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Syntheses, structures and luminescent properties of six divalent metal terephthalate coordination polymers based on three new flexible bis(imidazole) ligands†

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Six coordination polymers based on terephthalate and one of three new symmetry-related ligands which contain two flexible -O-CH_2-CH_2- chains and rigid naphthalene ring of bis (imidazole) (2,7-bis(ethoxyimidazole)-naphthalene (L1), 2,7-bis(ethoxybenzimidazole)-naphthalene(L2), 1,5-bis (ethoxybenzimidazole)-naphthalene (L3)), formulated as [Cd(L1)(*p*-bdc)]·DMF·H_2O (**1**), [Co(L1)(*p*-bdc)$(H_2O)_2$]·H_2O (**2**), [$Zn_2$$(L1)_2$(*p*-bdc)$_2$]·3$H_2O$ (**3**), [Zn(L2)(*p*-bdc)]·DMF (**4**), [Co(L2)(*p*-bdc)]·H_2O (**5**), [Co(L3)(*p*-bdc)(H_2O)]·2DMF (**6**) have been prepared under hydrothermal conditions. Compound **1** shows a two-dimensional (2D) (4^4)-network with a 2-fold interpenetration structure. Compound **2** possesses a three-dimensional (3D) framework and can be simplified as **qzd** (quartz-dual) “dense” net with point (*Schläfli*) symbol $\{7^5.9\}$. Compound **3** displays an infinite one-dimensional (1D) structure containing three different rings, exhibiting a “cryptand ring” structure. Compound **4** presents a 2D framework and exhibits slightly undulating (4^4) topology. Compound **5** exhibits a 2D network with point (*Schläfli*) symbol $\{12\}\{4.12^5\}\{4\}$. Compound **6** demonstrates a 2D network with point (*Schläfli*) symbol $\{8^4.12^2\}\{8\}_2$. A comparison of six complexes shows that the coordination mode of terephthalate plays key role in the construction of coordination polymers and three N-containing ligands beautify and enrich the structures. In addition, the powder X-ray diffraction (PXRD), elemental analysis, IR, thermal stability and optical properties of all compounds have also been investigated.

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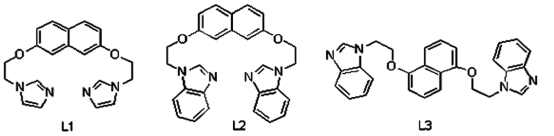
[†] Electronic supplementary information (ESI) available: NMR spectrograms, X-ray crystallographic data, selected bond lengths and bond angles, additional crystal figures, powder X-ray patterns, TGA curves for complexes **1**–**6** and the emission spectra of the free ligands and complexes **1**–**6**. CCDC: 919450-919452, 9194449, 919448, 919447 for **1**–**6**. For ESI and crystallographic data in CIF or other electronic format see DOI:

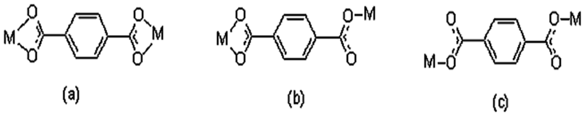
Introduction

Currently, metal-organic frameworks (MOFs) have attracted more attention not only for their novel topologies and intriguing structural diversities but also for their structure related potential applications, such as catalysis, gas storage, ion exchange, sensors, magnetism, luminescence and so on.[1-7] In theory, it is difficult for the researcher to get the corresponding structure and the desired property because a lot of factors affect the self-assembly process. However, the designer by rational designing of organic ligands and metal centers have synthesized some target crystals with specific crystal structural characteristics in resent years (e.g. MOF-5), therefore, the synthesis strategy of designing ligand and metal is being a main stream of active research to construct MOFs.[8] In recent years, N-donor ligands have increasingly become a topic, which is mainly because of their diversiform coordination modes and fascinating topology architectures, such as 1, 10-phenanthroline, 4, 4'-bipyridine, triazole, tetrazole, pyrazole, etc.[9] In a large number of N-ligands, bis(imidazole) ligands with flexible chain have played an important role in building coordination polymers,[10] and many rigid imidazole ligands are also reported in the literature.[11] Owing to the mixed ligand with flexible chain and rigid functional group, possessing new coordination advantages, which can be a better way to produce more variable structures compared with single mode of ligands. Nowadays, using the mixed ligand is being a good choice to construct new metal organic compounds.[12] In additional, imidazole-based ligands are usually used to build more complicated coordination polymers in company with ancillary carboxylic acid ligands. There are mainly two kinds of acids: aliphatic-carboxylate acids and aromatic-carboxylic acids. For the former, because of the carbon chains have the ability to rotate freely, the carboxyl group could meet the metal ions in various coordination directions during the assembly process, such as malonic acid, glutaric acid, suberic acid and so on.[13] For the latter, the most common acids are 1,4-benzenedicarboxylic acid (p-H_2bdc), 1,3-benzenedicarboxylic acid (m-H_2bdc), 1,3,5-benzentricarboxylic acid (H_3btc), biphenyl-4,4'-dicarboxylic and so on, which are good candidates as organic linkers in the construction of coordination polymers because of they have rigid coordination modes.[14]

As an extension of previous work, we synthesize three new ligands, namely, 2,7-bis(ethoxyimidazole)-naphthalene (L1), 2,7-bis(ethoxybenzimidazole)-naphthalene (L2), 1,5-bis(ethoxybenzimidazole)-naphthalene (L3) (Scheme 1), which contain bis(imidazole) units with flexible chains and rigid naphthalene ring simultaneously. Two flexible -O-CH_2-CH_2- chains with imidazol functional groups can rotate freely to meet metal ions, which would dramatically increase the diversity.[15] Further, the naphthalene ring is a multifunctional group, which is a big rigid group with almost all atoms existing in the same plane and can fix the conformation of the bis(imidazole) ligand to a certain extent, therefore, which probably enhance conformational stable performance of the ligand to a certain degree, though the flexible alkoxy chains in the skeleton may decrease the stability during the self-assembly process and fluorescence characteristic as a luminophore.[15d] At the same time, we choose a symmetrical rigid terephthalate as a coligand and successfully construct six coordination polymers: [Cd(L1)(p-bdc)]·DMF·H_2O (**1**), [Co(L1)(p-bdc)$(H_2O)_2$]·H_2O (**2**), [$Zn_2(L1)_2$(p-bdc$)_2$]·3H_2O (**3**), [Zn(L2)(p-bdc)]·DMF (**4**), [Co(L2)(p-bdc)]·H_2O (**5**), [Co(L3)(p-bdc)(H_2O)]·2DMF (**6**). All compounds are characterized by single-crystal X-ray diffraction, elemental analysis, IR, thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD). We have discussed the influence of terephthalate (Scheme 2) and N-containing ligand on the final structures. In addition, optical properties have also been investigated.



Scheme 1. Three kinds of bis(imidazole) ligands in this work.



Scheme 2. Three coordination modes of p-bdc^{2-} in compounds **1**-**6**.

Experimental

Materials and Characterization

All chemicals were commercially available and used without any further purification except L1, L2 and L3. NMR analyses were recorded with a Bruker Advance □ 400 NMR spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz, respectively). Elemental analyses (C, H, N) were performed on a Perkin-

Elmer 240 elemental analyzer. FT-IR spectra were recorded on a Nicolet 6700 using KBr disk in the region of 400-4000 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were measured on Dmax/Ultima IV. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449 F3 thermal analyzer from room temperature to 800 °C at a heating rate of 10 °C/min in a N_2 atmosphere. The solid-state fluorescence emissions were obtained with an F-4600 FL Spectrophotometer. The UV-vis diffuse reflectance spectra in the solid state were recorded on a UV-2550 ultraviolet-visible spectrophotometer in the region of 200-800 nm.

Synthesis

Synthesis of 2,7-bis [ethoxyimidazole]- naphthalene (L1). A mixture of NaOH (6.00 g, 150 mmol), tetrabutylammonium bromide (TBAB, 0.40 g, 1.2 mmol), 2,7-dihydroxynaphthalene (4.00 g, 25 mmol) and 1,2-dibromoethane (80 mL) in a 250 mL two-necked round bottom flask stirred at 80 °C for 36 hours. Solvent was removed in vacuo and the reside was purified by silica column chromatography, afforded the product 2,7-bis(bromoethoxy)-naphthalene 5.80 g, 63%.[16] To a flame-dried two-necked flask charged with NaH (in 60% oil dispersion, 3.40 g, 81 mmol) and imidazole (4.08 g, 60 mmol), then anhydrous THF (30 mL) was added with stirring under N_2 atmosphere. The mixture was stirred overnight at room temperature. A solution of 2,7-bis(bromoethoxy)naphthalene (1.50 g, 4.03 mmol) in 30 mL of THF was added dropwise, and the result mixture was refluxed over 72 hours and monitored by TLC. The mixture was evaporated to get the crude product and recrystallized by ethyl acetate and petroleum ether to give the title compound. Yield: 1.05 g, 75%; mp: 43-45 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 4.31 (t, J = 4.8 Hz, 4H), 4.39 (t, J = 5.0 Hz, 4H), 6.97-6.99 (m, 4H), 7.09 (d, J = 3.2 Hz, 4H), 7.66 (t, J = 10.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 46.43, 67.19, 106.38, 116.30, 119.41, 124.95, 129.53, 135.47, 139.59, 156.63 (Fig. S1-S2).

Synthesis of 2,7-bis [ethoxybenzimidazole] -naphthalene (L2). The L2 was prepared by a similar process to obtain L1 except imidazole was replaced by benzimidazole (7.08 g, 60 mmol), gained the white powder. Yield: 1.1 g, 61%; mp: 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 4.39 (d, J = 4.4 Hz, 4H), 4.62 (t, J = 4.6 Hz ,4H), 6.94 (t, J = 11.4 Hz, 4H), 7.33 (t, J = 8.4 Hz, 2H), 7.51 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 8.8 Hz, 2H), 7.84 (d, J = 7.2 Hz, 2H), 8.07 (s, 2H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 44.39, 66.09, 106.36, 109.44, 116.23, 120.55, 122.06, 123.05, 124.96, 129.48, 143.53, 143.83, 156.55 (Fig. S3-S4).

Synthesis of 1,5-bis[ethoxybenzimidazole]-naphthalene (L3). When 2,7-dihydroxy-naphthalene of L2 was replaced by 1,5-dihydroxynaphthalene, the white powder of L3 was prepared. Yield: 1.20 g, 67%; mp: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 4.47 (t, J = 5.2 Hz, 4H), 4.70 (t, J = 5.0 Hz, 4H), 6.77 (d, J = 7.6 Hz, 2H), 7.28-7.37 (m, 6H), 7.51 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 7.6 Hz, 2H), 8.14 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 44.42, 66.15, 105.72, 109.33, 114.98, 120.60, 122.31, 123.11, 125.28, 143.46, 153.39 (Fig. S5-S6).

Synthesis of [Cd(L1) (*p*-bdc)]·DMF·H_2O (1). A mixture of L1 (0.0348 g, 0.1 mmol), $Cd(NO_3)_2{\cdot}4H_2O$ (0.0308 g, 0.1 mmol), *p*-H_2bdc (0.0332 g, 0.2 mmol), DMF (7 mL), and H_2O (2 mL) was placed in a Teflon reactor (25 mL) and heated at 160 °C for 4 days. Then the mixture had been cooled to room temperature in 40 hours. Crystals of **1** were obtained by filtration and washed with DMF and water, and dried in air (yield: 69%, based on L1). Anal. Calcd for $C_{31}H_{33}CdN_5O_8$ (*Mr* = 716.02): C, 52.00; H, 4.65; N, 9.78. Found: C, 52.49; H, 4.42; N, 9.86. IR (KBr, cm^{-1}): 3420(w), 3120(w), 3060(w), 2930(w), 2880(w), 1660(m), 1570(vs), 1520(s), 1460(m), 1390(vs), 1210(s), 1090(m), 1170(m), 1060(w), 839(m), 837(m), 750(m), 660(w).

Synthesis of [Co(L1) (*p*-bdc) $(H_2O)_2$]·H_2O (2). A mixture of L1 (0.0348 g, 0.1 mmol), $Co(NO_3)_2{\cdot}6H_2O$ (0.0291 g, 0.1 mmol), *p*-H_2bdc (0.0166 g, 0.1 mmol), CH_3CN (4mL), and H_2O (4 mL) was placed in a Teflon reactor (25 mL) and heated at 160 °C for 4 days. Then the mixture had been cooled to room temperature in 40 hours. Crystals of **2** were obtained by filtration and washed with acetonitrile and water, and dried in air (yield: 71%, based on L1). Anal. Calcd for $C_{28}H_{30}CoN_4O_9$ (*Mr* = 625.44): C, 53.77; H, 4.83; N, 8.96. Found: C, 53.94; H, 4.85; N, 9.13. IR (KBr, cm^{-1}): 3420(m), 3130(w), 3060(w), 2940(w), 2880(w), 1690(m), 1630(s), 1600(vs), 1520(s), 1380(m), 1270(m), 1210(vs), 1090(s), 1050(m), 853(m), 835(m), 748(s), 660(m).

Synthesis of $[Zn_2(L1)_2$ $(p\text{-bdc})_2]{\cdot}3H_2O$ (3). A mixture of L1 (0.0348 g, 0.1 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.0297 g, 0.1 mmol), *p*-H_2bdc (0.0166 g, 0.1 mmol), CH_3OH (4 mL) and H_2O (4 mL) was placed in a Teflon reactor (25 mL) and heated at 120 °C for 3 days. Then the mixture had been cooled to room temperature in 35 hours. Crystals of **3** were obtained by filtration and washed with methanol and water, and dried in air (yield: 58%, based on L1). Anal. Calcd for $C_{56}H_{48}N_8O_{15}Zn_2$ (*Mr* = 1203.81): C, 55.60; H, 4.50; N, 9.26. Found: C, 55.87; H, 4.02; N, 9.45. IR (KBr, cm^{-1}): 3440 (w), 3130(w), 2940(w), 2880(w), 1630(vs), 1520(m), 1360(vs), 1260(s), 1210(m), 1160(m), 1100(m), 1050(m), 953(w), 833(w), 750(m), 658(m).

Synthesis of [Zn(L2)(*p*-bdc)]·DMF (4). A mixture of L2 (0.0448 g, 0.1 mmol), Zn $(NO_3)_2·6H_2O$ (0.0297 g, 0.1 mmol), *p*-H_2bdc (0.0332 g, 0.2 mmol), DMF (7 mL), and H_2O (4 mL) was placed in a Teflon reactor (25 mL) and heated at 120 °C for 3 days. Then the mixture had been cooled to room temperature in 35 hours. Crystals of **4** were obtained by filtration and washed with DMF and water, then dried in air (yield: 68%, based on L2). Anal. Calcd for $C_{39}H_{35}N_5O_8Zn$ (*Mr* = 767.11): C, 60.91; H, 4.85; N, 9.11. Found: C, 60.97; H, 4.86; N, 9.15. IR (KBr, cm^{-1}): 3450(w), 3100(w), 3160(w), 2950(w), 2800(w), 1630(vs), 1520(s), 1470(m), 1390(vs), 1360(vs), 1260(m), 1210(s), 1160(m), 1090(m), 829(w), 748(s), 634(w).

Synthesis of [Co(L2)(*p*-bdc)]·H_2O (5). A mixture of L2 (0.0448 g, 0.1 mmol), $Co(NO_3)_2·6H_2O$ (0.0297 g, 0.1 mmol), *p*-H_2bdc (0.0332 g, 0.2 mmol), DMF (7 mL) and H_2O (4 mL) was placed in a Teflon reactor (25 mL) and heated at 120 °C for 4 days. Then the mixture had been cooled to room temperature for 48 hours. Crystals of **5** were obtained by filtration and washed with DMF and water, and dried in air (yield: 71%, based on L2). Anal. Calcd for $C_{36}H_{28}CoN_4O_8$ (*Mr* = 703.55): C, 61.46; H, 4.01; N, 7.96. Found: C, 61.69; H, 4.17; N, 8.23 IR (KBr, cm^{-1}): 3400(w), 3110(w), 2940(w), 2870(w), 1660(m), 1630(m), 1550(m), 1510(s), 1470(m), 1390(vs), 1260(m), 1210(s), 1170(w), 1060(w), 958(w), 835(w), 748(s), 633(w).

Synthesis of [Co(L3) (*p*-bdc) (H_2O)]·2DMF (6). A mixture of L3 (0.0448 g, 0.1 mmol), $Co(NO_3)_2·6H_2O$ (0.0297 g, 0.1 mmol), *p*-H_2bdc (0.0332 g, 0.2 mmol), DMF (7 mL) and H_2O (4 mL) was placed in a Teflon reactor (25 mL) and heated at 160 °C for 3 days. Then the mixture had been cooled to room temperature for 35 hours. Crystals of **6** were obtained (yield: 52%, based on L3). Anal. Calcd for $C_{42}H_{46}CoN_6O_{10}$ (*Mr* = 853.78): C, 59.08; H, 5.43; N, 9.84. Found: C, 60.24; H, 5.46; N, 9.98. IR (KBr, cm^{-1}): 3390(m), 3110(w), 3060(w), 2930(w), 1660(vs), 1590(s), 1510(s), 1370(vs), 1270(s), 1210(m), 1070(m), 1010(w), 955(w), 777(s), 750(s).

X-ray Crystallography

The X-ray crystallographic data of **1-6** were collected on Bruker APEX-II CCD diffractometer with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) at room temperature using the ω-scan mode. All of the structures were solved by direct methods with SHELXS-97[17] and refined with the full-matrix least-squares procedures on F^2 using the SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all the hydrogen atom positions were generated geometrically at idealized positions onto the specific atoms and refined by using the riding model. Owing to the disorder problem at date collection, some solvent molecules not crystallographically defined successfully. The relevant crystallographic crystal data and corresponding structures refinement parameters for compounds **1-6** are summarized in Table 1. Selected bond distances and angles for compounds **1-6** are listed in Table S1-S6.

Result and discussion

Crystal structure of [Cd(L1) (*p*-bdc)]·DMF·H_2O (1)

X-ray diffraction analyses reveal that **1** is monoclinic crystal system with *P2(1)/c* space group. The asymmetric unit contains one six-coordinated Cd(II) cation, one L1 ligand, two half *p*-bdc^{2-} ligands each in independent inversion center, a lattice DMF molecules and one lattice water molecule. As depicted in Fig. 1a, Cd(II) displays a distorted octahedral coordination geometry, and was defined by four carboxyl oxygen atoms from two symmetry-related ligands (Cd-O = 2.230(3)-2.704(4) Å) and two nitrogen atoms from two L1 ligands (Cd-N = 2.250(2)-2.265(3) Å). The bond angle for cadmium atom and the adjacent two nitrogen atoms is almost perpendicular (N1-Cd-N4 = 92.31(9)°). L1 ligand adopts an asymmetrical *trans*-configuration with the dihedral angles between imidazole and naphthalene of 69.06(1)° and 80.07(1)°, respectively. The *p*-bdc^{2-} ligand adopts bidentate coordination mode (Scheme 2a), which connects the Cd ions to form an infinite linear chain (Fig. S7). Meanwhile, L1 ligands by cadmium atoms as nodes connected adjacent chains forming a two dimensional structure (Fig. 1b). From the topological point of view, compound **1** exhibits a uninodal four-connected (4^4) 2-fold interpenetrating network (Fig. 1c).

Table 1. Crystal data and structure refinement data for compounds **1-6.**

complexes	**1**	**2**	**3**	**4**	**5**	**6**
formula	$C_{31}H_{33}CdN_5O_8$	$C_{28}H_{30}CoN_4O_9$	$C_{56}H_{48}N_8O_{15}Zn_2$	$C_{39}H_{35}N_5O_8Zn$	$C_{36}H_{28}CoN_4O_8$	$C_{42}H_{46}CoN_6O_{10}$
Formula weight	716.02	625.44	1203.81	767.11	703.55	853.78
Crystal system	monoclinic	trigonal	triclinic	orthorhombic	triclinic	monoclinic
Space group	*P2(1)/c*	*P3(2)*	*P-1*	*Pbca*	*P-1*	*P2(1)/c*
a/Å	16.982(4)	11.473(3)	9.779(4)	18.724(7)	9.753(6)	12.937(8)
b/Å	10.725(2)	11.473(3)	13.952(6)	19.302(7)	14.101(8)	11.150(7)
c/Å	22.521(4)	19.268(5)	21.144(9)	20.004(8)	14.740(8)	17.445(8)
α/deg	90.00	90.00	92.178(9)	90.00	116.334(10)	90.00
β/deg	128.552(1)	90.00	92.178(9)	90.00	108.889(10	126.80(3)
γ/deg	90.00	120.00	109.309(8)	90.00	90.034(10)	90.00
V/Å3	3207.8(11)	2196.4(8)	2698(2)	7229(5)	1694.0(17)	2015(2)
T/K	293(2)	296(2)	296(2)	296(2)	296(2)	293(2)
Z	4	3	2	8	2	2
Dcalc/g cm^{-3}	1.483	1.405	1.482	1.410	1.379	1.407
μ/mm^{-1}	0.738	0.644	0.967	0.740	0.564	0.493
F(000)	1464.0	957.0	1240.0	3184.0	726.0	894.0
Reflections collected	17136	12286	14979	38432	9011	10677
Independent reflections	6270	4923	10469	7109	6455	3922
R(int)	0.0283	0.0560	0.0417	0.0902	0.0548	0.0588
GOF on F^2	1.027	1.100	1.018	1.004	1.069	1.010
Flack	-	0.13(4)	-	-	-	-
$^aR_1$, [I>2σ(I)]	0.0335	0.0778	0.0613	0.0534	0.1153	0.0694
$^bwR_2$, (all date)	0.0849	0.2195	0.1444	0.1462	0.2598	0.1213

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

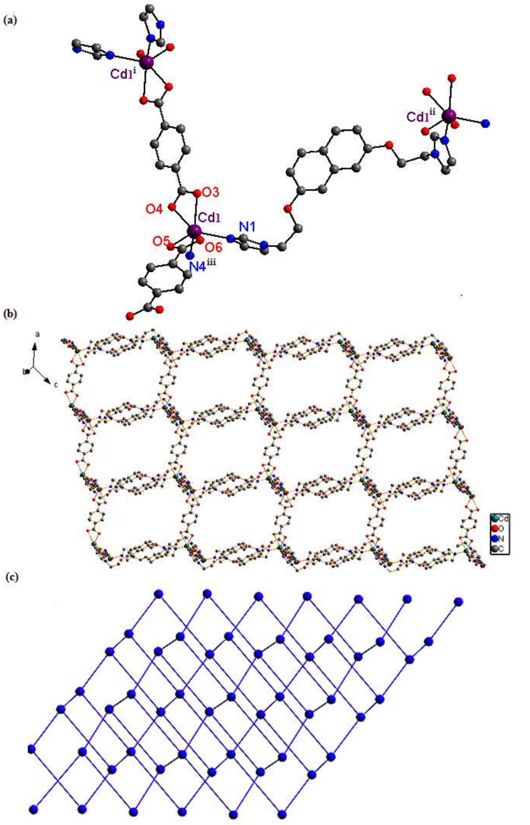


Fig. 1. (a) Coordination environment of the Cd(II) cation in **1**. The hydrogen atoms and solvent molecules are omitted for clarity. Symmetry code: i = -x, 2-y, 1-z; ii = 1+x, y, 1+z; iii = -1+x, y, -1+z. (b) Schematic representation of a puckered 2D network. (c) Topological representation of the 2D 2-fold interpenetrating framework of **1**.

Crystal structure of $[Co(L1)(p\text{-}bdc)(H_2O)_2]\cdot H_2O$ (2)

The structure of **2** is a three-dimensional metal-organic frameworks constructed by mutually staggered carboxylate groups and imidazole ligands. The asymmetric unit of **2** contains one Co(II) cation, a L1 ligand, one *p*-bdc^{2-}, two coordinated water molecules (O1W, O2W) and a lattice water molecule (O3W) which are a litter disordered and whose share is 50%, H atoms cannot be obtained by Fourier differential peak synthesis. As showed in Fig. 2a, the Co atom is six-coordinated with an octahedral geometry, composed of four oxygen atoms from carboxyl oxygen atoms of *p*-bdc^{2-} and two water molecules (O3, O6, O1W, O2W. Co-O = 2.082(5)-2.157(8) Å), and two nitrogen atoms (N1, N4) from two L1 ligands (Co-N1 = 2.089(1) Å, Co-N4 = 2.094(0) Å). N1 and N4, O1W and O2W, O3 and O6 are almost the axial atoms with N1-Co-N4 bond angle of 178.54(3)°, O1W-Co-O2W bond angle of 175.60(3)°, O3-Co-O6 bond angle of 176.60(3)°. The N-Co-O angles vary from 87.96(3)° to 90.77(3)°, which are almost perpendicular. The *p*-bdc^{2-} ligand adopts the monodentate coordination mode (Scheme 2c). The imidazole rings of **2** adopt an almost symmetric *trans*-configuration in which the dihedral angles between imidazole and naphthalene are 60.95(3)° and 63.38(3)°, respectively. In compound **2**, *p*-bdc^{2-} and Co ions are connected to form a linear metal carboxylate chain the same as compound **1** (Fig. S8). However, the arrangement of the chains is completely different from compound **1**, which is mutually staggered. And then, the ligand

L1 connects the remaining binding sites of metal carboxylate chain, extending forward or backward, to generate a 3D framework structure (Fig. 2b). The phenomenon is mainly because of free expansion of L1 in space. From the topological point of view, compound **2** forms a **qzd** (quartz-dual) "dense" net coordination framework with topology symbol{7^5.9}(Fig. 2c).

Crystal structure of [$Zn_2(L1)_2(p\text{-bdc})_2$]·$3H_2O$ (3)

Single-crystal X-ray diffraction analysis reveals that compound **3** is a 1D coordination polymer. The asymmetric unit is composed of two Zn(II) cations, two L1 ligands, one *p*-bdc^{2-} ligand and three lattice water molecules. As illustrated in Fig. 3a, two Zn(II) cations are in different coordination environments. The Zn1 is five-coordinated by three carboxylate oxygen atoms (O3, O4, O5) from two *p*-bdc^{2-} (Zn-O distances range from 1.987 (4) Å to 2.622 (4) Å) and two nitrogen atoms from two L1 ligands (Zn1-N1 = 1.982(4) Å, Zn1-N5 = 1.978(5) Å) with tetragonal pyramid coordination geometry. The minimum and maximum bond angles for Zn1 are 54.36(1)° and 120.22(2)°, respectively (O3-Zn1-O4 = 54.36(1), N5-Zn1-N1 = 120.22(2)°). The Zn2 is also in a distorted tetrahedral geometry defined by two carboxylate oxygen atoms (O8, O9) and two nitrogen atoms (N4, N8) (Zn2-O8 = 1.929(3) Å, Zn2-O9 = 1.920(4) Å, Zn2-N4 =1.957(0) Å, Zn2-N8 = 1.968(4) Å). N8-Zn2-N4 angle is 111.96(2)°. The *p*-bdc^{2-} ligand adopts the monodentate coordination mode (Scheme 2c). Interestingly, four deprotonated terephthalic acid molecules are linked by four zinc metal centers forming an almost all atoms are flat 36-membered ring. Furthermore, the rings are connected through the L1 ligands (*trans*-) in the adjacent zinc for the node and then stretching infinitely. In addition, the adjacent zinc atoms are linked by a L2 Ligand (*cis*-). Therefore, three kinds of rings coexist in compound **3**, the member numbers of rings are 56, 36, 28, forming "cryptand ring" of three dimensional holes (Fig. 3b). There are *trans*-configuration, in which the dihedral angles between imidazole and naphthalene are 65.84(2)° and 40.49(2)°, and *cis*-configuration, in which the dihedral angles between imidazole and naphthalene are 86.82(1)° and 47.76(3)° coexisting for L1 ligand. 1D topological network represent the buckle chain structure (Fig. S9).

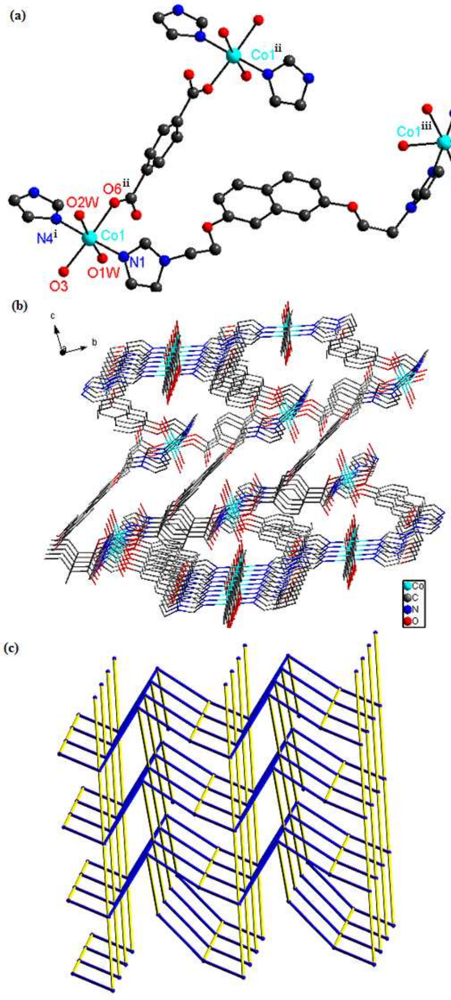


Fig. 2. (a) Coordination environment of the Co(II) cation in **2** with the ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity. Symmetry code: i = 1-y, 2+x-y, -1/3+z; ii = -1+x, y, z; iii = 1-x+y, 1-x, 1/3+z. (b) The viewing of 3D framework constructed by metal chain and L1 ligands. (c) Topological representation of the **qzd** net (The yellow sticks represent the *p*-bdc^{2-} ligand and blue sticks represent L1 ligand).

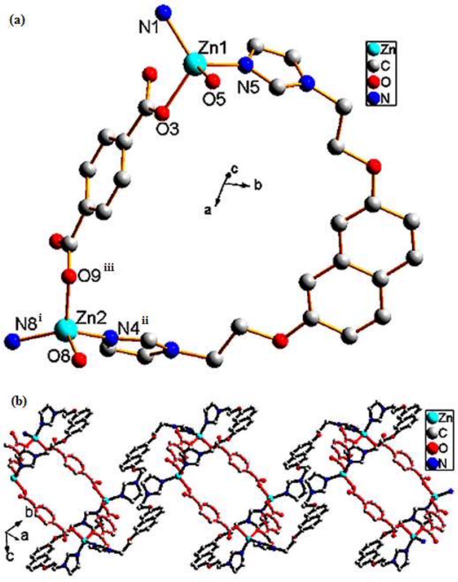


Fig. 3. (a) Coordination environment of the Zn(II) cations in **3**. The hydrogen atoms and solvent molecules are omitted for clarity. Symmetry code: i = 2+x, 1+y, z; ii = 3-x, 1-y, z; iii = 3-x, 1-y, 1-z. (b) Schematic representation of three kinds of rings of **3**.

Crystal structure of [Zn(L2)(*p*-bdc)]·DMF (4)

Single-crystal X-ray analysis reveal that the asymmetric unit is composed of one Zn(II) cation, one L2 ligand, one *p*-bdc^{2-} ligand and a lattice DMF molecule. As depicted in Fig. 4a, the Zn(II) center is located in a distorted square pyramidal geometry and coordinated by one monodentate carboxylate oxygen atom (O4) and two bidentate coordination carboxylate oxygen atoms (O5 and O6) from two *p*-bdc^{2-} ligands (Zn-O = 1.930(3)-2.007(4) Å) and two nitrogen atoms (N4, N1) from two L2 ligands (Zn-N = 2.005(3)-2.034 (3) Å). There are two coordination modes for *p*-H_2bdc ligands (Scheme 2b). Neighboring Zn cations are coordinated by *p*-bdc^{2-} ligands and come into a wavelike chain (N1-Zn-N4 angle is 102.83 (1)°) (Fig. S10). The L2 ligand adopts an asymmetric *cis*-configuration and the dihedral angles between benzimidazole and naphthalene are 75.92(6)° and 87.94(1)°, respectively, which connect remaining binding sites of Zn atoms extending upward or downward to generate a 2D reticular framework (Fig. 4b). The reticular net is composed by two L2 ligands and two *p*-bdc^{2-} ligands (Fig. S11). From the topological point of view, compound **4** shows slightly undulating with (4^4) topology (Fig. 4c).

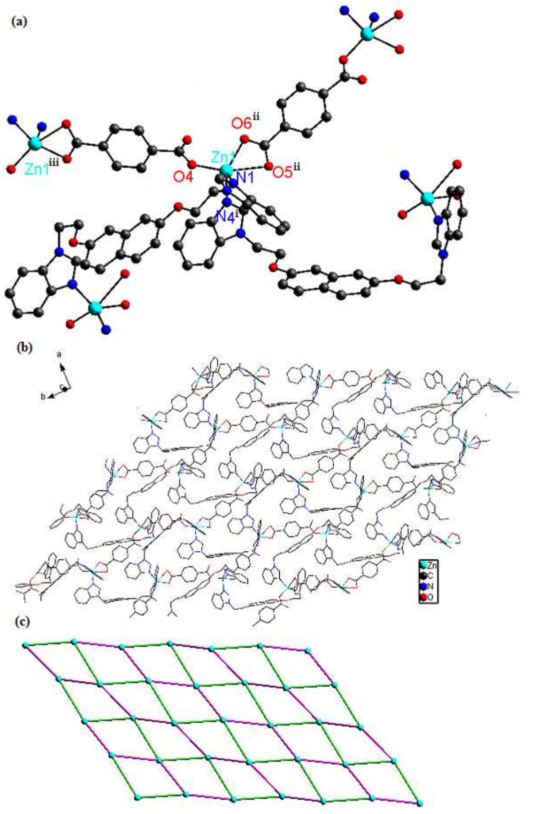


Fig. 4. (a) Coordination environment of the Zn(II) cation in **4**. The hydrogen atoms and solvent molecules are omitted for clarity. Symmetry code: i = 3/2-x, -1/2+y, z; ii = 1-x, -1/2+y, 3/2-z; iii = 1-x, 1/2+y, 3/2-z. (b) Schematic view of a 2D reticular framework. (c) Topological representation of 2D (4^4) network of **4** (The green sticks represent the L2 ligands and pink represent the *p*-bdc^{2-} ligands).

Crystal structure of [Co(L2)(*p*-bdc)(H_2O)]·H_2O (5)

Single-crystal X-ray analysis reveal that the asymmetric unit of **5** consists of one Co(II) cation, a L2 ligand, two half *p*-bdc^{2-} ligands each in independent inversion center, one coordinated water molecule and a lattice water molecule (O3W lies on an inversion center). As depicted in Fig. 5a, the six-coordinated Co center has an octahedral environment from four oxygen atoms (three oxygen atoms of O3, O4, O5 from two carboxyl oxygen atoms of *p*-bdc^{2-} and the fourth oxygen atom O1W from water molecule) and two nitrogen atoms(N1, N4) from two L2 ligands. Co-O distances are in the rang from 2.041(6) Å to 2.246(6) Å, the Co-N bond distances are 2.087(7) Å and 2.113(9) Å, respectively. There are two types of coordination modes for *p*-H_2bdc ligand (Scheme 2a, 2c). The L2 ligand is *trans*-configuration with the dihedral angles between benzimidazole and naphthalene of 55.93(2)° and 88.45(2)°, respectively. A particularly interesting feature of this structure is that two L2 ligands connect two Co centers to form a ring which was further linked by terephthalate ligands to form a larger ring. Therefore, the large ring contains two identical small rings, which just like a pair of handcuffs (Fig. S12) and the larger rings are mutually connected to form a 2D structure (Fig. 5b). The 2D net can be described as a special (4, 4)-connected framework with topology symbol {12}{4.12^5}{4} (Fig. 5c).

Crystal structure of [Co(L3)(*p*-bdc)(H_2O)]·2DMF (6)

The asymmetric unit of compound **6** consists of one crystallographically unique Co(II) cation lies on an inversion center, a L3 ligand and one *p*-bdc^{2-} lie on other independent inversion center, one coordinated water molecule and two lattice DMF molecules. As depicted in Fig. 6a, the coordination environment of compound **6** is similar to compound **2**. The Co(II) cation is six-coordinated and shows an octahedral environment from four oxygen atoms (two oxygen atoms from carboxyl group and the other two oxygen atoms from two water molecules) and two nitrogen atoms from two L3 ligands. The coordination mode of *p*-bdc^{2-} is similar to compound **2** (Scheme 2c). But their frameworks are totally different. Interestingly, two groups of O-Co-O and N-Co-N are all in the axial position, corresponding to the angles are all 180.00°. The L3 ligand adopts a symmetric *trans*-configuration with the dihedral angles between benzimidazole and naphthalene are almost equal (83.78(8)° and 83.77(8)°). The neighboring Co cations are coordinated by *p*-bdc^{2-} ligands to form a linear chain (Fig. S13). Then the chains are connected by L3 ligands to produce a planar structure (Fig. 6b). The 2D framework of **6** can be described as (4, 4)-connected framework with topology symbol $\{8^4.12^2\}\{8\}_2$ (Fig. S14).

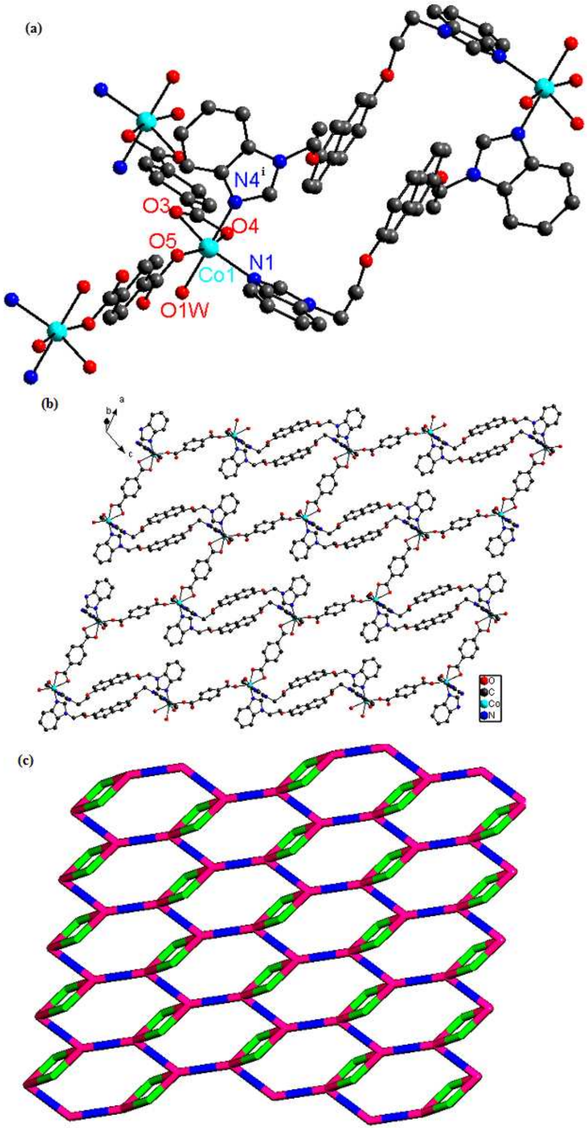


Fig. 5. (a) Coordination environment of the Co(II) cation in **5**. The hydrogen atoms are omitted for clarity. Symmetry code: i = -x, 1-y, -z. (b) Schematic view of a plane structure. (c) Schematic representation of 2D topological network of **5** (The pink spheres represent the Co center, green sticks represent the L2 ligands and blue sticks represent *p*-bdc^{2-}).

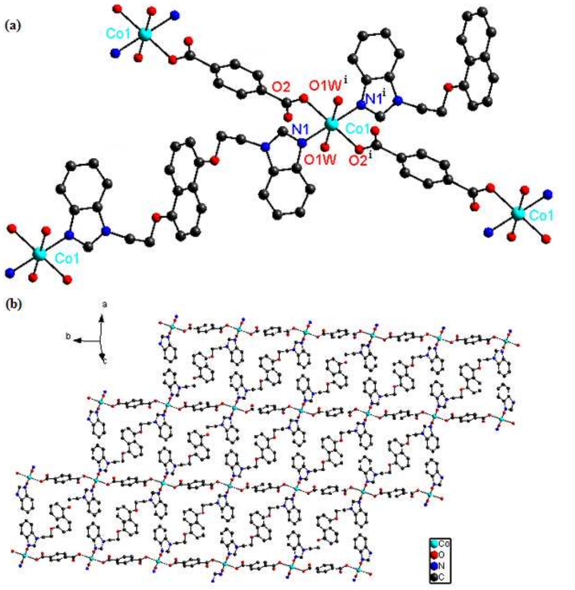


Fig. 6. (a) Coordination environment of the Co(II) cation in **6**. The hydrogen atoms and solvent molecules are omitted for clarity. Symmetry code: i = -x, 2-y, 2-z. (b) Schematic view of a 2D framework of **6**.

Effect of bis(imidazole) ligands and terephthalate coligand on the structures of complexes 1-6

Based on the character of the three bis(imidazole) ligands containing two flexible -O-CH$_2$-CH$_2$- chains and rigid naphthalene ring of bis(imidazole) can present a *cis/trans*-conformation and symmetric (with the same dihedral angles between imidazole arm and the naphthalene ring)/asymmetric (with different dihedral angles between imidazole arm and the naphthalene ring) conformations. From the structural descriptions above, the nature of naphthalene ring is rigid and flat, which can fix the conformation of the bis(imidazole) ligand to a certain extent, though the flexible alkoxy chains may have the opposite effect, therefore, which probably enhance conformational stability performance of the ligand to a certain degree during the self-assembly process. Ligands of L1, L2 or L3 exhibit an asymmetric *trans*-conformation in **2** and **5**, a symmetric *trans*-conformation in **1** and **6** as well as an asymmetric *cis*-conformation in **4**, but the asymmetric *cis* and *trans*-configuration coexist in the complex **3**. In addition, all of the dihedral angles between imidazole arm and the naphthalene ring among the various materials are different in **1**–**6**. Because the free conformations of the -O-CH_2-CH_2- chains with imidazol functional groups can rotate freely to meet metal ions, which beautify and enrich the structures of complexes. Moreover, we select terephthalate as coligand, which have an important influence on the construction of the resultant 1D, 2D, 3D structures. In these compounds, the terephthalate bridge adjacent Zn(II)/Cd(II)/Co(II) ions, leading to the formation of an infinite chain except forming a ring made of terephthalate and metal in complex **3**. Hence, in **1**, **4**, **5** and **6**, the bis(imidazole) ligand serve as bidentate bridging pillars showing a good stability to connect the remaining binding sites of metal carboxylate chains to generate 2D net. In complex **2**, for the arrangement of the chains is mutually staggered, the L1 ligand links the chains to produce a 3D framework. In complex **3**, the L2 ligand connects rings made of terephthalate and metal forming a wavelike 1D structure. Due to the formation of 2D compounds used in DMF/H_2O as solvent system, for 3D complex of **2** and 1D complex of **3**, CH_3CN/H_2O and CH_3OH/H_2O solvent systems are used, respectively, therefore, the appreciable structural differences of six crystals reveal that different solvent system probably influence the coordination of terephthalate and bis(imidazole) ligand as well as overall structures of the resultant complexes. These results show that the various coordination modes of the carboxylate group play key role in the construction of 2D frameworks and bis(imidazole) ligand exert an influence on the features and overall structures of six compounds.

PXRD analysis and thermogravimetric analysis (TGA)

In order to confirm the phase purity of compounds **1-6**, the powder X-ray diffraction (PXRD) patterns were carried out. Their peak positions were comparable to the corresponding simulated results from the single-crystal diffraction, indicating the phase purity of bulk synthesized materials (Fig. S15 -S20).

To examine the thermal stability of the compounds **1-6**, TG analyses were carried out (Fig. S21). The experiments were performed on samples consisting of numerous single crystals with a heating rate of 10 °C/min in N_2 atmosphere. Compound **1** shows two weight loss processes, the first weight loss which is attribute to the loss of lattice DMF molecule up to 171 °C (weight loss: measured 12.52%, theoretical 12.29%) and the second weight loss process is assigned to the decomposition of framework (starting from 345 °C). For compound **2**, it begins to release of water molecular at 89 °C (weight loss: measured 4.63%, theoretical 5.1%) and the complex starts to decompose at 349 °C. Compound **3** shows that the weight loss of 4.02% in the range of 87-349 °C which is probably due to releasing three lattice water molecules (theoretical 5.1%) and then the coordination polymer starts to decompose at 355 °C. The TGA curve of **4** displays a weight loss of 9.3% (theoretical 9.5%) at 256 °C, corresponding to the release of DMF molecule, and then the complex starts to decompose at 355 °C. Compound **5** exhibits a water loss of 2.01% between 95 and 110 °C which may be attributed to the release of lattice water molecular (theoretical 2.26%) and starts to decompose at 351 °C. For compound **6**, the weight loss of 17.01% (theoretical 17.12%) is consistent with the removal of a lattice DMF molecule, and then the framework begins to decompose at 349 °C. It is interesting that the six polymers do not thermally decompose below 345 °C, which may be attributed to the rigidity and planar nature of the naphthalene moiety in the N-containing ligand and terephthalate enhancing the coordinational stability with metal ions.[8a,8b]

Photoluminescent properties

Luminescent behaviors of compounds **1-6** were showed in the solid state at room temperature (Fig. S22). The excitation wavelengths of all compounds were at 265 nm. The emission peaks of the free ligands L1, L2 and L3 are observed at 379 nm in L1, 381 nm in L2, and 352 nm in L3, which may be attributed to the π*-n or π*-π transitions.[14a] The emission peak of terephthalic acid is 387 nm. The emission peaks of compounds **1** and **3** at 381 nm and 387 nm, respectively, in comparison to their bis(imidazole) ligand L1, which show a small red shift (2 nm, 8 nm) probably attributed to the π-π* or n-π* intraligand emission and enhanced conjugation in the ligands upon metal coordination.[18,19] For compound **4**, the emission peak at 348 nm, exhibiting strongest emission intensity compared with other compounds, which is mainly due to effectively increasing the rigid structure of the ligand.[20] Notably, compared with the corresponding ligand L2, complex **4** exhibits strong blue-shift (33 nm), which may be assigned to the intraligand π-π*or n-π* transition.[21] Compounds of **2**, **5** and **6** exhibit relatively weak emission band with a maximum at

389 nm, 420 nm and 381 nm, respectively. Because of corresponding paramagnetic metal effect, luminescence emission of the compounds **2**, **5**, **6** were severely quenched.[22] In view of the strong luminescence of Cd and Zn compounds, **1** and **4** may be good candidates for luminescent materials.

In addition, UV-vis diffuse reflectance spectra were investigated in the solid-state at room temperature (Fig. S23). The absorption spectrum of L1, L2, L3 and complexes **1-6** exhibit intense absorption peaks at 220-320 nm, which can be ascribed to π-π* transition between ligand and metal-to-ligand charge-transfer (MLCT) transition.[23] Meanwhile, the absorbance of complexes **1-6** are all stronger than the corresponding ligands. The splitting of the 3d levels transfers to the ligand which was accompanied by energy transfer in the UV-vis range of the electromagnetic spectrum.[24] Lower energy bands from 310 to 350 nm were assigned to metal-to-ligand charge-transfer (MLCT) transition.[14]

Conclusion

In summary, based on three new bidentate symmetry-related bis (imidazole) derivative ligands L1, L2 and L3 and coligand of terephthalic acid, six coordination polymers have been successfully constructed under hydrothermal conditions. All of the N-donor ligands contain two flexible -O-CH_2-CH_2- chains and a rigid naphthalene ring. For this reason, the imidazole group can rotate freely and generate different conformation to connect metal ions, which beautify and enrich the structures of complexes **1**–**6**, meanwhile, the rigid naphthalene ring enhanced the conformational stable property of the ligand and fluorescence characteristic. In addition, the various coordination modes of terephthalates play key roles in the construction of coordination polymers. Moreover, compounds of **1** and **4** display well fluorescence properties and may be good candidates for luminescent materials. We look forward that these approaches can be applied to build more coordination polymers.

Acknowledgments

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Short text and illustration for table of contents:

Six coordination polymers based on terephthalate and one of three bis(imidazole) ligands as well as their optical properties are reported.