24}\cdot6^4$) topology of **4**. All hydrogen atoms are omitted for clarity. The green, red and blue represent cobalt, oxygen and nitrogen atoms, respectively.

Crystal structure of $[Cd_2(NO_3)_2(1,4\text{-ndc})(L3)_2]\cdot H_2O$ (5).

5 crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of **5** is composed of two Cd(II) ions, one 1,4-ndc ligand, two L3 ligands and one water molecule. The two Cd(II) ions have two different coordination modes where Cd1 is surrounded by two O atoms from one 1,4-ndc ligand, three O atoms from two different NO_3^- anions and two N atoms from two different L3 ligands and Cd2 is six-coordinated with a distorted octahedral geometry surrounded by two O atoms from one 1,4-ndc ligand, two O atoms from two different NO_3^- anions and two N atoms from two different L3 ligands. The Cd-O distances are from 2.367(5) Å to 2.571(8) Å and the Cd-N distances rang from 2.21(5) Å to 2.260(5) Å. (Fig. 4a). The two neighboring Cd(II) ions are linked by two NO_3^- anions forming a binuclear {Cd2} unit. This {Cd2} unit is further connected by two 1,4-ndc ligands along [0 0 1] direction and four L3 ligands along [-1 1 0] direction to form a 2D layer (Fig. 4b). Thus, each 2D net is further crossed by L3 ligands along [1 2 0] direction and form a 3D framework. The 3D framework is interpenetrated by a crystallographic equivalent net to form a two-fold interpenetrating 3D framework (Fig. 4c). Topologically, if the {Cd2} clusters are viewed as 4-connected nodes, the overall motif of **5** will be a 3D uninodal 4-connected network with a CdS ($CdSO_4$) with point symbol ($6^5\cdot8$) topology (Fig. 4d). Some networks with CdS ($CdSO_4$) topology have been reported.[17]

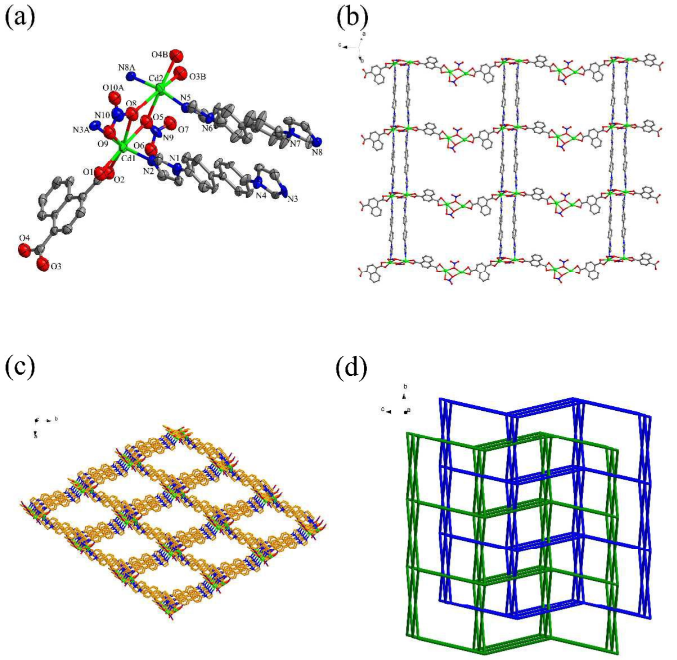

Fig. 4 (a) Cd(II) coordination environments of **5**. Symmetry codes: (A) x − 1, y − 1, z; (B) x, −y + 1/2, z − 1/2; (b) View of the 2D layer of **5**. (c) 2D layer of **5**. (d) 3D uninodal 4-connected network with a CdS ($CdSO_4$) with point symbol ($6^5\cdot8$) topology of **5**. All hydrogen atoms are omitted for clarity. The green, red and blue represent cadmium, oxygen and nitrogen atoms, respectively.

PXRD Results

Powder X-ray diffraction (PXRD) was used to check the phase purity of the compounds in the solid state. The identities of **1**-**5** were further confirmed by PXRD. For **1**-**5**, the measured PXRD patterns are closely agreement with the simulated patterns generated from the results of single-crystal diffraction data which indicate the good purity and homogeneity of the synthesized samples (Fig. S1, ESI†).

Thermal Analysis

In order to study the thermal stabilities of the five compounds, thermogravimeric analyses (TGA) of **1**-**5** were carried out. The thermogravimetric (TG) measurements were performed in N_2 atmosphere on polycrystalline samples, TG curves for **1**-**5** are shown in Fig. S2. The five compounds demonstrated high thermal stabilities. For **1**, the weight loss corresponding to the release of lattice water molecule is observed from 57 to 100 °C (obsd 0.98%, calcd 0.92%), and then the framework is stable up to 354 °C, where the framework begins to collapse. The remaining residue corresponds to the formation of CdO (obsd 13.84%, calcd 13.17%). The TG curves for **2** and **5** are similar to **1**. They show a gradual weight loss between 57 to 100 °C, which can be ascribed to the release of lattice water molecule (obsd 1.85%, calcd 1.74%) for **2** and (obsd 1.94%, calcd 1.56%) for **5**, and the residue of 24.05% beyond 375 °C for **2** and the residue of 12.08% beyond 363 °C for **5** are assigned to CdO (calcd 24.90%) and (calcd 11.13%), respectively. For **3**, the departure of coordinated water molecule is observed to 100 °C (obsd 2.39%, calcd 2.12%), and the decomposition of the compound occurs at

271 °C with CuO residue (obsd 10.64%, calcd 11.52%). The TG curve for **4** shows the framework is stable to 218 °C and a small weight loss of 1.36% from 218 to 343 °C can be assigned to the release of coordinated water molecules (calcd 1.20%). From 343 °C, the framework begins to collapse. The remaining residue is the formation of CoO (obsd 4.74%, calcd 4.98%).

Magnetic Properties

The temperature-dependent magnetic susceptibilities were measured on powdered samples of 3 and 4 at 1000 Oe in the range of 2-300 K. The $\chi_M T$ and χ_M versus T plots of 3 and 4 are shown in Fig. 5.

In the structure of **3**, the distance between two Cu ions within a dimer unit is about 2.711 Å, which is smaller than 3 Å, indicating the existence of the strong super-exchange coupling interactions among the metal centers. The $\chi_M T$ and χ_M versus T plots are shown in Fig. 5a. At 300 K, the $\chi_M T$ value is 0.69 cm^3 mol^{-1} K, which is smaller than that expected for two magnetically isolated S = 1/2 spin carriers (0.75 cm^3 mol^{-1} K).[18] As the temperature decreases to 2 K, $\chi_M T$ promptly decreases to the minimum of 0.01 cm^3 mol^{-1} K, indicating a strong antiferromagnetic coupling between Cu^{2+}. In **3**, two magnetic exchange pathways may be considered: one is within the dimer {Cu2} and the other is the 1,4-ndc and L1 bridges which connect adjacent dimer entities. Taking into account that the distance between the nearest {Cu2} units (10.821 Å) is much longer than that within the {Cu2} unit, the exchange interaction between {Cu2} units can be expected to be very weak.

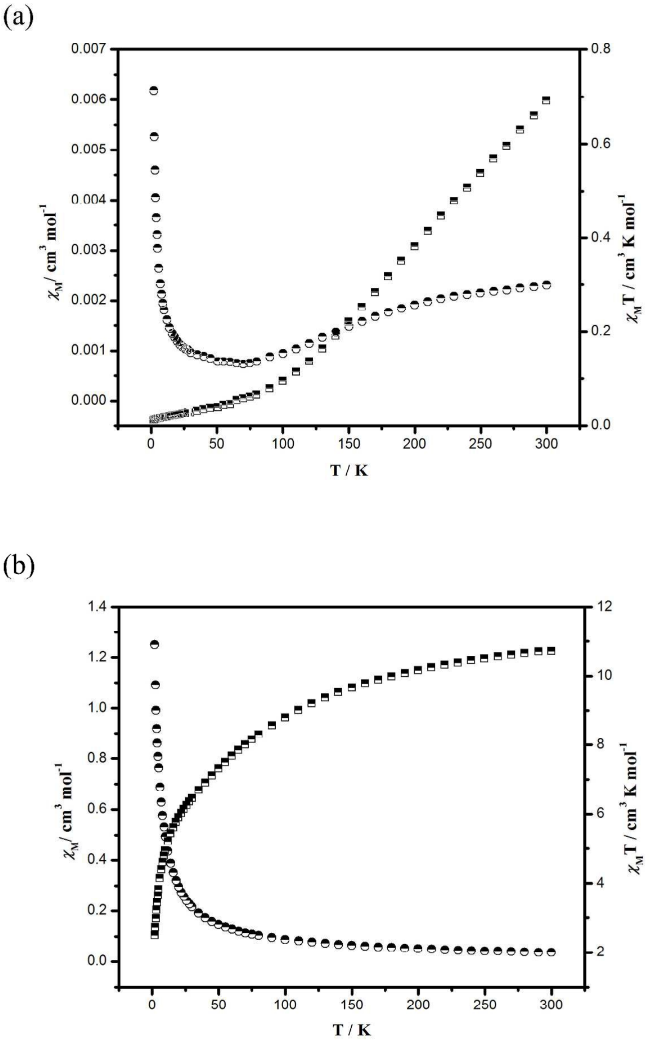

Fig. 5 Temperature dependence of $\chi_M T$ and χ_M versus T plots of **3** and **4**, (a) **3**, (b) **4**.

For **4**, the $\chi_M T$ and χ_M versus T plots are shown in Fig. 5b. The $\chi_M T$ value at 300 K is 10.72 cm^3 mol^{-1} K, which is larger than the calculated spin-only value (5.625 cm^3 mol^{-1} K) for three Co(II) (S = 3/2) ions,[19] indicating the orbital contribution arising from the high-spin octahedral Co(II). Upon cooling, $\chi_M T$ decreases monotonously to achieve a minimum value of 2.50 cm^3 mol^{-1} K at 2 K, indicating an appreciable antiferromagnetic exchange between the Co(II) ions connected through μ_2-O and O-C-O bridges. The magnetic susceptibility conforms to the Curie-Weiss law with C = 1.60 cm^3 mol^{-1} K and $\Theta = -17.68$ K, revealing dominant antiferromagnetic interactions between the Co(II) ions and the presence of spin-orbit couplings.

Photoluminescence Properties

The luminescent properties of **1**, **2** and **5**, 1,4-H_2ndc ligand, bpy, phen and L3 ligands were investigated in the solid state at room temperature. The main emission peaks of 1,4-H_2ndc ligand is at 475 nm and of three N-donor ligands are at 360, 390, 378 nm, respectively for N-donor ligands. As shown in Fig. 6, the emission peaks of **1**, **2** and **5** are at 383, 376 and 374 nm (λ_{ex} = 320 nm), respectively. Obviously, 1,4-H_2ndc ligand is nearly nonfluorescent in the range 400-800 nm at ambient temperature. In comparison with the N-donor ligands, the emissions maximum of three compounds may be attributed to the π*-π transitions because similar peaks appears for the three N-donor ligands.[20-21] Meanwhile, the complexation of the N-donor ligands with metal ions may be also affect the emissions of the compounds because of the different red or blue shifts and intensities of the emission peaks of these compounds compared with the three N-donor ligands.[22] The photoluminescence behavior is closely relative to the coordinated ligands and metal ions.[23]

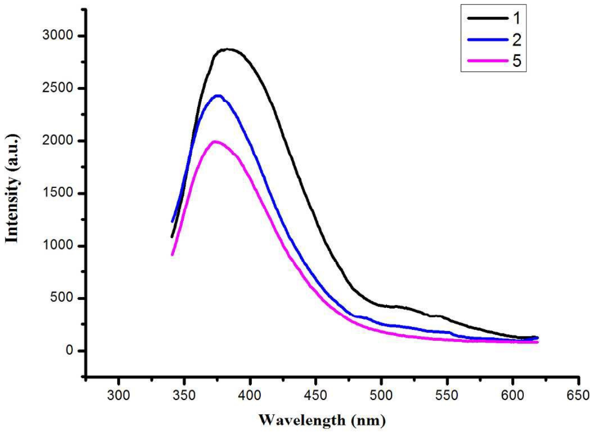

Fig. 6 Emission spectra of **1**, **2** and **5** in solid state at ambient temperature.

Conclusions

In summary, five new coordination polymers constructed from 1,4-naphthalenedicarboxylic and N-donor ligands have been successfully obtained by hydrothermal method. These compounds exhibit intriguing 2D and 3D structural motifs. The diversities of these structures demonstrate that 1,4-naphthalenedicarboxylic can act as a versatile building block to form diverse structural motifs. Additionally, the choices of the N-donor ligands and the pH of the final reaction system are vital to form targeted coordination polymers with promising properties and potential applications. In addition, **3** exhibits antiferromagnetic interactions between the adjacent copper ions and **4** shows antiferromagnetic interactions between the Co(II) ions and the presence of spin-orbit couplings. The solid-state fluorescence spectra shows that **1**, **2** and **5** have strong emissions at room temperature. Further studies on the coordination polymers based on 1,4-naphthalenedicarboxylic and other N-donor ligands are underway.

Acknowledgements

This work was financially supported by the NSFC of China (No. 21471027, 21171033, 21131001, 21222105), National Key Basic Research Program of China (No. 2013CB834802), Changbai mountain scholars of Jilin Province and FangWu distinguished young scholar of NENU.

Notes and references

Institute of Functional Material Chemistry ; Key Laboratory of Polyoxometalate Science of Ministry of Education, Northeast Normal University, Changchun, 130024 Jilin, People's Republic of China. E-mail: qinc703@nenu.edu.cn, zmsu@nenu.edu.cn; Fax: + 86 431-85684009; Tel: + 86 431-85099108

† Electronic Supplementary Information (ESI) available: Schemes, figures and CIF files giving selected Bonds and angles, PXRD, TGA and crystallographic data (CCDC 1053072-1053076). See DOI: 10.1039/b000000x/

1 (a) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (b) Z. J. Lin, D. S. Wragg, J. E. Warren and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 10334; (c) L. Mihalces, N. Henry, T. Bousquet, C Volkringer and T. Loiseau *Cryst. Growth Des.*, 2012, **12**, 4641; (d) B. F. Abrahams, S. R. Batten, B. F. Hoskins and R. Robson, *Inorg. Chem.*, 2003, **42**, 2654; (e) L. R. Yang, H. M. Zhang, Q. Q. You, L. Z. Wu, L. Liu and S. Song, *CrystEngComm*, 2013, **15**, 7505; (f) N. Y. Li, Y. Ge, T. Wang, S. J. Wang, X. Y. Ji and D. Liu, *CrystEngComm*, 2014, **16**, 2168.

2 (a) X. L. Wang, C. Qin, E. B. Wang and Z. M. Su, *Angew. Chem., Int. Ed.*, 2004, **43**, 5036; (b) X. L. Wang, E. B. Wang, Y. G. Li, Z. M. Su, L. Xu and L. Carlucci, *Angew. Chem., Int. Ed.*, 2005, **44**, 5824; (c) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (d) M. Fang, L. Chang, X. Liu, B. Zhao, Y. Zuo and Z. Chen, *Cryst. Growth Des.*, 2009, **9**, 4006; (e) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (f) S. R. Batten and K. S. Murray, *Coord. Chem. Rev.*, 2003, **246**, 103.

3 (a) D. R. Xiao, E. B. Wang, H. Y. An, Y. G. Li, Z. M. Su and C. Y. Sun, *Chem.–Eur. J.*, 2006, **12**, 6528; (b) M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (c) J. P. Zhang, Y. B. Zhang and J. B. Lin, *Chem. Rev.*, 2012, **112**, 1001; (d) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (e) Z. Zhang, J. F. Ma, Y. Y. Liu, W. Q. Kan and J. Yang, *Cryst. Growth Des.*, 2013, **13**, 4338; (f) P. M. Forster, N. Stock and A. K. Cheetham, *Angew. Chem., Int. Ed.*, 2005, **44**, 7608.

4 (a) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastre, *J. Mater. Chem.*, 2006, **16**, 626; (b) E. Q. Gao, Y. F. Yue, S. Q. Bai, Z. He and C. H. Yan, *J. Am. Chem. Soc.*, 2004, **126**, 1419; (c) R. Q. Zou, H. Sakurai and Q. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 2542; (d) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (e) S. R. Batten, *CrystEngComm*, 2001, **3**, 67; (f) X. J. Kong, L. S. Long, Z. Zheng, R. B. Huang and L. S. Zheng, *Acc. Chem. Res.*, 2010, **43**, 201.

5 (a) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 17; (b) D. Braga, L. Maini, M. Polito, L. Scaccianoce, G. Cojazzi and F. Grepioni, *Coord. Chem. Rev.*, 2001, **216**, 783; (c) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; (d) L. X. Sun, Y. Qi, Y. M. Wang, Y. X. Che and J. M. Zheng, *CrystEngComm*, 2010, **12**, 1540; (e) S. K. Ghosh, J. Ribas and P. K. Bharadwaj, *CrystEngComm*, 2004, **6**, 250; (f) T. K. Maji, M. Ohba and S. Kitagawa, *Inorg. Chem.*, 2005, **44**, 9225.

6 (a) D. Liu, Z. G. Ren, H. X. Li, J. P. Lang, N. Y. Li and B. F. Abrahams, *Angew. Chem., Int. Ed.*, 2010, **49**, 4767; (b) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (c) Y. Ling, M. L. Deng, Z. X. Chen, B. Xia, X. F. Liu, Y. T. Yang, Y. M. Zhou and L. H. Weng, *Chem. Commun.*, 2013, **49**, 78; (d) O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. Ö. Yazaydin and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 15016; (e) M. C. Das, S. Xiang, Z. Zhang and B. Chen, *Angew. Chem., Int. Ed.*, 2011, **50**, 10510; (f) B. J. Burnett, P. M. Barron and W. Choe, *CrystEngComm*, 2012, **14**, 3839.

7 (a) Y. X. Tan, Y. P. He and J. Zhang, *Inorg. Chem.*, 2012, **51**, 9649; (b) T. N. Nguyen, W. Wernsdorfer, K. A. Abboud and G. Christou, *J. Am. Chem. Soc.*, 2011, **133**, 20688; (c) Y. Liu, K. Mo and Y. Cui, *Inorg. Chem.*, 2013, **52**, 10286; (d) M. N. Kopylovich, T. C. O. Mac Leod, K. T. Mahmudov, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Dalton Trans.*, 2011, **40**, 5352; (e) J. W. Han and C. L. Hill, *J. Am. Chem. Soc.*, 2007, **129**, 15094; (f) J. G. Lin, Y. Su, Z. F. Tian, L. Qiu, L. L. Wen, Z. D. Lu, Y. Z. Li and Q. J. Meng, *Cryst. Growth Des.*, 2007, **7**, 2526.

8 (a) L. Hou, W. J. Shi, Y. Y. Wang, Y. Guo, C. Jin and Q. Z. Shi, *Chem. Commun.*, 2011, **47**, 5464; (b) N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dybtsev, V. P. Fedin and O. A. Kholdeeva, *J. Catal.*, 2008, **257**, 315; (c) B. V. Harbuzaru, A. Corma, F. Rey, J. L. Jorda, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem., Int. Ed.*, 2009, **48**, 6476; (d) X. L. Wang, C. Qin, E. B. Wang and Z. M. Su, *Chem.–Eur. J.*, 2006, **12**, 2680; (e) A. J. Fletcher, K. M. Thomas and M. J. Rosseinsky, *J. Solid State Chem.*, 2005, **178**, 2491.

9 (a) J. C. Bailar, Jr., in *Preparative Inorganic Reactions*, ed. W. L. Jolly, Interscience, New York, 1964, **1**, 1; (b) S. Mann, *J. Chem. Soc., Dalton Trans.*, 1993, 1; (c) L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325; (d) K. Biradha, M. Sarkar and L. Rajput, *Chem. Commun.*, 2006, 4169.

10 X. Q. Lu, J. J Jiang, H. C. zur Loye, B. S. Kang and C. Y. Su, *Inorg. Chem.*, 2005, **44**, 1810.

11 (a) X. L. Wang, C. Qin and E. B. Wang, *Cryst. Growth Des.*, 2006, **6**, 439; (b) J. Jia, M. Shao, T. T. Jia, S. R. Zhu, Y. M Zhao, F. F Xing and M. X. Li, *CrystEngComm*, 2010, **12**, 1548.

12 (a) X. J. Jiang, J. H. Guo, M. Du and J. S. Li, *Polyhedron*, 2009, **28**, 3759; (b) K. H. He, W. C. Song, Y. W. Li, Y. Q. Chen and X. H. Bu, *Cryst. Growth Des.*, 2012, **12**, 1064; (c) J. Yang, G. B. Che, B. Liu, Y. Y. Liu and J. F. Ma, *Inorg. Chem. Comun.*, 2010, **13**, 112; (d) Z. L. Liao, G. D. Li, M. H. Bi and J. S. Chen, *Inorg .Chem.*, 2008, **47**, 4844; (e) X. J. Zheng, L. P. Jin, S. Gao and S. Z. Lu, *Inorg. Chem. Comun.*, 2005, **8**, 72; (f) Y. W. Li, H. Ma, Y. Q. Chen, K. H. He, Z. X. Li and X. H. Bu, *Cryst. Growth Des.*, 2012, **12**, 189; (g) J. Yang, J. F. Ma, Y. Y. Liu, J. C. Ma and S. R. Batten, *Cryst. Growth Des.*, 2008, **8**, 4383

13 (a) G. M. Sheldrick. SHELXS97, A Program for the Solution of Crystal Structures from X-ray Data, University of Gӧttingen, Germany, 1997; (b) G. M. Sheldrick. SHELXL97, A Program for the Refinement of Crystal Structures from X-ray Data , University of Gӧttingen, Germany, Gӧttingen, Germany, 1997.

14 (a) E. Yang, L. Wang and J. Zhang, *CrystEngComm*, 2014, **16**, 2889; (b) X. X. Xu, X. Zhang, X. X. Liu, L. S. Wang and E. B. Wang, *CrystEngComm*, 2012, **14**, 3264; (c) Q. X. Yao, X. H. Jin, Z. F. Ju, H. X. Zhang and J. Zhang, *CrystEngComm*, 2009, **11**, 1502.

15 (a) Z. H. Yan, W. Wang, L. L. Zhang, X. W. Zhang, L. Wang and D. F. Sun, *RSC Adv.*, 2015, **5**, 16190; (b) J. T. Jia, F. X. Sun, Q. R. Fang, X. Q. Liang, K. Cai, Z. Bian, H. J. Zhao, L. X. Gao and G. S. Zhu, *Chem. Commun.*, 2011, **47**, 9167; (c) S. Hu, J. L. Liu, Z. S. Meng, Y. Z. Zheng, Y. H. Lan, A. K. Powell and M. L. Tong, *Dalton Trans.*, 2011, **40**, 27.

16 (a) S. Goswami. S. Sanda and S. Konar, *CrystEngComm*, 2014, **16**, 369; (b) H. Q. Hao, J. Wang, W. T. Liu and M. L. Tong, *CrystEngComm*, 2008, **10**, 1454.

17 (a) G. E. Kostakis, L. Casella, N. Hadjiliadis, E. Monzani, N. Kourkoumelis and J. C. Plakatouras, *Chem. Commun.*, 2005, 3859; (b) Y. W . Li, D. C. Li, J. Xu, H. G. Hao, S. N. Wang, J. M. Dou, T. L. Hu and X. H. Bu, *Dalton Trans.*, 2014, **43**, 15708.

18 J. H. Nettleman, P. J. Szymanski, L. K. Sposato and R. L. L. Duca, *Inorg. Chim. Acta*, 2010, **363**, 225.

19 T. Ding, L. D. Ren. X. D. Du, L. Quan, Z. W. Gao, W. Q. Zhang and C. Z. Zheng, *CrystEngComm*, 2014, **16**, 7790.

20 (a) X. Shi, G. Zhu, G. Fang, G. Wu, G. Tian, R. Wang, D. Zhang, M. Xue and S. Qiu, *Eur. J. Inorg. Chem.*, 2004, 185; (b) L. Wen, Z. Lu, J. Lin, J. Tian, H. Zhu and Q. Meng, *Cryst. Growth Des.*, 2007, **7**, 93;

21 Z. H. Yan, L. L. Han, Y. Q. Zhao, X. Y. Li, X. P. Wang, L. Wang and F. D. Sun, *CrystEngComm*, 2014, **16**, 8747.

22 B. Valeur, *Molecular Fluorescence: Principles and Application*, Wiley VCH, Weinheim, 2002.

23 (a) O. Kahn, Molecular Magnetism, Wiley−VCH, New York, 1993; (b) B. N. Figgis, Wiley Interscience, New York, 1961.

Graphical Abstract

Syntheses, structures, magnetic and luminescent properties of a series of coordination polymers constructed from 1,4-naphthalenedicarboxylic and N-donor ligands

Liu Yang, Chao Qin, Bai-Qiao Song, Xiao Li, Chun-Gang Wang and Zhong-Min Su**

Institute of Functional Materials Chemistry, Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun 130024, China. E-mail: zmsu@nenu.edu.cn; qinc703@nenu.edu.cn

A series of coordination polymers constructed from 1,4-naphthalenedicarboxylic and N-donor ligands have been synthesized which forms four topological types. The thermal, magnetic and photoluminescent properties in solid state were also investigated.