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Hydrothermal synthesis, structure characterization and luminescence property of three porous coordination polymers using a flexible tripodal amide containing linker

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ABSTRACT

Use of a C_3-symmetric facial ligand N,N',N"-tris(3-pyridyl)-1,3,5-benzenetricarboxamide (L1), three porous MOFs, $[CdCl_2(aas\text{-}L1)]_n$ (**1**), $[HgI_2(sss\text{-}L1)]_n$ (**2**) and $[CoCl_2(ass\text{-}L1)(EtOH)]_2$ (**3**), were obtained under solvothermal conditions. Complex **1** exhibits a fascinating 2D two interwoven nets consisting of sandwich-like channels. Compound **2** shows an infinite 1D polymeric chain in herringbone fashion running along *a*-axis. The hydrogen-bonding interactions further link the molecules into 2D extended structure with 48-membered macrocycles. In the binuclear complex **3**, two metal centers are bridged by two ligands, producing a 28-membered ring. The macrocyclic subunits further self-assemble into an open-framework structure with porous system via the hydrogen-bonding interactions. Furthermore, the luminescence properties of these compounds have been studied.

During the past decade, the porous metal-organic frameworks (MOFs) with intriguing variety of architectures and topologies were investigated quite intensively [1–7]. The ultimate goal of designing rational and novel porous MOFs is to synthesize new materials and discover practical applications that use their functional aspects, including catalysis, nonlinear optics, gas storage, separation, molecular sensor technology, and electrochemistry, nevertheless it is still cumbersome for this purpose. More research is still required before final goal can be completed.

Tripodal ligands have proven useful for the construction of a wide range of one-, two-, three- dimensional infinite solid-state coordination architectures as well as discrete molecular structure with nanosized cavities, and it has been used to stabilize unusual coordination geometries, unusual inorganic functionalities, and catalytically active species [8–12]. In addition, the presence of the amide group in a tripodal ligand has gained much attention due to the advantages of the organic amides in assembling supramolecular networks organized by hydrogen bond, which can be used as driving force to give interesting nanotubes or zeolite-like frameworks through inter-ring or inter-tube hydrogen bonding [13–19]. Considering these aspects aforementioned, much work has been done over the past years with the ligands such as N,N',N"-Tris(3-pyridinyl)-1,3,5-benzenetricarboxamide (L1), N,N',N"-Tris(4-pyridinyl)-1,3,5-benzenetricarboxamide (L2), N,N',N"-Tris(2-pyridinyl)-1,3,5-benzenetricarboxamide (L3), and so on, to produce novel porous MOFs [13–19]. For example, lah and coworkers have reported the novel single-crystal structure of the truncated octahedral $[Pd_6L1_8]^{12+}$ and $[Cu_6L1_8]^{12+}$ nanocages [17–18]. They also have reported an unprecedented twoford interpenetrating (3,4)-connected of the Cu_3L2_4-type MOF with L2 as a trigonal three-connected node and copper(II) ion as a square planar four-connection node [19]. Stang and coworkers have utilized L2 to construct a Pd^{II} coordination cage with the $(Pd_3L2_2)^{6+}$ moiety [20]. Different from the cage structure, we report here the solid-state structure and luminescence properties of three new porous MOFs, namely, $[CdCl_2(aas\text{-}L1)]_n$ (**1**), $[HgI_2(sss\text{-}L1)]_n$ (**2**) and $[CoCl_2(ass\text{-}L1)(EtOH)]_2$ (**3**) based on the tridentate ligand L1, with three pyridylamides as functional appendages [21–22].

A single crystal X-ray diffraction study performed on **1** revealed that the complex crystallizes in the triclinic space group $P\bar{1}$ and contains a fascinating 2D polymeric architecture consisting of two interwoven nets. The symmetric unit of **1** consists of six Cd centers, two Cl^- ions, and two ligands (Fig. 1a). Two crystallographically independent six-connected Cd^{2+} centers, Cd1 adopts a slightly distorted octahedral coordination geometry through bonding to four Cl atoms (Cl1B, Cl1C, Cl2A, and Cl2B) and two N atoms (N6A and N6B) from one ligand, however, Cd2 is six-coordinate by binding four N atoms (N1A, N1B, N4A, and N4B) from two ligands and two bridging Cl atoms (Cl1A and Cl1B).

In **1**, the C_3-symmetric triangular facial ligand L adopts *aas* conformation (Scheme 1). The ligand L acts as a trigonal three-connection node. Cd2A, Cd1B and Cd2B coordinated with one ligand, while Cd1A, Cd2C and Cd2D are connected by another ligand, thus, forming a 2D two interwoven nets with sandwich-like channels (Fig. 1b). Cd1 and Cd2 atoms are further connected with the bridging Cl1 atoms to form a 1D -Cl-Cd-Cl- chain. The angle of Cd(1)- Cl(1)-Cd(2) are 143.019(47), and the Cd1-Cl1 and Cd2-Cl1 distances are 2.7123(11)

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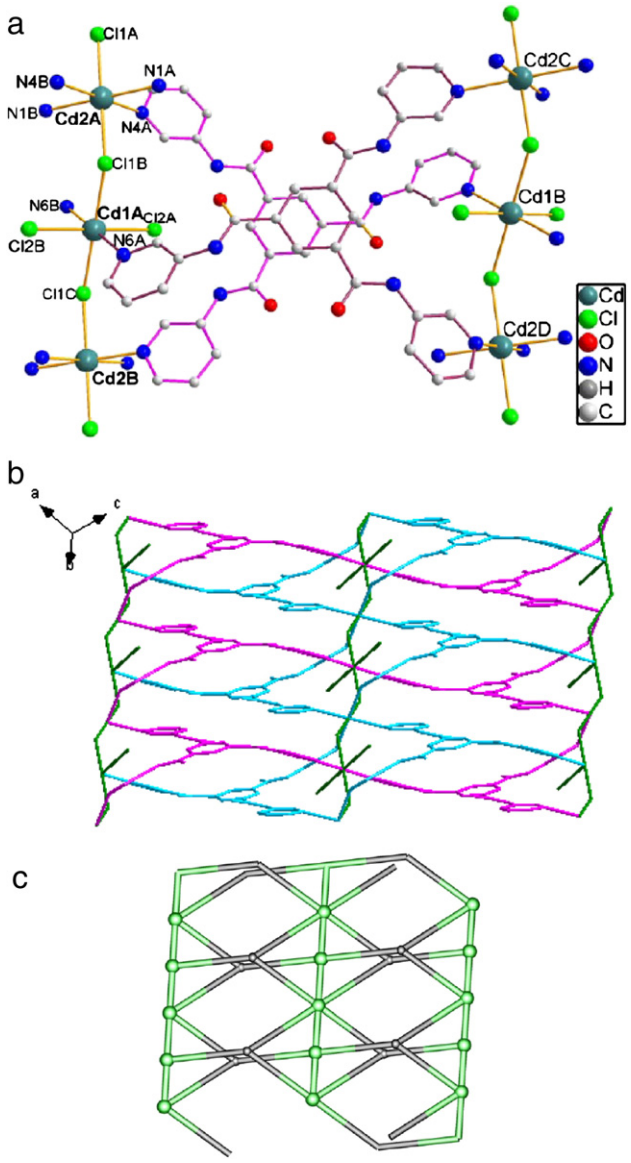


Fig. 1. (a) View of one layer of compound **1**. All hydrogen atoms are omitted for clarity; (b) 2D framework of **1** showing its two interwoven nets; (c) Topological representation of the structure.

and 2.6051(11) Å, respectively. While the Cl2 atoms being a terminal group coordinates with Cd1 atoms, which are appended in the channels through hydrogen-bonding interactions with the amide nitrogen atom [N5–H5A···Cl2: N5···Cl2 = 3.454 Å, N5–H5A···Cl2 143.2 º].

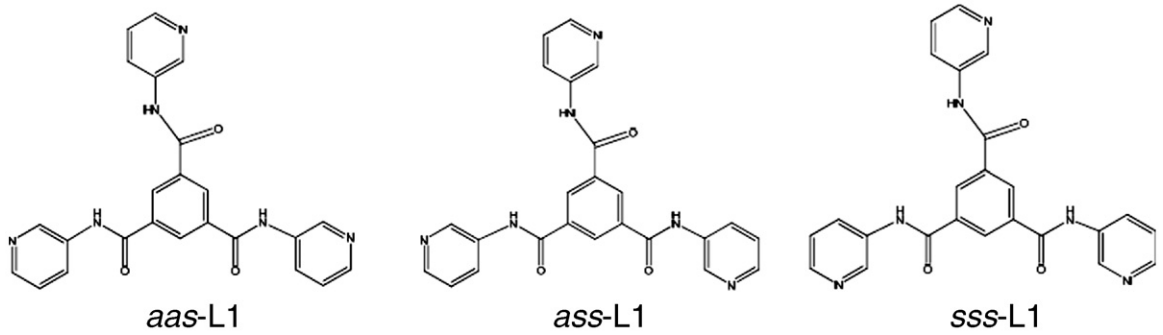
Thus, when the C_3-symmetric triangular facial ligand L1 combined with the hexatopic Cd(II) ion in the presence of chlorine as a bridging linker, a fascinating 2D two interwoven nets consisting of sandwich-like channels is formed. When the tetrahedral coordinated Cd(II) centers are regarded as nodes, and the organic ligands and Cl^- ions are regarded as connectors, the network of the complicated structure can be described topologically in a straight-forward way with node-and-connector approach. As shown in Fig. 1c, the 2D framework structure of **1** can be described as a (3,4,6)-connected topology with Schläfli symbol of a $4^6.6^7.8^2$, with Cd1 ion as a 4-connected node, Cd2 ion as a 6-connected node and L1 as a 3-connected node.

X-ray diffraction reveals that **2** belongs to the monoclinic space group $P2_1/c$. Each Hg(II) is in a distorted tetrahedral coordination environment and the Hg center is combined via two iodide atoms and two nitrogen atoms (N1 and N4) of two ligands. The bond lengths of Hg-N1 and Hg-N4 are 2.452 and 2.391 Å, respectively. In **2**, the C_3-symmetric triangular facial ligand L1 acts as a bridging linker with *sss* conformation. The three pyridine nitrogen atoms and the amide oxygen atoms are all in the opposite side. The Hg(II) ions are bridged by ligands forming an infinite 1D polymeric chain in herring-bone fashion running along *a*-axis. Furthermore, the hydrogen-bonding interactions between the uncoordinated pyridine nitrogen atom (N6) and the amide nitrogen atom (N2) in the next chain [N2–H2A···N6: N2···N6 = 3.000(7) Å, N2–H2A···N6 159.0 º] link complex molecules into 2-D extended structure with 48-membered macrocycles (Fig. 2). Besides, hydrogen bonding interactions between the amide moieties (N5-H5A···O2) are observed in the solid state.

Compound **3** crystallises in the triclinic space group Pī. The crystal structure can be described as a bimetallic macrocycle formed by coordinating two Co(II) metal centres with two ligands which are in *ass* conformation. Co(II) is four-coordination which exits in a slightly distorted tetrahedral configuration combining via two Cl atoms (Cl1 and Cl2) and two nitrogens (N1 and N6) of two ligands (Fig. S2). The Co(II)-N distances are 2.0358(33) and 2.0348(40) Å, and the Co···Co distance is about 11.88 Å.

The C_3-symmetric triangular facial ligand L1 acts as a bridging linker which coordinates with two Co (II) ions to form a 28-membered nonplanar ring. In addention, the hydrogen-bonding interactions between the uncoordinated pyridine nitrogen atom (N4) and the amide nitrogen atom (N2) in the neighboring metallo-macrocycle [N2–H2A···N4: N2···N4 = 3.055(6) Å, N2–H2A···N4 151.8 º] link **3** into 1D extended structure. Furthermore, the chains are further packed on top of each other in an offset fashion mediated by hydrogen bonding interactions (N3-H3A···Cl2 = 3.507 (4) Å and N5-H5A···Cl2 = 3.597 Å) of the amide nitrogen atom with the coordinated Cl^- anions (Fig. 3).

The XRD powder patterns of the complex **1** and **2** were collected on a PANalytical X'prtPro diffractormeter using graphite-monochromated Cu-Kα radiation in the angular range 2θ = 5-30º. Their powder patterns match with the ones calculated from their sing crystal structure data



Scheme 1. The conformations of the ligand in crystal structures (*a* and *s* are defined based on the relative orientation of the amide oxygen and the pyridyl nitrogen. *a*-conformation means the two atoms are in the opposite side. *s*-conformation means that the pyridine nitrogen atom and the amide oxygen atom of the ligand are in the same side).