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Constructing various metal-organic frameworks by mixed pyridine-acylamide and carboxylate ligands: ring-like or helical building blocks

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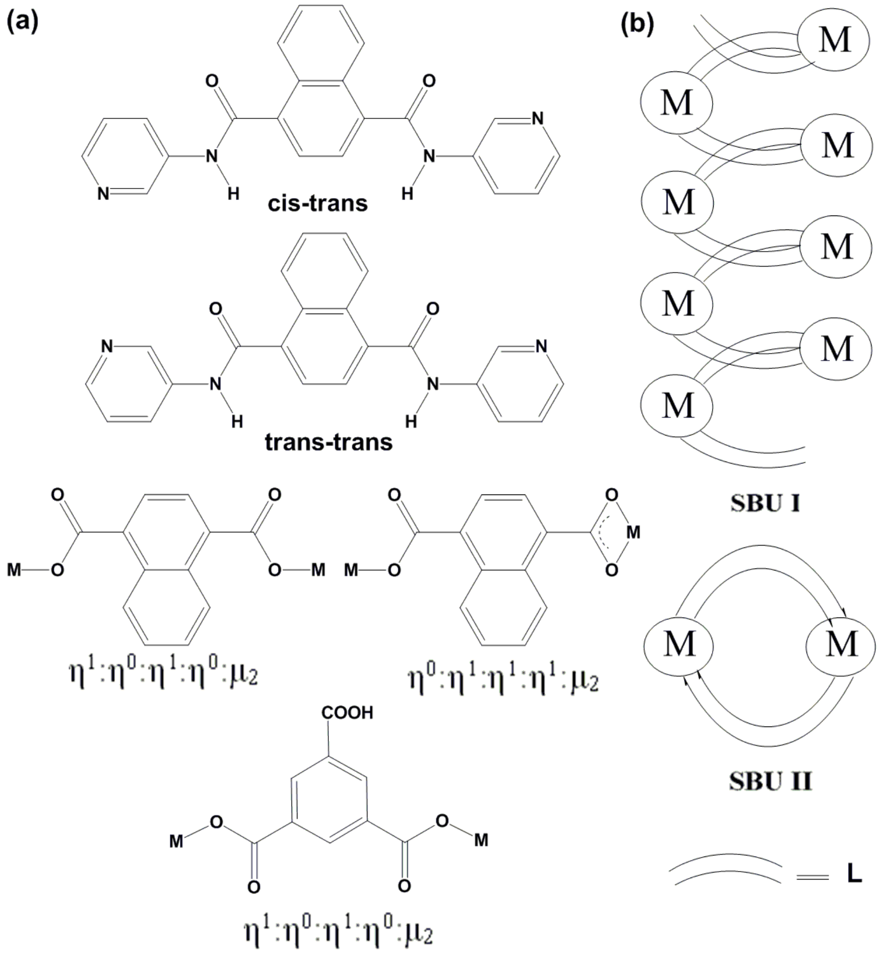
ABSTRACT: A new pyridine-acylamide ligand, L=L=N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide, has been synthesized. Based on L, four kinds of carboxylate ligands as co-ligands and two metal ions (Zn(Π) and Cd(Π)), seven new metal-organic frameworks have been synthesized and structurally characterized. Compounds **1** and **2** are constructed by SBU I (a helical $\{Zn(L)\}_n$ chain), while compounds **3-7** are assembled by SBU II (a M_2L_2 metallocycle). In **1**, with Hbtc^{2-} anions connected to the neighboring Zn(II) ions of one SBUs I, an infinite 1D chain is formed. While in **2**, the neighboring SBUs I are bridged by ip^{2-} anions forming a 2D structure. With SBUs II extended by oba^{2-} ligands, compound **3** shows a 2D network. Compound **4** exhibits a 1D infinite chain with SBUs II bridged by nap^{2-} ligands. Compound **5** and **6** are isomers, in which SBUs II are extended by nap^{2-} ligands to afford a 2D network. In compound **7**, SBUs II are linked together by Hbtc^{2-} ligands featuring an infinite 1D chain. All of these compounds have 3D framework governed by hydrogen bonds interactions. Compared all compounds, it demonstrates that the structural characteristics of L ligand and organic counteranions simultaneously play an important role in the construction of the compounds. Moreover, their thermostability and photoluminescence properties were explored.

Introduction

Metal-organic frameworks (MOFs) continue to progress at an explosive pace driven primarily by their intriguing structures, topologies, interesting properties and wide applications in the field of catalysis, magnetism, optics, gas storage and so on.[1-6] However, controllable synthesis of MOFs is still a great challenge, due to the fact that the self-assembly process of crystals are frequently influenced by various factors, including time, pH value, reaction temperature, template agents, the solvent system, metal-to-ligand ratio, the reactant stoichiometry, the method of crystallization, the chemical structure of the ligands chosen, the coordination geometry preferred by the metal, and so on.[7-10] In this field, it is still a major challenge to control the construction of MOFs. Even though, it is wise to carefully select the structure of organic ligands and the coordination geometry of metal ions to construct desirable MOFs.



Scheme 1. View of the configuration of L ligand, the coordination mode of carboxylate ligands, and the SBU involved in this work.

Mixed-ligand MOFs constructed from N-donor linkers, such as pyridine-acylamide ligand and carboxylate acids have attracted intensive interest because of their ability to incorporate the virtues of different functional groups and to easily obtain controlled architecture by changing one of the ligands.[11-13] With that in mind, we designed a new pyridine-acylamide ligand, N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide, as an organic linker, which features special characteristics, such as the free rotation of the pyridyl ring and naphthalene ring can improve the flexibility of the polymeric frameworks, the structures can be modified by changing the spacer groups, for instance, the length and angle of the spacer, and the good fluorescent characteristic of fluorene group may endow the resulting products some excellent luminescent properties. On the other hand, multidentate O-donor organic carboxylate ligands, such as 1,3,5-benzenetricarboxylate have been extensively employed in the construction of a rich variety of structures attributing to the diversity of the coordination modes.[12] Successfully, the combination of this new pyridine-acylamide ligand, L, that combines with different organic carboxylate ligands to generate diverse MOFs, namely, $\{[Zn(L)(Hbtc)]\cdot 2(H_2O)\}_n$ (**1**), $\{[Zn(L)(ip)]\cdot(H_2O)\}_n$ (**2**), $\{[Zn(L)(oba)]\cdot 2(H_2O)\}_n$ (**3**), $\{[Zn(L)(nap)]\cdot(H_2O)\}_n$ (**4**), $\{[Cd(L)(nap)(H_2O)]\cdot(DMF)\}_n$ (**5**), $\{Cd((L)(nap)(H_2O)\}_n$ (**6**), $\{[Cd(L)(Hbtc)(H_2O)]\cdot 2(H_2O)\}_n$(**7**) ($H_2oba$=4,4'-oxydibenzoic acid, H_2ip=isophthalic acid, H_3btc= benzene-1,3,5-tricarboxylic acid, H_2nap=naphthalene-1,4-dicarboxylic acid, DMF=N,N-dimethylformamide). These compounds have been characterized by elemental analysis and X-ray crystallography. Their photoluminescence properties were also studied in detail.

Experimental Section

Materials and Methods. The N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide was prepared by the reported method.[13] All other commercially available reagents are used as received without further purification. The characteristic IR bands of acylamide group around 3100 cm^{-1}, 1689 cm^{-1}, 1531 cm^{-1} and 1290 cm^{-1} were observed.[14]

Physical Measurements. We carried out thermogravimetric analyses (TGA) on METTLER TOLEDO TGA850 instrument in the temperature range of 20-800 °C under nitrogen atmosphere (flow rate of 50 mL min^{-1}) at a heating rate of 5 °C min^{-1}. Elemental analysis for C, H and N was performed on a Perkin-Elmer 240 analyzer. Steady-state photoluminescence spectra were measured on a SHIMADZU RF-5301PC spectro-Fluorophotometer. The infrared spectroscopy were carried out by Avater-360 Fourier infrared spectroscopy (KBr tablet) in 4000-400cm^{-1}.

The synthesis of 1. $Zn(NO_3)_2$ (0.2 mmol), N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide (0.2 mmol), benzene-1,3,5-tricarboxylic acid (0.2 mmol), H_2O (8 ml) was sealed in a 25 ml Teflon reactor, and heated at 160 ºC for 3000 min, and then cooled to room temperature at 3 ºC/h. Subsequently, colorless block crystals were obtained in 79% yield based on Zn, respectively. The phase purity of **1** is confirmed by both EA and XRD studies (Figure S1). Calcd for $C_{31}H_{24}N_4O_{10}Zn$ (%): C, 54.92; H, 3.57; N, 8.26. Found: C, 54.83; H, 3.49; N, 8.41.

The synthesis of 2. $Zn(NO_3)_2$ (0.2 mmol), N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide (0.2 mmol), isophthalic acid (0.2 mmol), H_2O (8 ml) was sealed in a 25 ml Teflon reactor, and heated at 160 ºC for 3000 min, and then cooled to room temperature at 3 ºC/h. Subsequently, colorless block crystals were obtained in 73% yield based on Zn, respectively. The phase purity of **2** is confirmed by both EA and XRD studies (Figure S2) Calcd for $C_{30}H_{22}N_4O_7Zn$ (%): C, 58.50; H, 3.60; N, 9.10. Found: C, 57.83; H, 3.56; N, 9.28.

The synthesis of 3. $Zn(NO_3)_2$ (0.2 mmol), N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide (0.2 mmol), 4,4'-oxydibenzoic acid (0.2 mmol), H_2O (8 ml) was sealed in a 25 ml Teflon reactor, and heated at 160 ºC for 3000 min, and then cooled to room temperature at 3 ºC/h. Subsequently, colorless block crystals were obtained in 65% yield based on Zn, respectively. The phase purity of **3** is confirmed by both EA and XRD studies (Figure S3) Calcd for $C_{36}H_{28}N_4O_9Zn$ (%): C, 59.55; H, 3.89; N, 7.72. Found: C, 60.03; H, 3.75; N, 7.68.

The synthesis of 4. $Zn(NO_3)_2$ (0.2 mmol), N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide (0.2 mmol), naphthalene-1,4-dicarboxylic acid (0.2 mmol), H_2O (8 ml) was sealed in a 25 ml Teflon reactor, and heated at 160 ºC for 3000 min, and then cooled to room temperature at 3 ºC/h. Subsequently, colorless block crystals were obtained in 29% yield based on Zn, respectively. The phase purity of **4** is confirmed by XRD studies (Figure S4).

The synthesis of 5. $Cd(NO_3)_2$ (0.1 mmol), N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide (0.1 mmol), naphthalene-1,4-dicarboxylic acid (0.1 mmol), H_2O (4 ml) was sealed in a 25 ml Teflon reactor, and heated at 85 ºC for 3000 min, and then cooled to room temperature at 3 ºC/h. Subsequently, colorless block crystals were obtained in 68% yield based on Cd, respectively. Calcd for $C_{37}H_{31}N_5O_8Cd$ (%): C, 56.53; H, 3.97; N, 8.91. Found: C, 56.41; H, 3.84; N, 8.78.

The synthesis of 6. $Cd(NO_3)_2$ (0.2mmol), N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide (0.2 mmol), naphthalene-1,4-dicarboxylic acid (0.2 mmol), H_2O(8 ml) was sealed in a 25 ml Teflon reactor, and heated at 180 ºC for 3000 min, and then cooled to room temperature at 3ºC/h. Subsequently, colorless block crystals were obtained in 76% yield based on Cd, respectively. The phase purity of **6** is confirmed by both EA and XRD studies (Figure S5). Calcd for $C_{34}H_{24}N_4O_7Cd$ (%):C, 57.28; H, 3.39; N, 7.86. Found: C, 57.16; H, 3.47; N, 7.79.

The synthesis of 7. $Cd(NO_3)_2$ (0.2 mmol), N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide (0.2 mmol), benzene-1,3,5-tricarboxylic acid (0.15mmol), H_2O (8 ml) was sealed in a 25 ml Teflon reactor, and heated at 180 ºC for 3000 min, and then cooled to room temperature at 3 ºC/h. Subsequently, colorless block crystals were obtained in 35% yield based on Cd respectively. The phase purity of **7** is confirmed by XRD studies (Figure S6).

Single-Crystal X-ray Diffraction. We collected X-ray single-crystal structural data of **1**−**7** on a Bruker Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source with graphite monochromated MoKα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The SAINT program was used for integration of diffraction profiles and absorption correction was made with the SADABS program. All the structures were solved by SIR 92 and refined by full matrix least-squares method using SHELXL 97. All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were fixed by HFIX and placed in ideal positions. All calculations were carried out using SHELXL 97, PLATON, and WinGX system, Ver 1.70.01. All crystallographic and structure refinement data of **1**−**7** are summarized in Table 1. CCDC number is 995445, 995446, 9954457, 995448, 995449, 995450, 995451 for compounds **1**-**7**, respectively.

Table 1. Crystallographic and Structure Refinement Parameters for **1−7.**

Compounds	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{31}H_{24}N_4O_{10}Zn$	$C_{30}H_{22}N_4O_7Zn$	$C_{36}H_{28}N_4O_9Zn$	$C_{34}H_{24}N_4O_7Zn$	$C_{37}H_{31}N_5O_8Cd$	$C_{34}H_{24}N_4O_7Cd$	$C_{31}H_{26}N_4O_{11}Cd$
Mr	677.95	615.93	726.04	665.99	786.08	712.99	742.96
crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
space group	*C2/c*	$P2_1/c$	$P2_1/c$	*P-1*	$P2_1/c$	$P2_1/n$	*P-1*
a (Å)	27.8066(4)	7.3644(18)	11.4423(3)	9.48340(10)	13.2139(5)	11.3580(2)	10.0055(5)
b (Å)	10.04640(10)	20.505(5)	13.6677(4)	10.6376(2)	21.7434(8)	18.7948(4)	10.2265(5)
c (Å)	22.2781(3)	18.269(4)	21.4571(5)	14.9133(2)	16.7754(6)	13.6608(3)	14.5845(8)
α (deg)	90	90	90	95.1910(10)	90	90	90.836(3)
β (deg)	109.2360(10)	101.628(4)	107.6760(10)	103.4170(10)	127.107(2)	100.4380(10)	93.894(3)
γ (deg)	90	90	90	96.8640(10)	90	90	90.720(3)
V ($Å^3$)	5876.06(13)	2702.1(11)	3197.25(15)	1441.99(4)	3843.9(2)	2867.93(10)	1488.56(13)
Z	8	4	4	2	4	4	2
D_{calc}(mg/m^{-3})	1.530	1.514	1.508	1.534	1.232	1.651	1.658
F(0 0 0)	2776	1264	1496	684	1440	1440	752
R_{int}	0.0295	0.0364	0.0301	0.0321	0.0286	0.0351	0.0580
GOF on F^2	1.082	1.096	1.136	1.075	1.048	1.137	1.118
$R1^a[I>2\sigma(I)]$	0.0374	0.0485	0.0419	0.0374	0.0301	0.0295	0.0383
$\omega R2^b$(all data)	0.0976	0.1391	0.1026	0.0907	0.0780	0.0664	0.0866

Results and Discussion

Crystal structure description

Structure of {[Zn(L)(Hbtc)]·2(H_2O)}$_n$ (1) Compound **1** crystallizes in a monoclinic, *C2/c* space group. The asymmetric unit of **1** is shown in Fig. 1a, the Zn(II) site is surrounded by four organic ligands, involving two L ligands and two $Hbtc^{2-}$ ligands. The Zn(II) ion exhibits a tetrahedral coordination geometry with two oxygen atoms of two $Hbtc^{2-}$ ligands and two nitrogen atoms of two L ligands. The Zn-O/N bond lengths (Zn-O/N 1.978(1)-2.047(9)Å) are all within the normal range found in the literature.[15] The L ligand adopts *trans-trans* configuration, where '*trans*' means that the pyridyl nitrogen atom and the nitrogen atom in the amide group have the different orientation and vice versa, it is '*cis*' (Scheme **1**). And it gives a Zn...Zn separation of 16.343 Å. The distortion degree of L ligand traced by the dihedral angle between pyridine and naphthalene rings is ca. 43.5° or 70.6°. Notably, H_3btc ligands are partially deprotonated with two -COOH group deprotonated.

Each Hbtc^{2-} ligand connects to two Zn(Π) ions adopting the coordination mode $\eta^1:\eta^0:\eta^1:\eta^0:\mu_2$ (Scheme 1). With Hbtc^{2-} ligands connecting neighboring Zn(Π) ions together, a helices [M(L)]$_n$ chains is formed (Fig. 1b). As shown in Fig. 1c, with one helices (SBUs I) and Hbtc^{2-} ligands connecting to adjacent zinc atoms of the helices, the infinite 1D chain is formed along the *b* direction. With the packing of 1D chains, then a 3D supramolecular framework is formed, governed by hydrogen bonds between water and Hbtc^{2-} ligand (O7-H2W...O10/2.8673Å/179.347º, O9-H9A...O7/2.610(0)Å/172.275º), between water and L ligand (O7-H1W...O1/2.930(0)Å/147.130º, N1-H1M...O8/2.943(5)Å/160.613º). (Fig. 1d)

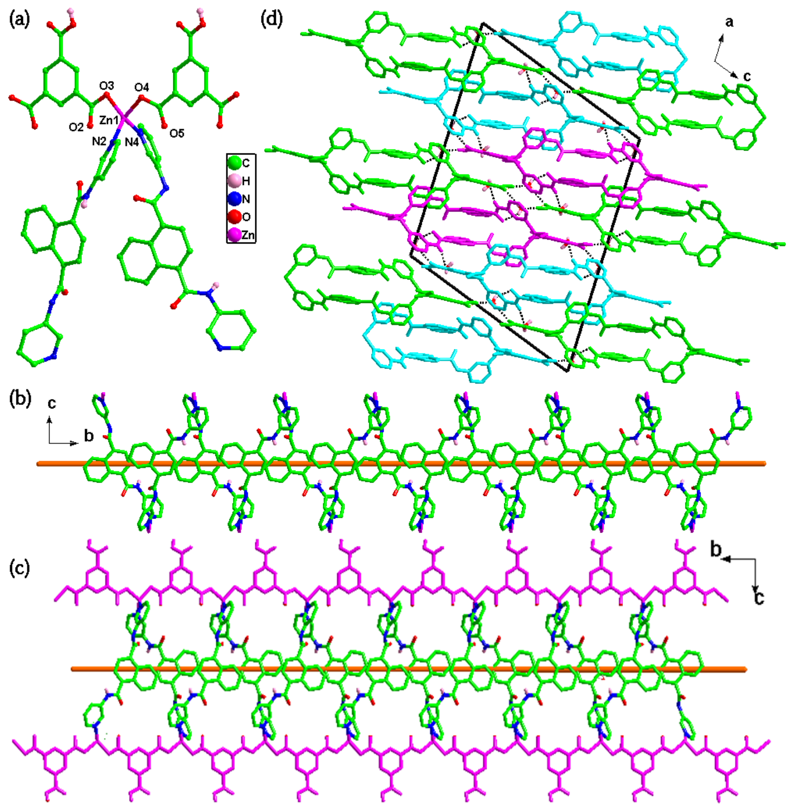


Fig. 1. Structure of **1**. (a) The coordination environment of **1**. Hydrogen atoms except on acylamide group are omitted for clarity. Atoms are colored as follows: C: green, H: purple, O: red, N: blue, Zn: pink. (b) 1D helical structure constructed by zinc centers and L ligands (SBU I). (c) The infinite 1D chain of **1** constructed by the Zinc centers, L ligands (SBU I), and the Hbtc^{2-} ligands (colored as pink). (d)Packing of the 1D chains(with different color) to 3D framework of **1** governed by hydrogen bonds(black dotted line).

Structure of {[Zn(L)(ip)]·H$_2$O}$_n$ (2) Compound **2** crystallizes in a monoclinic, *P2$_1$/c* space group. The asymmetric unit is shown in Fig. 2a, the Zn(II) site binds to two nitrogens from two

L ligands and two oxygens from two ip^{2-} ligands, creating a tetrahedral geometry. The Zn-O/N bond lengths of 1.917(6)-2.051(3) Å are in the normal range.[15] The L ligand adopts *cis-trans* configuration (Scheme 1), and the distortion degree of L ligand can be traced by the dihedral angle between pyridine and naphthalene rings, giving ca. 19.3º or 7.5º. With neighboring Zn(Π) ions are connected by L ligands, a helical chain, that is, SBUs I is formed (Fig. 2b). Through ip^{2-} spacers, neighboring (SBUs I) helical polymeric chains are connected together (Fig. 2c), and this kind of connectivity finally results in the overall 2D net. If L and ip^{2-} are considered as linkers, Zn centers can be clarified as four-connected nodes. Thus the topology of the structure can be simplified as a 2D ($4^4.6^2$) network (Fig. 2d). Three are three kinds of hydrogen bonds in the 2D network, that is, between the acylamide group of L ligand and water oxygen atom (N4-H2M...O7/2.826(1)Å/159.661º), between water group and acylamide nitrogen atom (O7-H1W...N4/2.826(1)Å/40.174º), between water group and ip^{2-} oxygen atom (O7-H2W...O4/2.835(4)Å/159.295º) (Fig. 2e). Then, governed by intermolecular hydrogen bonds between the acylamide group of L ligand and ip^{2-} oxygen atom (N3-H1M...O1/2.939(6) Å/149.548º), the 2D net are connected to obtain a 3D supramolecular net (Fig. 2e).

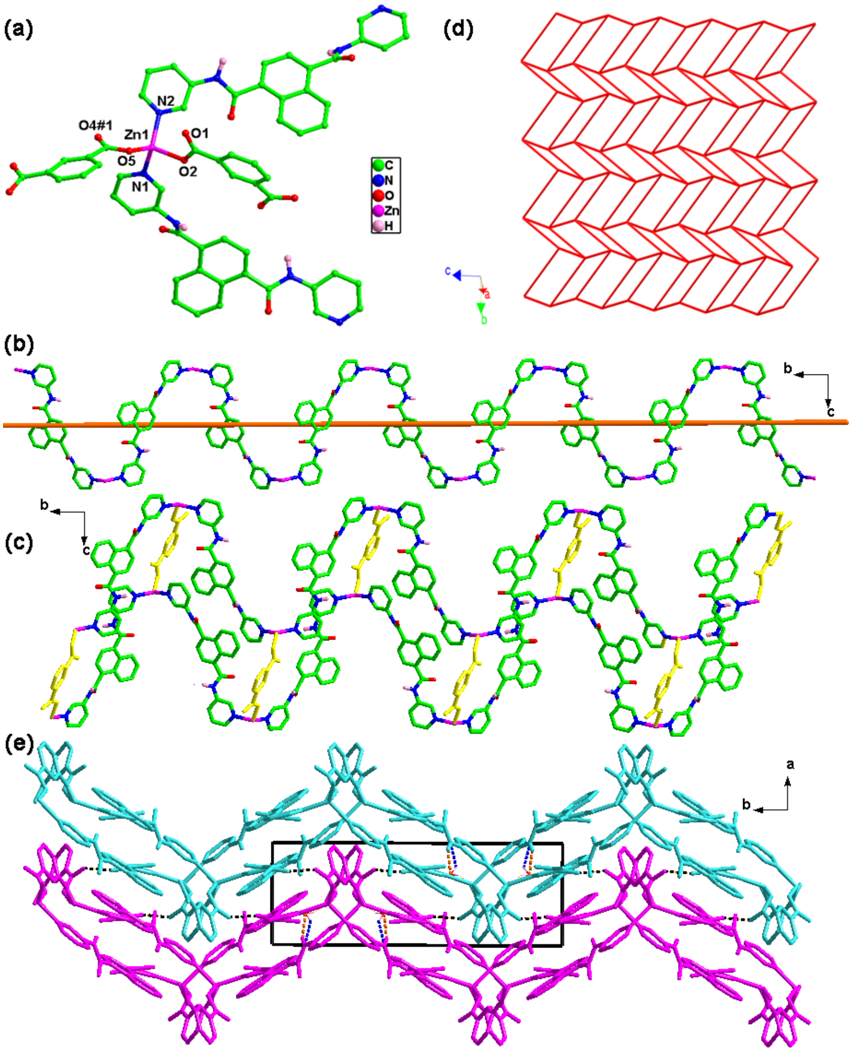


Fig. 2. Structure of **2**. (a) The coordination environment of **2**. Hydrogen atoms except on acylamide group are omitted for clarity. Atoms are colored as follows: C: green, H: purple, O: red, N: blue, Zn: pink. The symmetry code #1: x, 0.5-y, z-0.5. (b) 1D helical structure constructed by zinc centers and L ligands (SBU I). (c) The adjacent 1D helical chains(SBU I) connected by ip^{2-} ligands(colored as yellow) in the 2D net of **2** and (d) its ($4^4.6^2$) topology. (e) The view of the 3D framework of **2** governed by intermolecular hydrogen bond interactions (N3-H2M...O1, black dotted line), hydrogen bonds between the free water molecule and L (blue and yellow dotted line), hydrogen bonds between the free water molecule and ip^{2-} (red dotted line), and the two 2D nets are colored as pink and sky blue, respectively.

Structure of {[Zn(L)(oba)]·2(H_2O)}$_n$ (3) The single crystal X-ray diffraction reveals that compound **3** crystallizes in monoclinic, *P2₁/c* space group. As shown in Fig. 3a, Zn(II) site is four-coordinated by two oba^{2-} oxygens and two L nitrogens, resulting in the tetrahedral geometry. The Zn-O/N bond lengths range from 1.941(1) Å to 2.085(3) Å. The L ligand adopts *cis-trans* configuration. And the distortion degree of L ligand can be traced by the dihedral angle between pyridine and naphthalene rings, giving ca. 41.1° or 57.9°. Note that two L ligands bind to two Zn(II) ions to generate a 30-membered $Zn_2(L)_2$ metallocyclic ring (Fig. 3b), which is considered as SBU II. The length and width of the ring is ca. 15.4 Å × 7.6 Å (Fig. 3b). And through four oba^{2-} ligands connecting to the two Zn(П) ions of the ring, other four neighboring identical $Zn_2(L)_2$ loops are linked to this one. (Fig. 3c) Then this structure extends into a 2D layer. There are two kinds of free water molecules. Furthermore, as shown in Fig. 3d, a 3D supramolecular framework is obtained, governed by three kinds of hydrogen bonds between the acylamide group and water oxygen atom (N3-H2M...O8/2.851(7)Å/176.150°, N4-H1M..O9/3.002(3)Å/164.366°), between water group and oba^{2-} oxygen atom (O8-H1W...O1/2.785(8)Å/172.125°, O8-H2W...O1/2.758(1)Å/168.611°, O9-H3W...O5/ 2.764(1)Å/165.584°), between water group and L oxygen atom (O9-H4W...O6 /2.975(1)Å/166.979°).

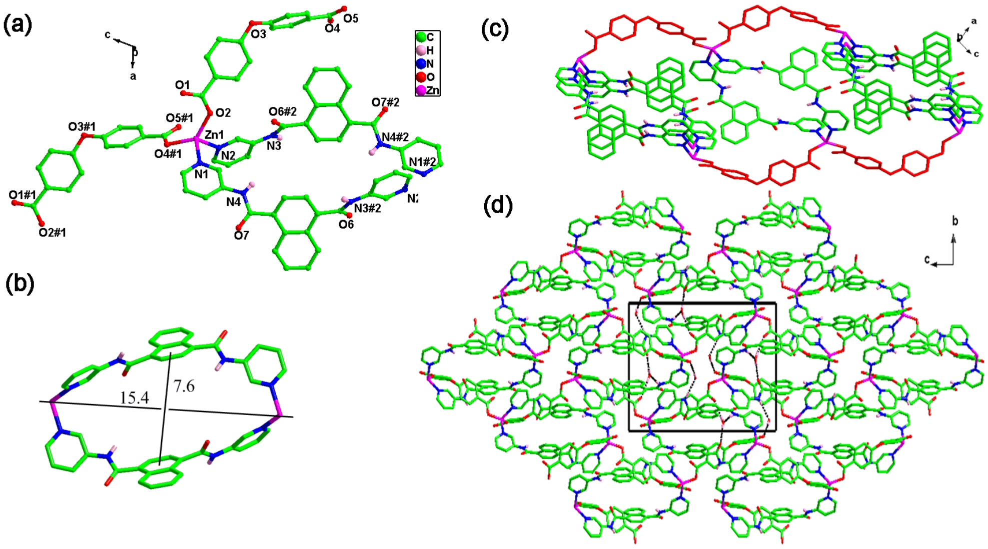


Fig. 3 (a)The coordination environment of **3**. Hydrogen atoms except on acylamide group are omitted for clarity. Atoms are colored as follows: C: green, H: purple, O: red, N: blue, Zn: pink. The symmetry code #1: 1+x, 0.5-y, 0.5+z; #2 1-x, 1-y, -z. (b) View of the 30-membered ring (SBU П). (c) One 30-membered ring (SBU II) connects to other four neighboring rings by four oba^{2-} ligands(colored as red) in the 2D net of **3**. (d) The 3D framework of **3** with hydrogen bond interactions(black dotted line).

Structure of $\{[Zn(L)(nap)]\cdot(H_2O)\}_n$ (4) Compound **4** crystallizes in a triclinic, *P-1* space group. As shown in Fig. 4a, the asymmetric unit of **4** consists of one independent Zn(II) ion, one L ligands and one crystallography-independent nap^{2-} ligands. The Zn(II) ion, connecting to two N atoms from two L ligands (Cd-N 2.086(9)-2.126(3) Å) and two O atoms from two nap^{2-} ligands (Cd-O 1.921(1)-1.956(6) Å), exhibits a tetrahedral geometry. The L ligand adopts *trans-trans* configuration. And the distortion degree of L ligand traced by the dihedral angle between pyridine and naphthalene rings give ca. 42.9º or 85.4º. Each nap^{2-} ligand connects to two Zn(II) ions adopting the coordination mode $\eta^1:\eta^0:\eta^1:\eta^0:\mu_2$ (Scheme 1). Through two L ligands, two Zn(II) atoms are linked together forming a 30-membered metallocyclic SBU II ring(Fig. 4b). The length and width of it is ca. 16.4 Å × 3.9 Å. And each ring is bridged to each other by two nap^{2-} ligands connecting to Zn(II) ions to generate an infinite 1D chain along the *b* direction (Fig. 4c). These 1D chains are bridged by hydrogen bonds(between L amide group and nap^{2-} oxygen atom (N2-H1M...O5/2.013(4)Å/169.501º), between water group and L oxygen atom(O6-H1W...O1/1.979(3)Å/171.634º), between L amide group and water oxygen atom (N4-H2M...O6/2.068(6)Å/176.057º)) to generate a 3D framework (Fig. 4c).

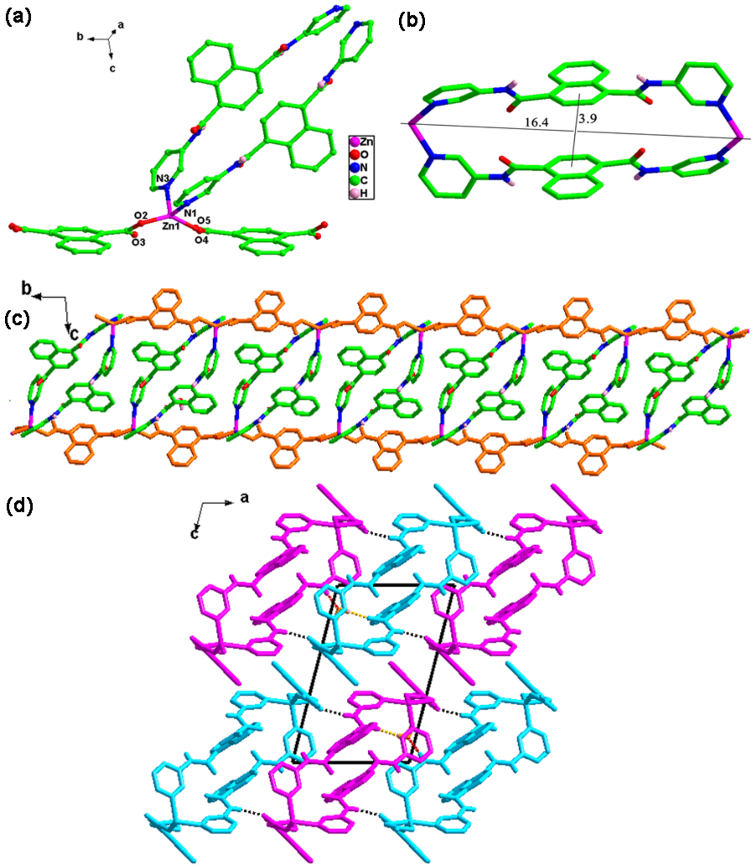


Fig. 4 Structure of (**4**). (a) The coordination environment of **4**. Hydrogen atoms except on acylamide group are omitted for clarity. Atoms are colored as follows: C: green, H: purple, O: red, N: blue, Zn: pink. (b) View of the 30-membered metallocyclic SBU П ring, and (c) the 1D chain of **4** with nap^{2-} ligands colored as orange. (d) View of the 3D framework of **4** governed by hydrogen bonds(intermolecular hydrogen bond interactions: blue dotted line, hydrogen bonds between water

and L ligand: red and yellow dotted line) with different colors to distinguish different 1D chains.

Structure of $\{[\mathrm{Cd(L)(nap)(H_2O)}]\cdot\mathrm{DMF}\}_n$ (5) Compound **5** crystallizes in a monoclinic, $P2_1/c$ space group. In the structure, there are one crystallographically unique Cd(II) atom, one nap^{2-} anion, one L ligand, one coordinated water molecule, and one free DMF molecule. According to the Platon calculation, the volume occupancy of per unit cell for solvent DMF molecule is 29.8%. As shown in Fig. 5a, the Cd atom is six-coordinated by three oxygen atoms from two nap^{2-} ligands(Cd-O 2.290(1)-2.417(3) Å), two nitrogen atoms from two L ligands(Cd-N 2.329(7)-2.369(0) Å), and one oxygen atom from the coordinated water molecule (Cd-O 2.341(8)Å). The L ligand adopts *trans-trans* configuration. And the distortion degree of L ligand traced by the dihedral angle between pyridine and naphthalene rings give ca. 32.5° or 75.7°. Bridged by two L ligands, two Cd(II) ions are connected together, forming a 30-membered metallocyclic SBU II ring (Fig. 5b). The length and width of it is ca. 16.9 Å × 4.7 Å. Each nap^{2-} ligand connects to two Cd(II) ions of two SBUs II with the coordination mode of $\eta^0:\eta^1:\eta^1:\eta^1:\mu_2$ (Scheme 1). And each SBU II is bridged to four adjacent SBUs II by four nap^{2-} ligands connecting to Cd(II) ions (Fig. 5c). This structure extends into a 2D brick-wall framework (Fig. 5c). Governed by hydrogen bonds between the acylamide group of L ligand and nap^{2-} oxygen atom (N2-H2M...O1/2.915(8)Å/162.040°, N3-H3M...O4/2.883(3)Å/167.876), a 3D framework is obtained (Fig. 5d).

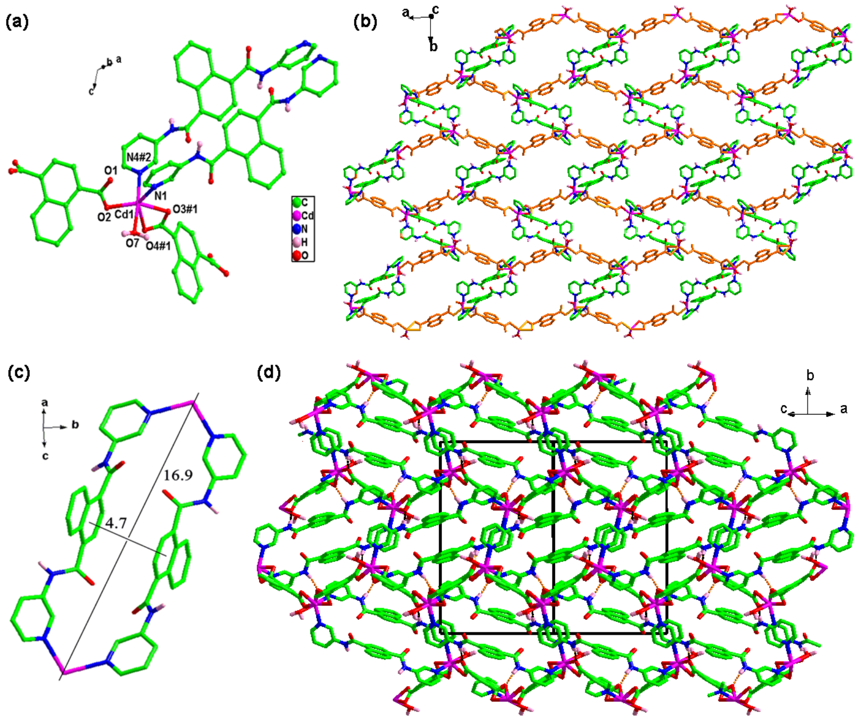


Fig. 5. Structure of (**5**). (a) The coordination environment of **5**. Hydrogen atoms except on

acylamide group are omitted for clarity. Atoms are colored as follows: C: green, H: purple, O: red, N: blue, Cd: pink. The symmetry code #1: 1+x, 0.5-y, 0.5+z. #2 2-x, 1-y, -z. (b) The 30-membered metallocyclic SBU Π ring. (c) The view of the 2D net with nap^{2-} ligands colored as orange. (d) The 3D framework of **5** governed by hydrogen bonds(yellow dotted line).

Structure of {Cd((L)(nap)(H_2O)}$_n$ (6) Compound **6** crystallizes in a monoclinic, *P2(1)/n* space group. In the structure, the asymmetric unit contains one crystallography-independent Cd(II) ions, one crystallography-independent L ligand and one crystallography-independent nap^{2-} ligand and one coordinated water molecule. The immediate coordination environment around the cadmium center is shown in Fig. 6a. Each Cd(II) is five coordinated by two oxygen atoms from two nap^{2-} ligands (Cd-O 2.261(4)-2.308(4) Å), two nitrogen atoms from two L ligands (Cd-N 2.295(8)-2.420(2) Å), and one oxygen atom from coordinated water molecule (Cd-O 2.364(1) Å). The L ligand adopts *trans-trans* configuration. And the distortion degree of L ligand traced by the dihedral angle between pyridine and naphthalene rings give ca. 12.3^{o} or 75.4^{o}. In **6**, each nap^{2-} ligand connects to two Cd(II) ions adopting the coordination mode $\eta^1:\eta^0:\eta^1:\eta^0:\mu_2$ (Scheme 1). Two Cd(II) atoms are bridged together by two L ligands, creating a 30-membered metallocyclic SBU II ring. The length and width of it is ca. 16.9 Å × 4.0 Å. Through four nap^{2-} ligands connecting to two Cd(II) ions of the SBU II, each SBU II bridges to other four neighboring ones. Then this structure extends into a 2D network (Fig. 6c). And the 3D net is obtained by hydrogen bonds between the water group and L oxygen atom (O7-H2W...O5/2.900(3)Å/170.038^{o}), between water group and nap^{2-} oxygen atom (O7-H1W...O1/2.767(1)Å/175.554^{o}), between acylamide group and nap^{2-} oxygen atom (N2-H2M...O3/3.151(1)Å/155.290^{o}).

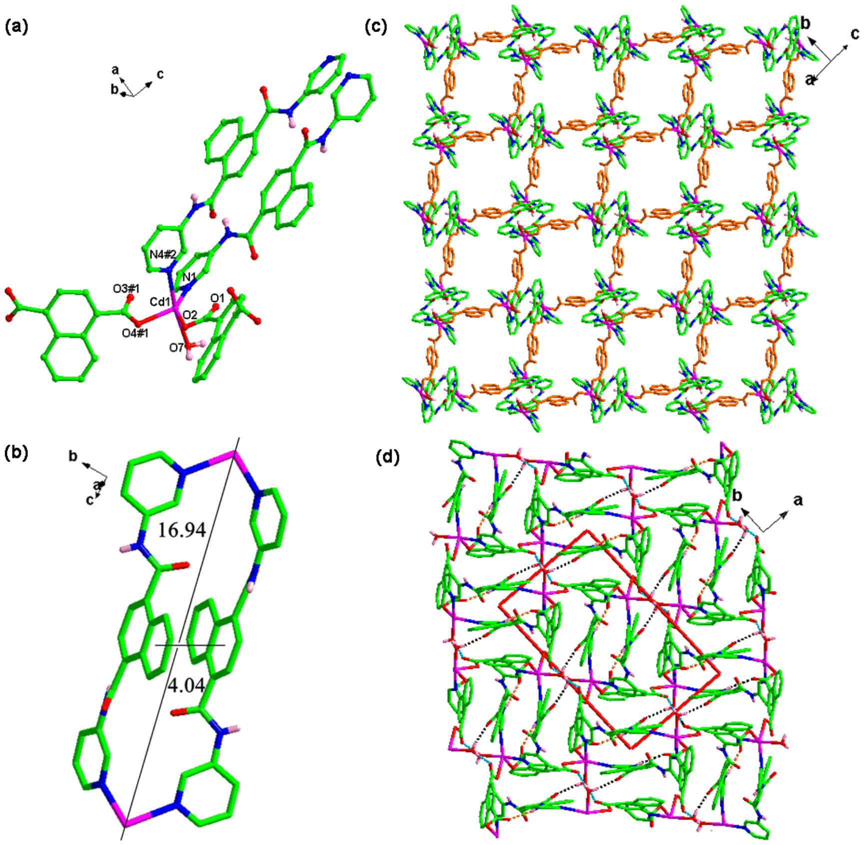


Fig. 6. Structure of (**6**). (a) The coordination environment of **6**. Hydrogen atoms except on acylamide group are omitted for clarity. Atoms are colored as follows: C: green, H: purple, O: red, N: blue, Cd: pink. The symmetry code #1: 0.5+x, 0.5-y, z-0.5. #2 2-x, -y, 1-z. (b) View of the 30-membered metallocyclic SBU Π ring, (c) the 2D net of **6** with the nap^{2-} ligands colored as orange. (d) View of the 3D framework of **6** governed by hydrogen bonds(O7-H1W...O1/sky blue dotted line, N2-H2M...O3/yellow dotted line, O7-H2W...O5/black dotted line).

Structure of {[Cd(L)(Hbtc)(H_2O)]·2(H_2O)}$_n$ (7) Compound **7** crystallizes in a triclinic, *P-1* space group. As shown in Fig.7a, the Cd(II) ion is five-coordinated by two oxygen atoms from two Hbtc^{2-} ligands, two nitrogen atom from two L ligands and one oxygen atom from the coordinated water molecule.The L ligand adopts *trans-trans* configuration. And the distortion degree of L ligand traced by the dihedral angle between pyridine and naphthalene rings give ca. 42.9° or 86.7°. Two Cd(Π) ions are bridged together by two L ligands forming a 30-membered metallocyclic SBU II ring, the length and width of which is ca. 17.0 Å × 3.9 Å (Fig. 7b). It similar to compound **1** that H_3btc ligand is partially deprotonated with two -COOH group deprotonated. By the coordination mode $\eta^1:\eta^0:\eta^1:\eta^0:\mu_2$, each Hbtc^{2-} ligand connects to two Cd(II) ions. And by two Hbtc^{2-} ligands, two adjacent SBUs II are linked together, then this unit extends into a infinite 1D chain along the *b* direction. (Fig. 7b). There are hydrogen bonds between the free water group and L oxygen atom (O11-H3W...O8/2.756(0)Å/178.595º), and between the free water group and $Hbtc^{2-}$ oxygen atom (O11-H4W...O2/2.897(1)Å/176.168º) in this 1D chain. With the packing of 1D chains, the 3D framework is obtained governed by hydrogen bonds between free water molecules (O10-H5W...O10#/3.017(8)Å/121.334º), between free water molecule group and coordinated water oxygen atom (O10-H5W...O7/2.818(4)Å/123.070º), between coordinated water group and $Hbtc^{2-}$ oxygen atom (O7-H1W...O3/2.743(4)Å/168.290º, O7-H2W...O6/2.830(2)Å/172.325º), between $Hbtc^{2-}$ group and free water oxygen atom (O5-H3M...O10/2.541(7)Å/141.620º), between free water molecule and $Hbtc^{2-}$ oxygen atom (O10-H6W...O2/2.734(7)Å/166.581º, O11-H4W...O2/2.897(1)Å/176.168º), between free water molecule and L ligand (O11-H3W...O8/2.756(0)Å/178.595º, N3-H2M...O11/2.808(6)Å/ 172.638º), between the acylamide group and $Hbtc^{2-}$ oxygen atom(N2-H1M...O1/3.137(6)Å/ 168.646º).

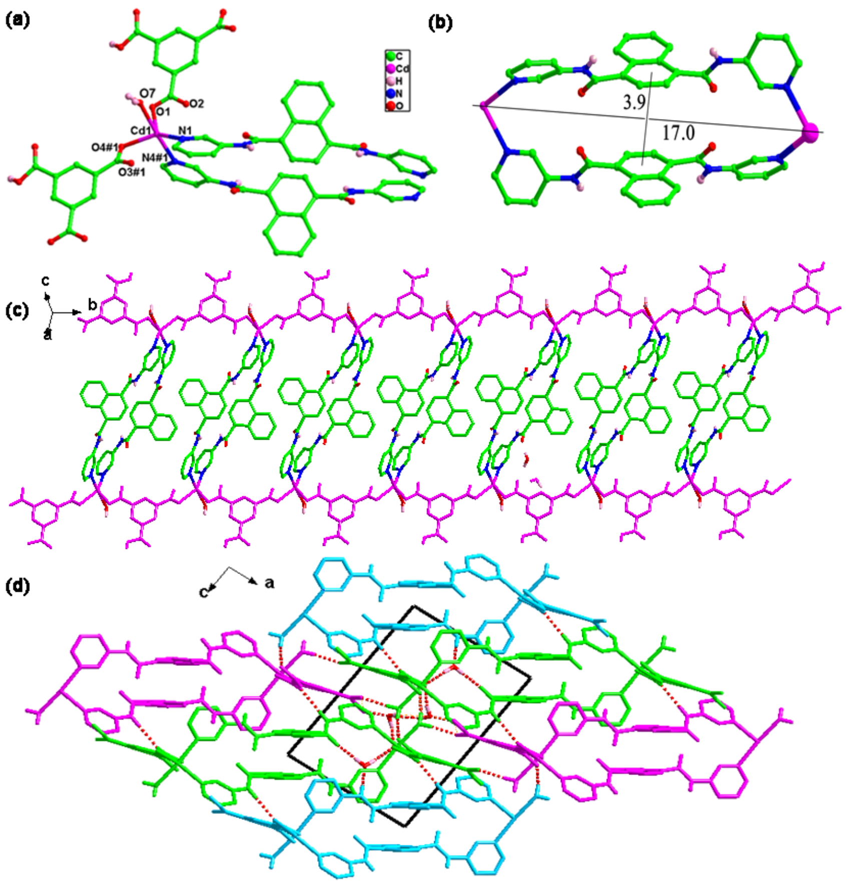


Fig. 7. Structure of (7). (a) The coordination environment of **7**. Hydrogen atoms except on acylamide group are omitted for clarity. Atoms are colored as follows: C: green, H: purple, O: red, N: blue, Cd: pink. The symmetry code #1: x, y-1, z. (b) View of the 30-membered metallocyclic SBU Π ring, and (c) the 1D chain of **7** with $Hbtc^{2-}$ ligands colored as pink. (d)

View of the 3D framework of **7** governed by hydrogen bonds(red dotted line) with different 1D chains are colored as different colors.

As mentioned above, both compound **1** and **2** contain SBUs I with different connectivity. In **1**, each $Hbtc^{2-}$ ligand connects two adjacent Zn(Π) ions in one SBUs I forming an infinite 1D chain, while each ip^{2-} ligand connects two adjacent Zn(Π) ions of two neighboring SBUs I extending into a 2D network in **2**. The L ligand adopts *trans-trans* configuration in **1**, while *cis-trans* in **2**. With different length and width of the metallocyclic SBU II, we obtained compound **3-5**. The L ligand in compound **3** adopts *cis-trans* configuration, while *trans-trans* in other compounds. And the nap^{2-} ligands in compound **4** and **6** adopt the coordination mode of $\eta^1:\eta^0:\eta^1:\eta^0:\mu_2$, while $\eta^0:\eta^1:\eta^1:\eta^1:\mu_2$ in compound **5**. In **3**, SBUs II are extended by oba^{2-} ligands forming a 2D net. Compound **4** features an infinite 1D chains by $Hbtc^{2-}$ ligands linked neighboring SBUs II together. Isomers **5** and **6** exhibit a 2D network in which five SBUs II are bridged together by four nap^{2-} ligands. In compound **7**, neighboring SBUs II are linked together by $Hbtc^{2-}$ ligands featuring an infinite 1D chain.

As discussed above, the L ligand act as a bidentate bridging ligands with *cis-trans* and *trans-trans* configuration. Moreover, the L ligand incorporates either $[Zn(L)_n]$ helical chain structure or M_2L_2 metallocycle which is apparently determined by the orientation of the C-N-C bond. Considering these two structural units as building blocks that are further linked by other ligands, unique MOFs are obtained. The various architectures of **1-7** are synthesized by the combination of these SBUs with four carboxylate anions ligands that show various position and quantities of carboxyl group and a diversity of coordination modes. It can't be ignored the significance of the metal coordination geometries in the formation of the product. The transition metal cations(Zn(Π) and Cd(Π)) adopt various coordinated geometries, that is, four-, five-, six-coordination. All these factors work together to influence the final structures, thus it is still difficult to separate and rationalize all these factors or to investigate the decisive reasons that each compound adopts a different configuration.

IR ,TG and Fluorescence Properties

We carried out IR studies for complex **1**, **2**, **3**, **4**, **6**, **7**. We observed characteristic IR bands of acylamide group in them (**1:** 3321, 3073, 1678; **2:** 3395, 3073, 1678; **3:** 3395, 3064, 1677; **4:** 3300, 3073, 1678; **6:** 3311, 3073, 1668; **7:** 3325, 3063, 1673cm^{-1}). And the characteristic IR bands of carboxyl group are also observed in them (**1:** 1719, 924; **2:** 1710, 933; **3:** 1740, 933; **4:** 1710, 913; **6:** 1711, 934; **7:** 1720, 913cm^{-1}).

Because the yield of polymers **4** and **7** is very low, we study the thermogravimetric and the fluorescence of the other compounds. As shown in Fig. 8, **1** is stable below 70 ºC, and free water molecules are lost during 71 ºC to 117 ºC (exp. 5.5%, calc. 5.3%). Chemical decomposition begins around 293 ºC with a sharp weigh loss. For **2**, below 150 ºC, there is no weight loss. During 151 ºC to 230 ºC, it is the weight loss of free water molecules (exp. 2.8%, calc. 2.9%). And the sharp weight loss above 325ºC is due to chemical decomposition. For **3**, it is stable below 100ºC, and the weight loss of free water molecules is during 100ºC to 170ºC (exp. 4.8%, calc. 4.9%). Around 300ºC, chemical decomposition begins with a sharp weight loss. Below 71ºC, **5** is stable, while the DMF solvent molecule is lost around 137ºC (exp. 9.5%, calc. 9.3%). And around 172ºC, the coordinated water molecule is lost (exp. 2.2%, calc. 2.3%). Then it begins to decompose gradually when the temperature increase. For **6**, it begins to gradually decompose around 53ºC. The coordinated water molecules are lost around 135ºC (exp. 5.8%, calc. 2.5%). The experiment value is lager than the theoretical value, suggesting somewhat phase impurity. Above 280 ºC, there is a sharp weight loss indicative of chemical decomposition.

Meanwhile, we also investigated the photoluminescence properties of compounds **1**, **2**, **3**, **5**, **6** in solid state at room temperature because of the excellent luminescent properties of d^{10} metal coordination compounds. As shown in Fig. 9a, for **2**, upon excitation at 337 nm, an intense emission spectrum is observed in the blue region at 420 nm. For **3**, upon excitation at 360 nm, an intense emission spectrum is observed in the ultraviolet region at 399.5 nm. When excited at 270 nm, **5** have an emission spectrum in the ultraviolet region at 404.6 nm. For **6**, it has an intense broad photoluminescence emission in the blue region at 439.2 nm when excited at 275 nm. Compared to others, **1** has a relatively weak emission spectrum in the blue region at 470.5 nm, when excited at 280 nm (Fig. 9b). As we know, the free L ligand in the solid state displays no luminescence.[14] Since the Zn^{2+} or Cd^{2+} ions are difficult to oxidize or to reduce due to their d^{10} configuration, the emission of these compounds could be attributed to intraligand (π-π^*) emission of carboxyalte ligand plus ligand-to-metal charge-transfer (LMCT).[16]

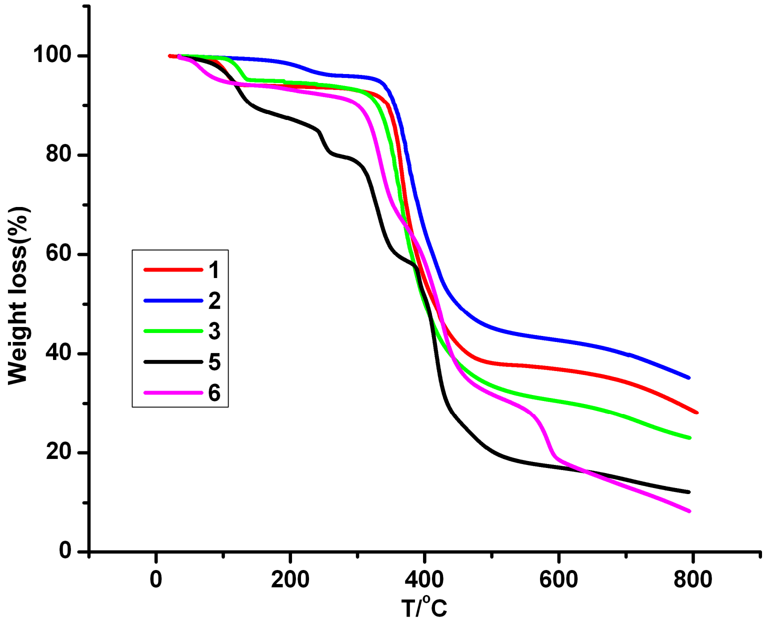


Fig. 8. The TG plot of **1**, **2**, **3**, **5**, **6**

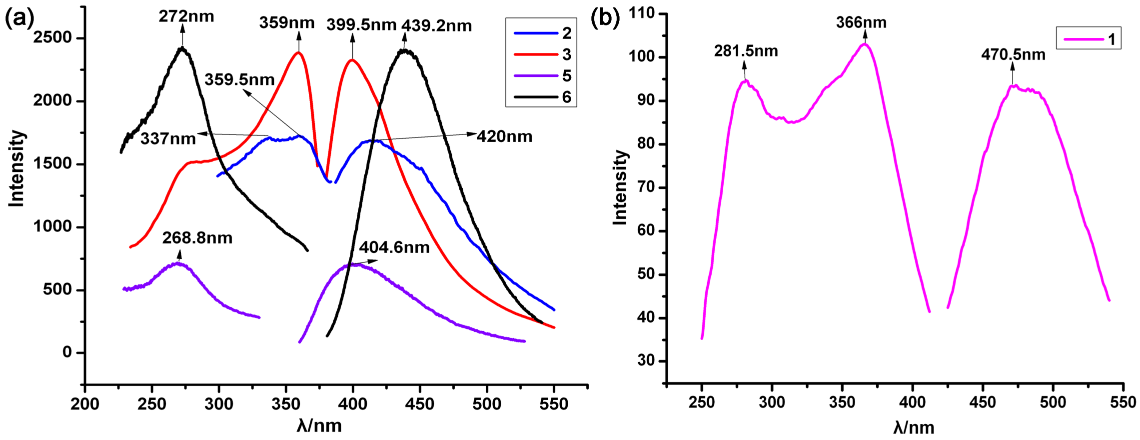


Fig. 9. (a) The solid-state photoluminescence spectrum of compound **2**, **3**, **5**, **6,** and (b) compound **1**.

Conclusions

In summary, a series of acylamide compounds based on acylamide ligand of N^1,N^4-di(pyridin-3-yl)naphthalene-1,4-dicarboxamide ligand and a series of carboxylate ligands were obtained. Interestingly, in these compounds, some similarity are observed, like that the combination of acylamide ligands and metal ions often generates helical or ring-type substructure. Furthermore, due to the diversities of carboxylate ligands employed here, final structural diversities were constructed. To some extent, this work has demonstrated the coordination affinity of L ligand, and gives us some insight to direct the next synthesis of L based compounds.

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