

Electronic Supplementary Information for MS:

Unusual self-threading and interdigitated architectures self-assembled from long flexible ligands and d¹⁰ metal salts

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Table S1 Crystal data and structure refinements for compound **4**.

Empirical formula	C ₂₃ H ₂₀ CdN ₄ O ₆ S
<i>M_r</i> (g·mol ⁻¹)	592.89
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.5434(8)
<i>b</i> (Å)	16.3088(12)
<i>c</i> (Å)	12.8836(10)
<i>α</i> (°)	90
<i>β</i> (°)	106.192(4)
<i>γ</i> (°)	90
<i>V</i> (Å ³)	2329.2(3)
<i>Z</i>	4
<i>ρ</i> _{calcd} (g·cm ⁻³)	1.691
<i>μ</i> (mm ⁻¹)	1.075
<i>F</i> (000)	1192
Reflections collected	18003
Unique data (<i>R</i> _{int})	5018 (0.0375)
GOF on <i>F</i> ²	1.079
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.1723
<i>wR</i> ₂ ^b (all data)	0.6109

$$^a R_1 = \sum ||F_0| - |F_C|| / \sum |F_0|; \quad ^b wR_2 = \sum [w(F_0^2 - F_C^2)^2] / \sum [w(F_0^2)^2]^{1/2}$$

Supporting Figures

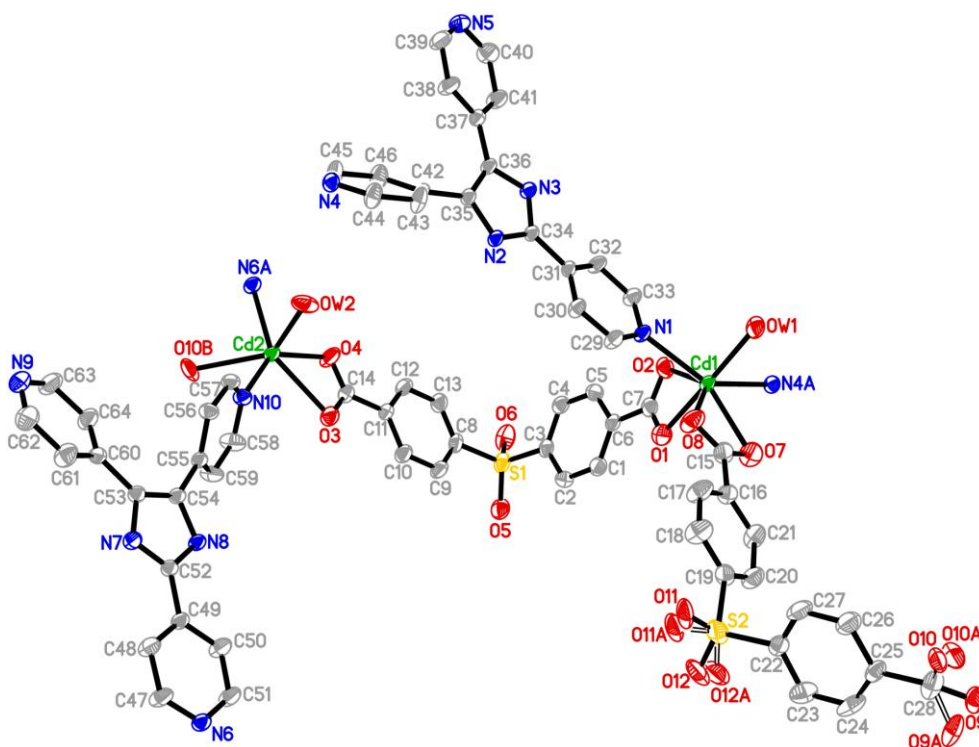
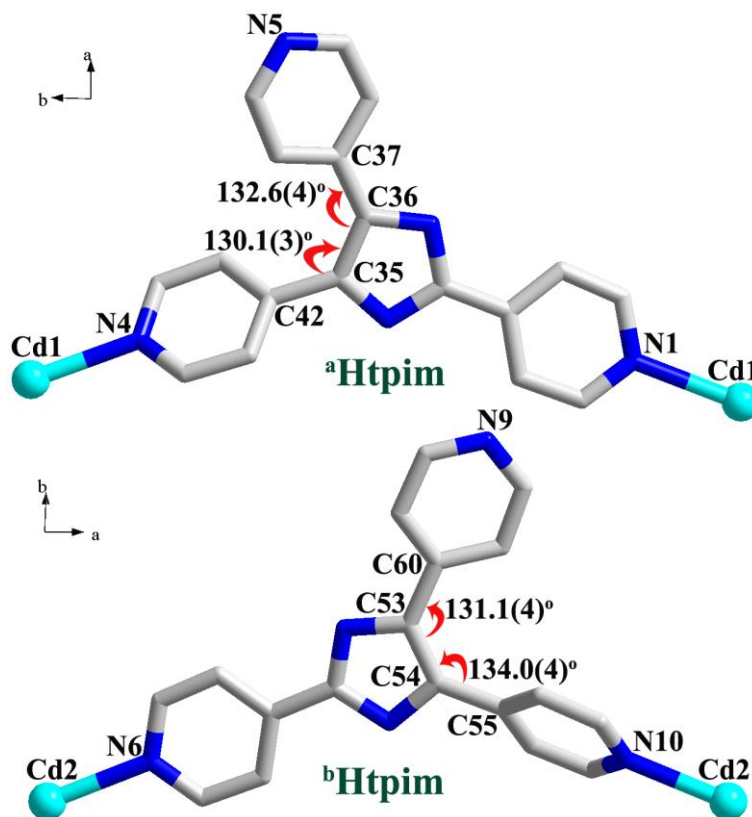


Fig. S1 ORTEP drawing of compound **1** with thermal ellipsoids at 30% probability.

The hydrogen atoms and free water molecules are omitted for clarity.



Scheme S1 View of the two different conformations of Htpim ligands in **1**.

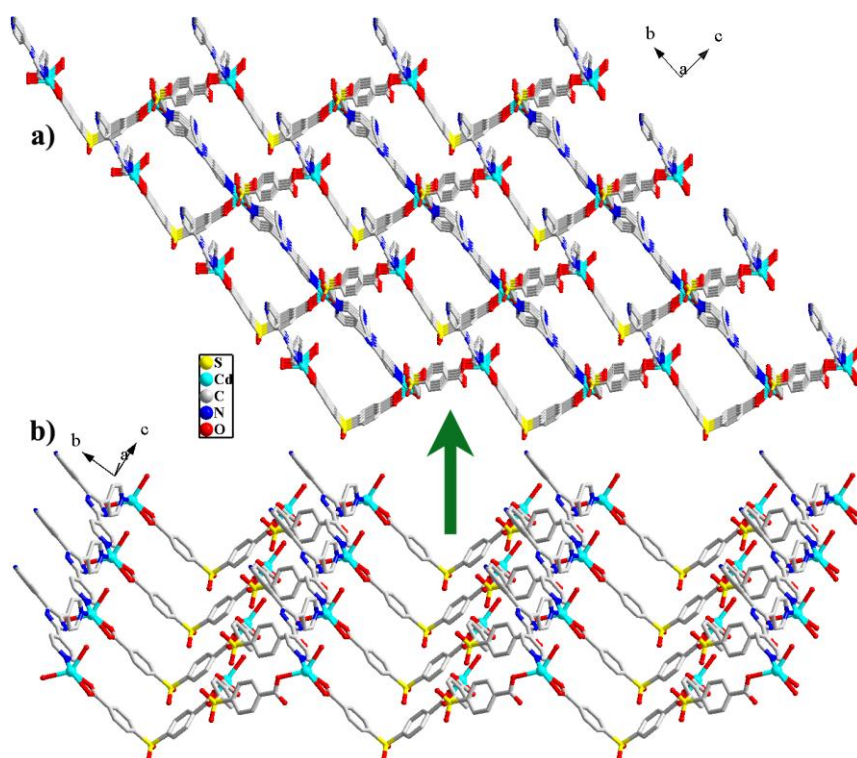


Fig. S2 Perspective views of (a) the single 3D self-threading network and (b) the undulating 2D network of **1**.

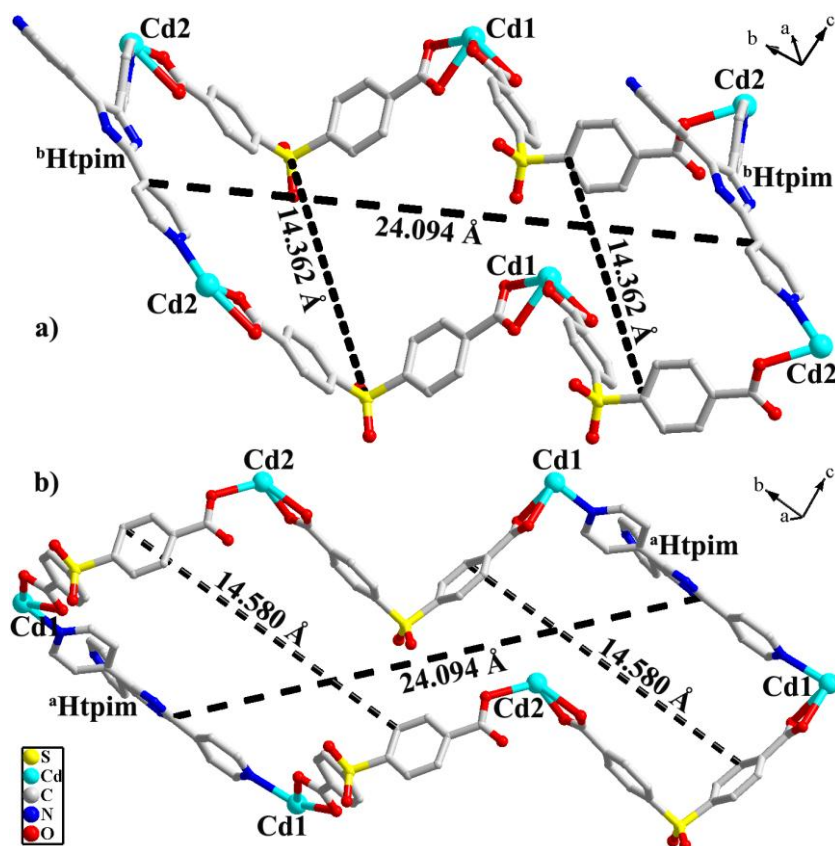
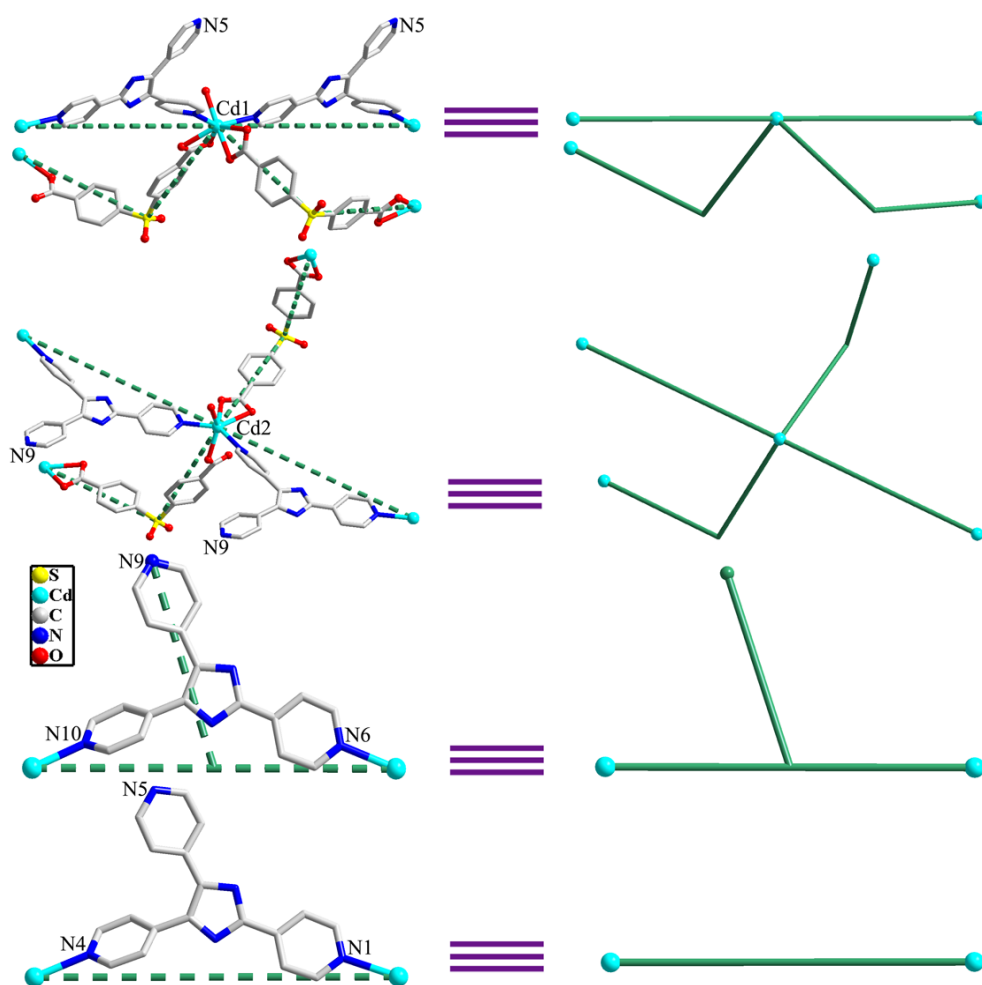
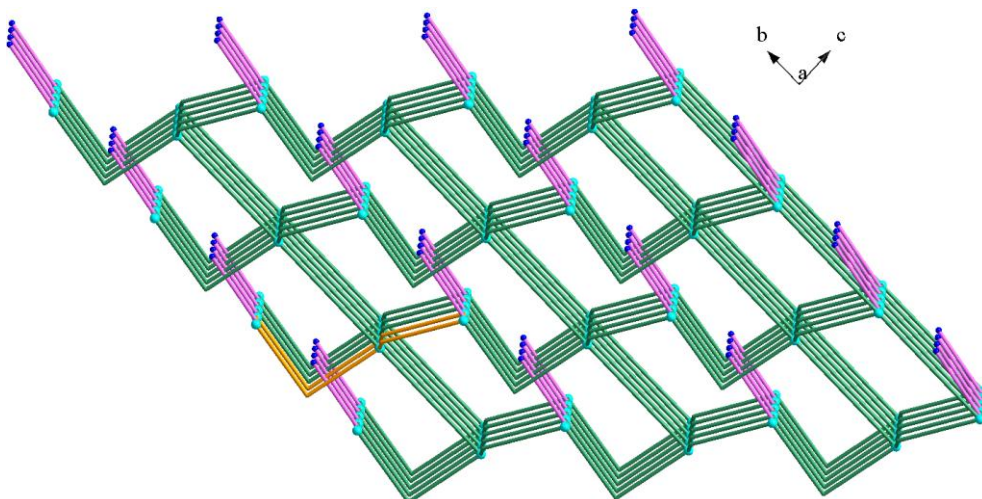


Fig. S3 Perspective views of the two types of hexagonal meshes: (a) the $[\text{Cd}_6(\text{sdba})_4(\text{}^b\text{Htpim})_2]$ unit and (b) the $[\text{Cd}_6(\text{sdba})_4(\text{}^a\text{Htpim})_2]$ unit in **1**.



(a)



(b)

Fig. S4 (a) Perspective (left) and simplified (right) views of the four-connected Cd centres and four types of linkers (Htpim and sdba ligands) in **1**. (b) Schematic representation of the single 3D self-threading framework with CdSO₄ topology.

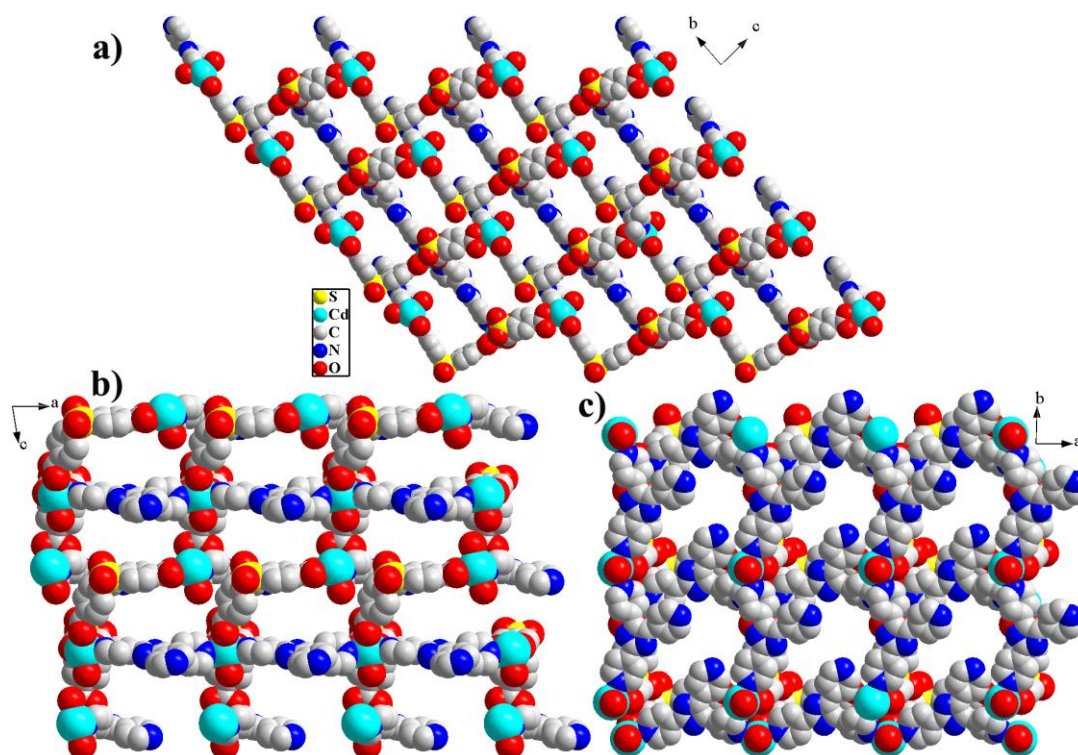


Fig. S5 Space-filling views of an individual 3D self-threading framework of **1**, possessing three-directional open channels of approximately $14.580 \times 8.782 \text{ \AA}$ along the *a* axis (a), of $14.362 \times 8.563 \text{ \AA}$ along the *b* axis (b), and of $14.850 \times 14.362 \text{ \AA}$ along the *c* axis (c).

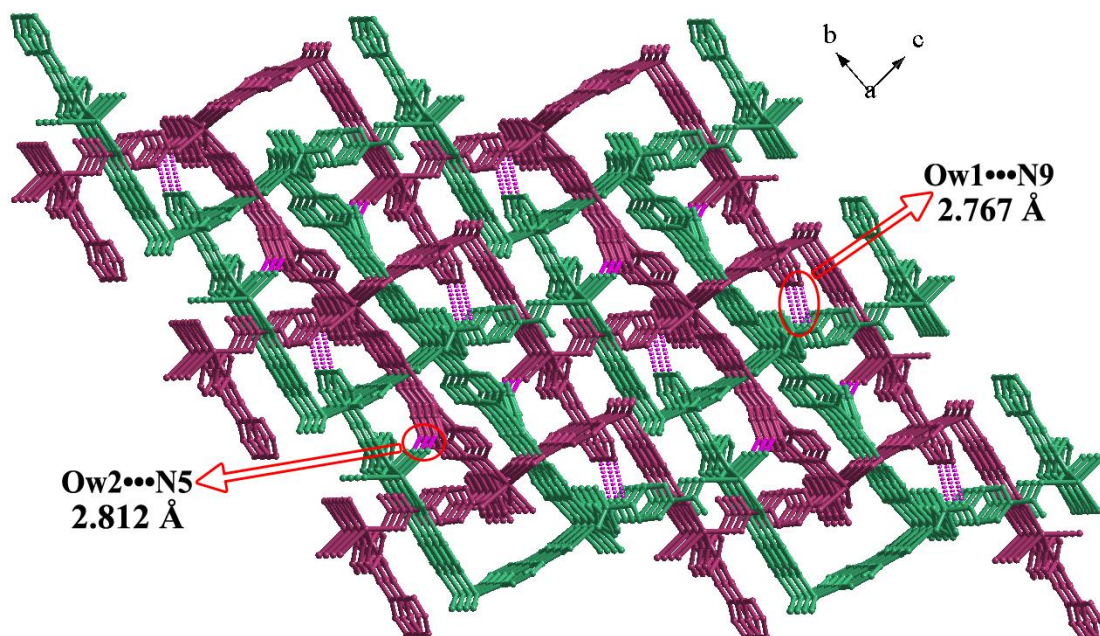


Fig. S6 Perspective view of the hydrogen bonding interactions ($\text{Ow}(1) \cdots \text{N}(9)$ 2.767 \AA and $\text{Ow}(2) \cdots \text{N}(5)$ 2.812 \AA) between two interpenetrated 3D self-threading networks of **1**. The hydrogen bonds are indicated by purple dashed lines.

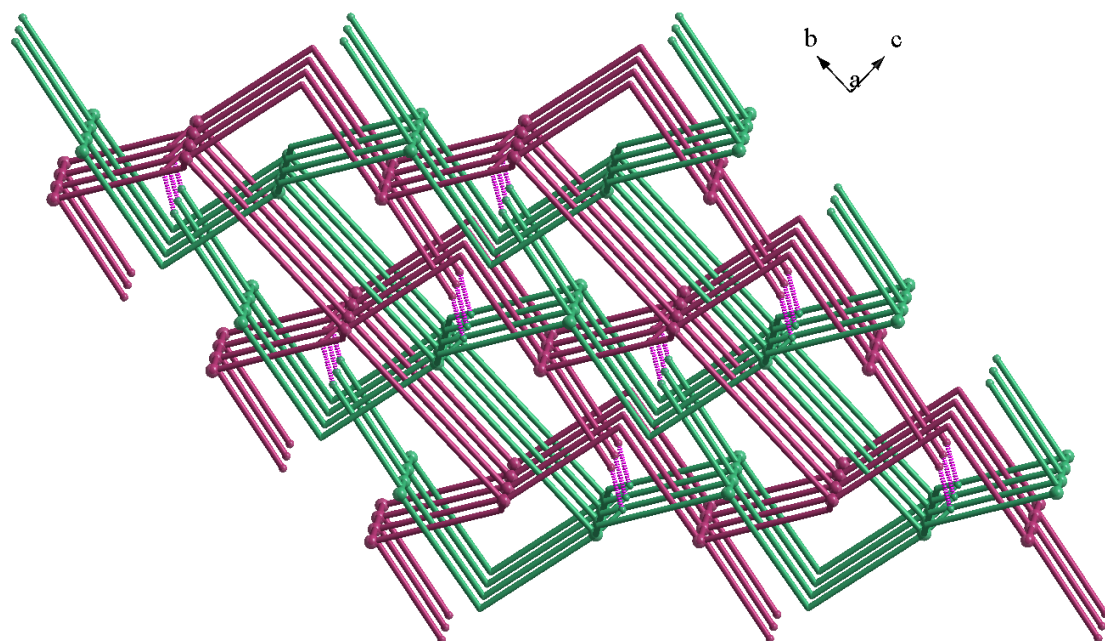


Fig. S7 Schematic view of the hydrogen bonding interactions ($\text{Ow}(1)\cdots\text{N}(9)$ 2.767 Å) between two interpenetrated 3D self-threading networks of **1**. The hydrogen bonds are indicated by purple dashed lines.

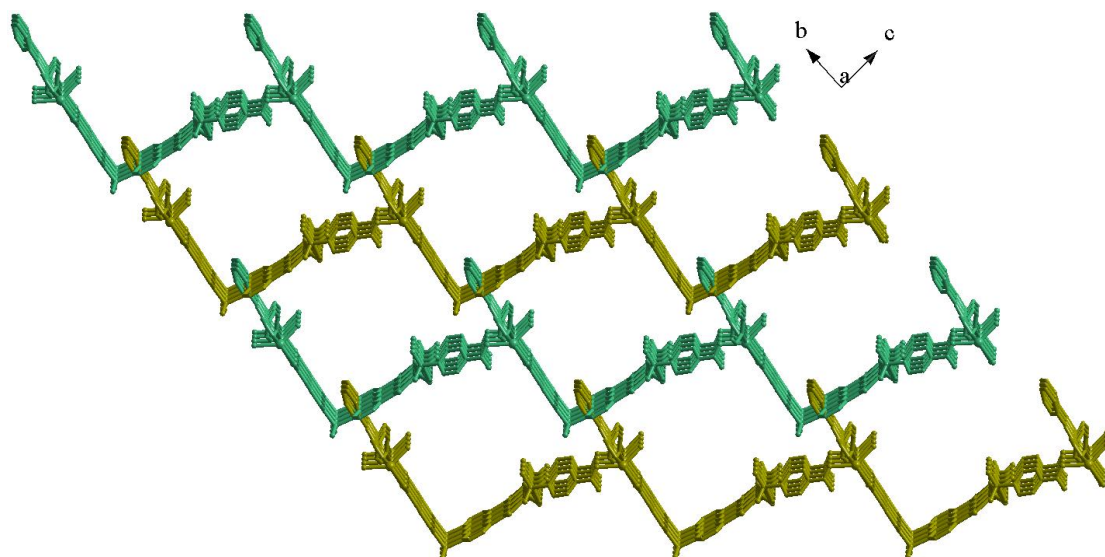


Fig. S8 Perspective view of the polythreading structure that is formed by removing the A-type Htpim ligands in **1**.

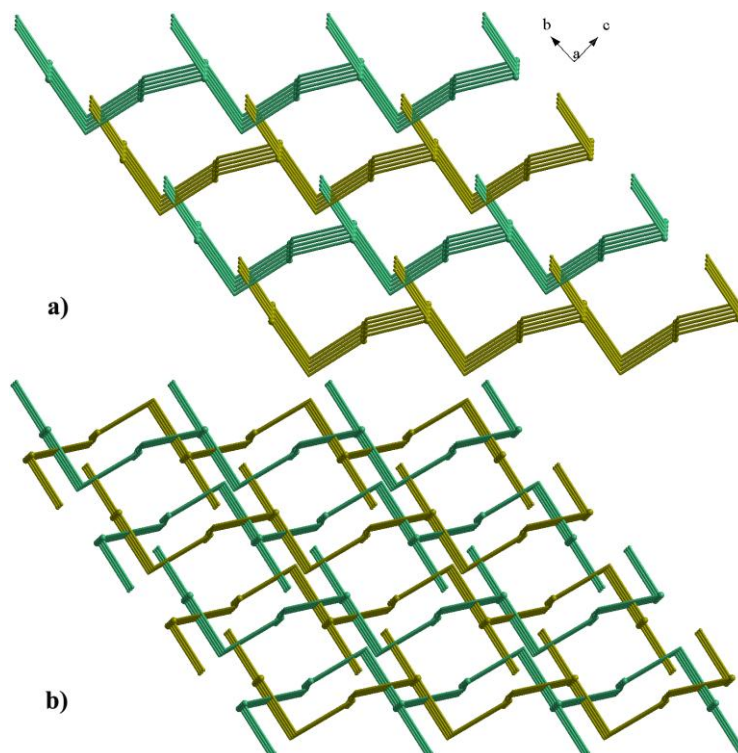


Fig. S9 Schematic representation of (a) the single polythreading structure and (b) the complicated 3D entangled architecture of **1**, that are both obtained by removing the A-type Htpim ligands.

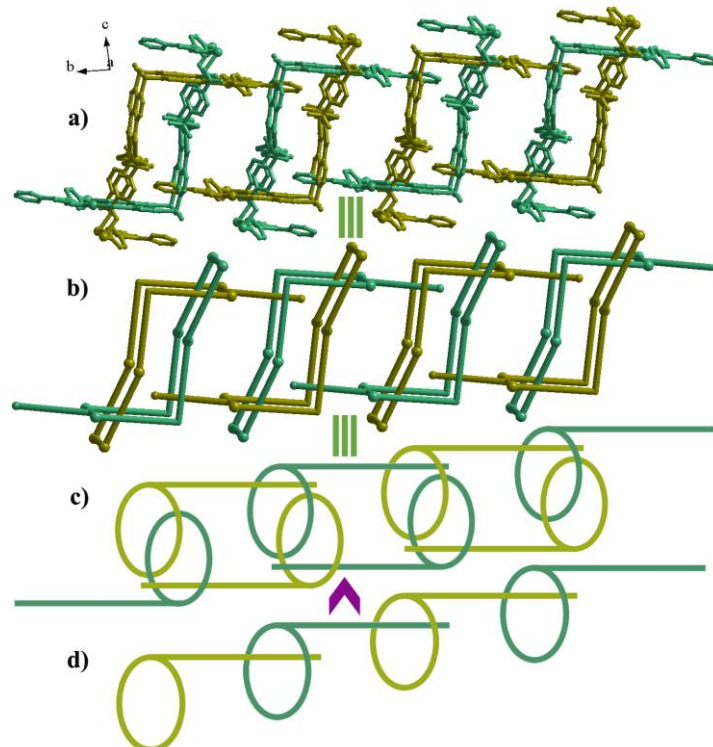


Fig. S10 Perspective (a) and schematic (b, c, d) views of the detail of the polycatination and polythreading characters in the remaining entangled architecture formed by removing the A-type Htpim ligands.

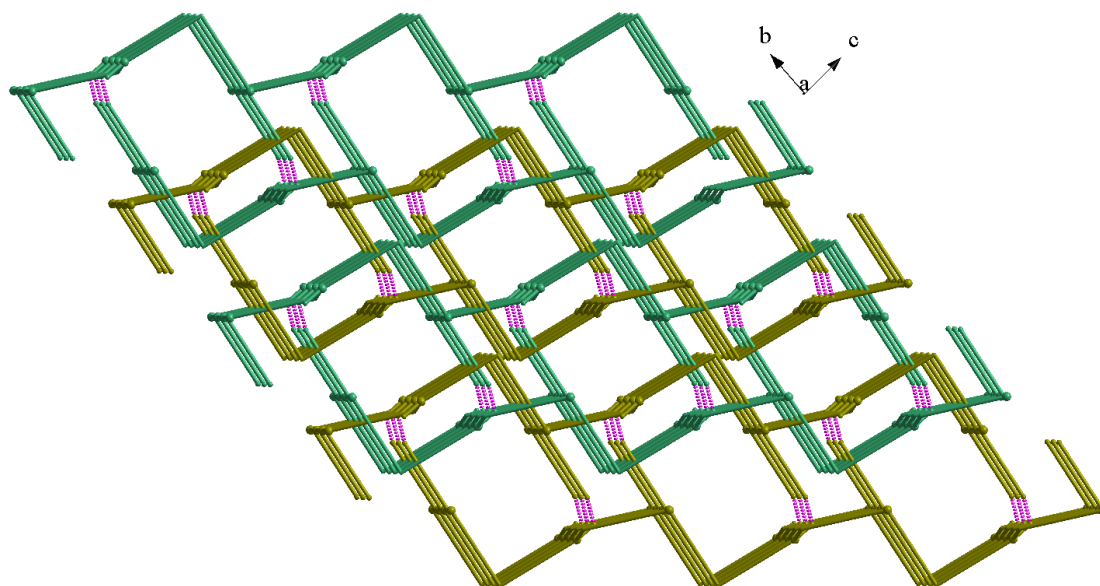


Fig. S11 Schematic view of the hydrogen bonding interactions ($\text{Ow}(1)\cdots\text{N}(9)$ 2.767 Å) in the complicated 3D entangled architecture that is isolated by removing the A-type Htpim ligands for the structure of **1**. The hydrogen bonds are indicated by purple dashed lines.

For the whole 3D structure of **1**, by removing the A-type Htpim ligands, the remainder is an especial and complicated entangled architecture both with polycatenation and polythreading characters, as shown in Figs. S9b and S10. At the same time, if we take account of the hydrogen bonding interactions ($\text{Ow}(1)\cdots\text{N}(9)$ 2.767 Å), the remaining complicated entangled architecture is therefore viewed as a (2D \rightarrow 3D) polycatenated network (Fig. S11), which is obtained by such a way that each hydrogen bonded 2D double-layer is interlocked with two nearest neighboring ones, that finally gives rotaxane feature besides polycatenation for the whole remaining structure (Fig. S12). This result also provides further evidence that the whole 3D structure of **1** is a preminent twofold interpenetration of two identical 3D self-threading networks.

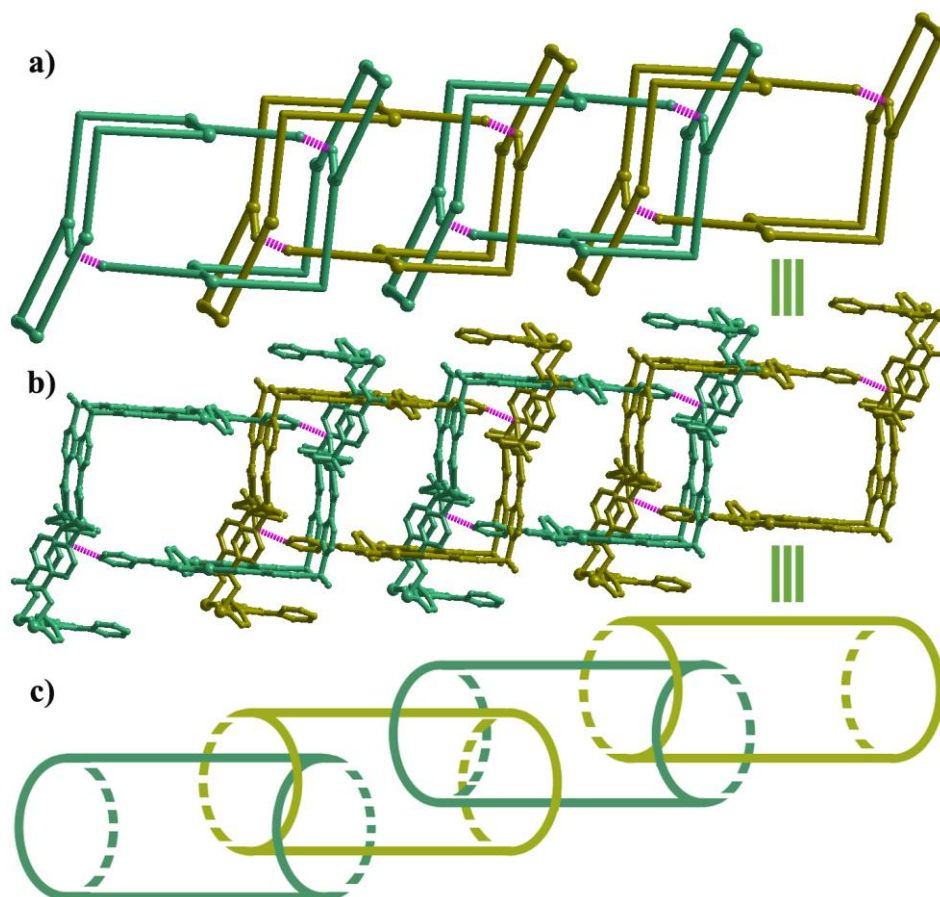
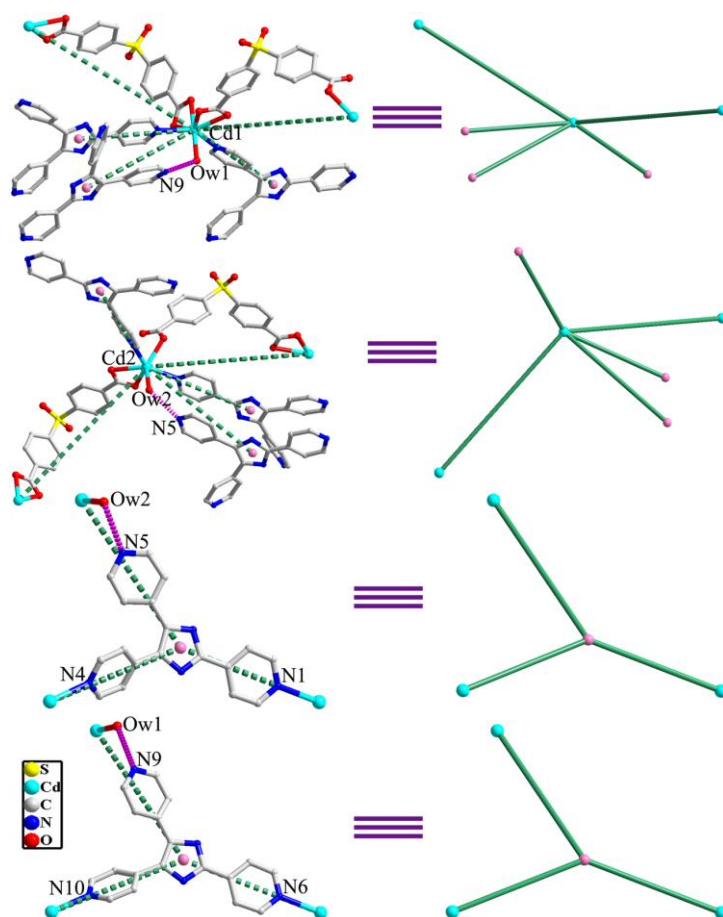
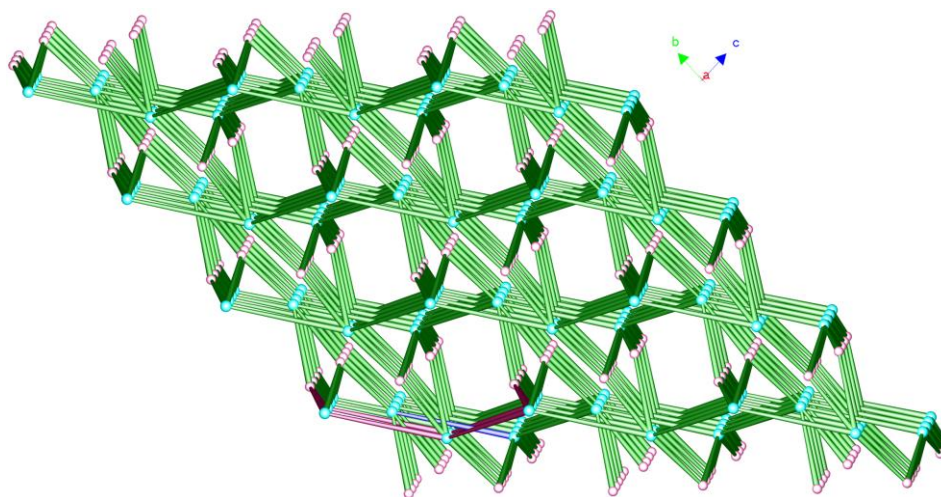


Fig. S12 Perspective (b) and schematic (a, c) views of the detail of the rotaxane and polycatenation characteristics for the whole remaining polycatenated network as depicted in Fig. S11. The hydrogen bonds are indicated by purple dashed lines.



(a)



(b)

Fig. S13 (a) Perspective (left) and simplified (right) views of the five-connected Cd centers and three-connected Htpim ligands in **1**. The hydrogen bonds Ow(2)···N(5) and Ow(1)···N(9) are both highlighted by purple dashed lines. (b) Schematic representation of the (3,5)-connected 3D self-penetrating network of $(4.6.8)(4.6^6.8^3)$ topology of **1**.

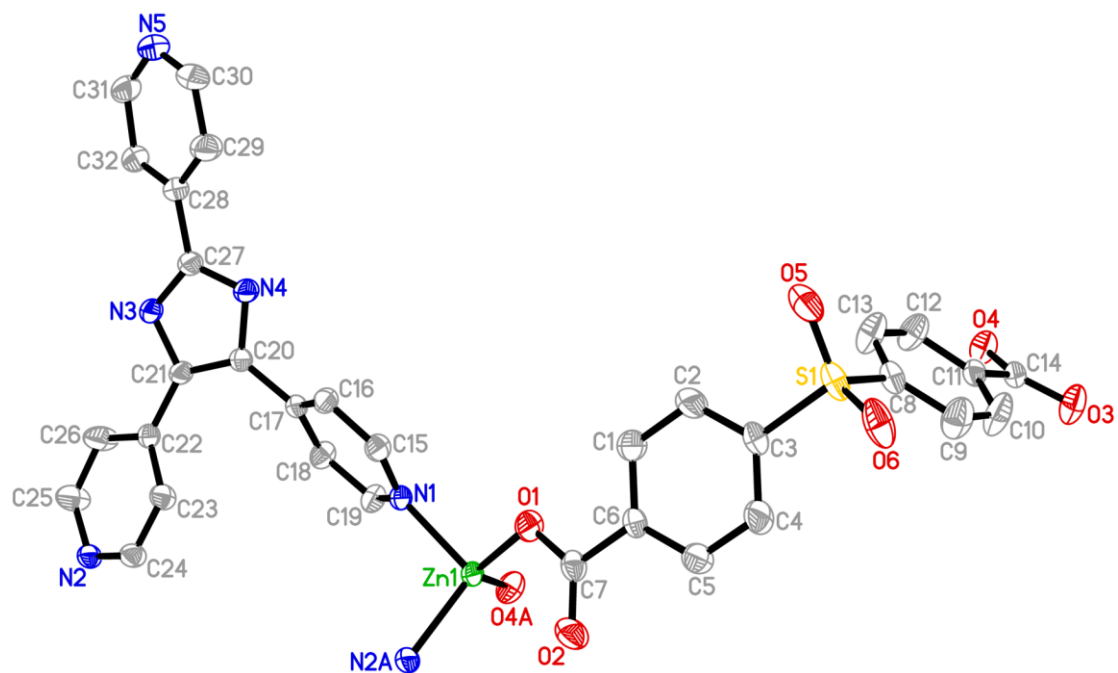


Fig. S14 ORTEP drawing of compound **2** with thermal ellipsoids at 30% probability.

The hydrogen atoms are omitted for clarity.

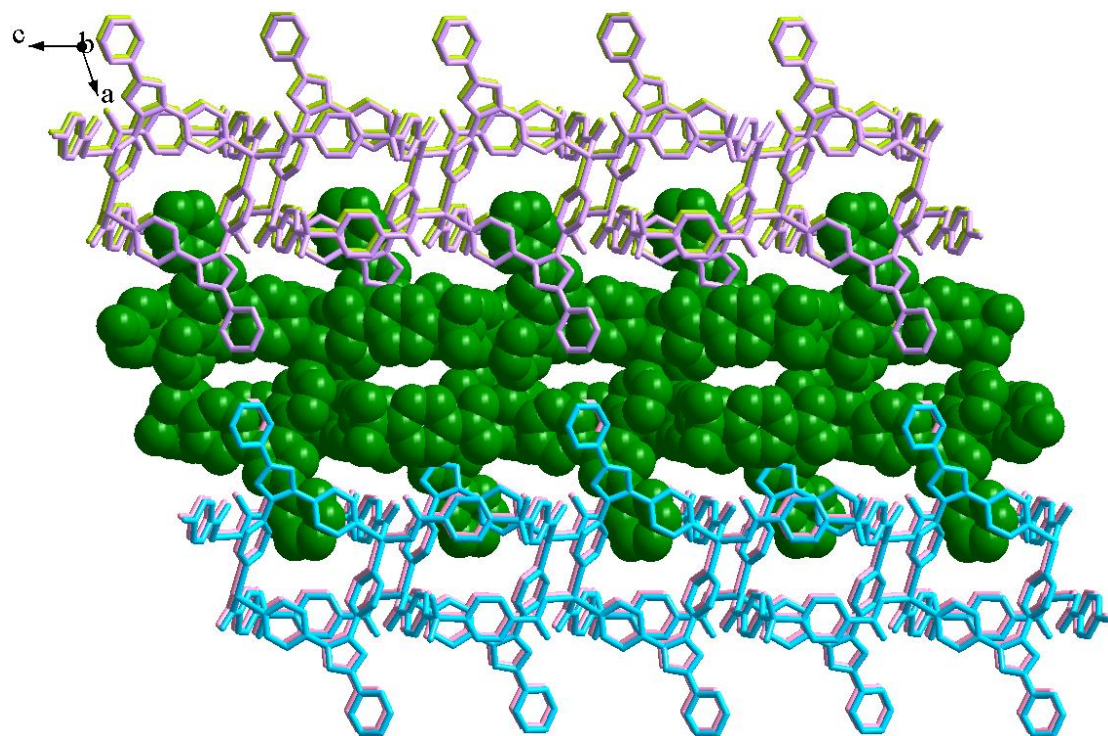


Fig. S15 View of the detail of the mutual interdigitation in compound **2**.

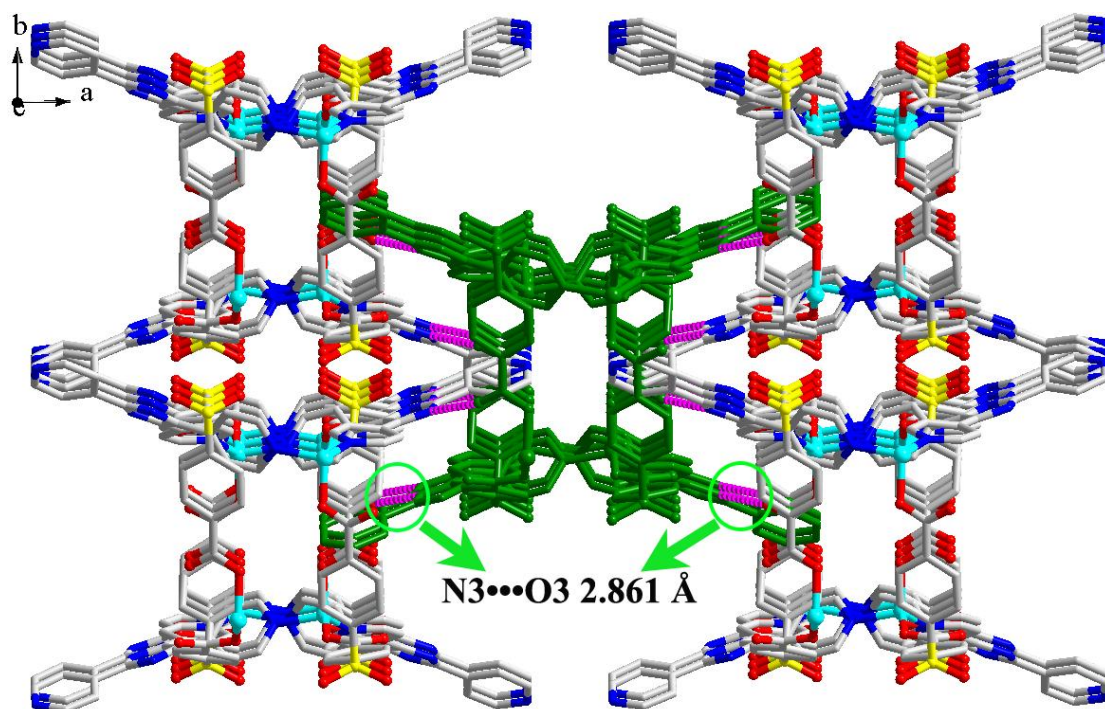
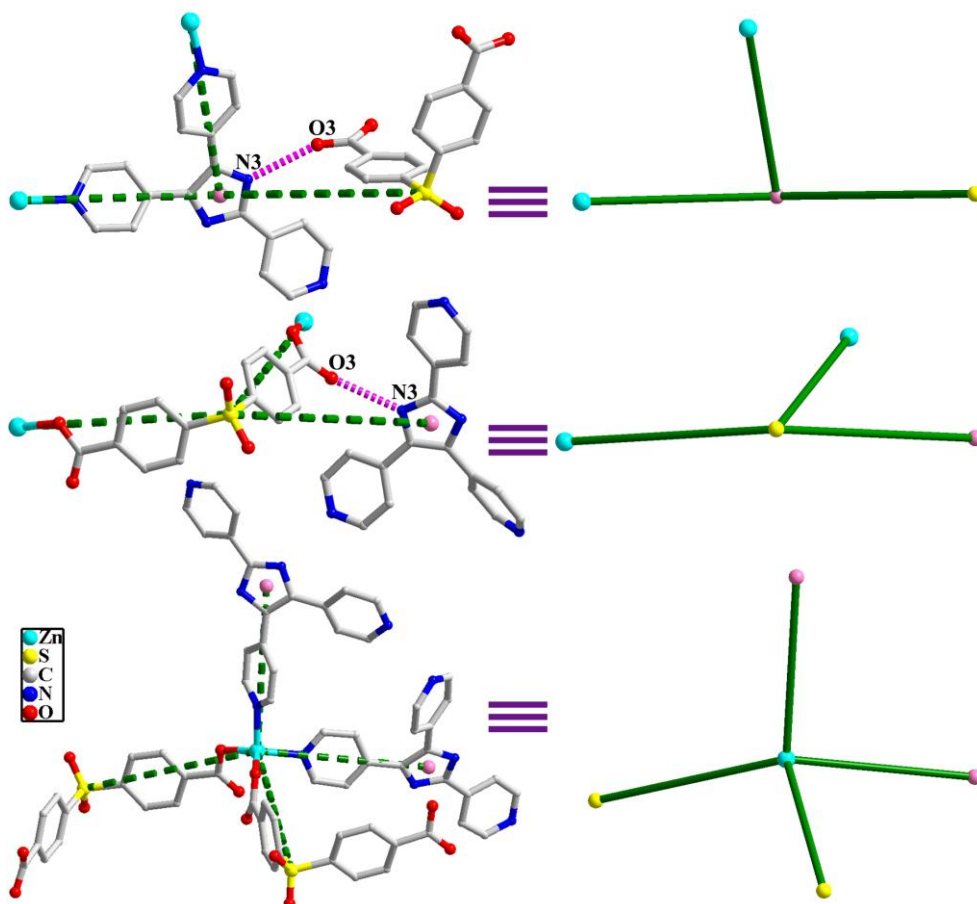
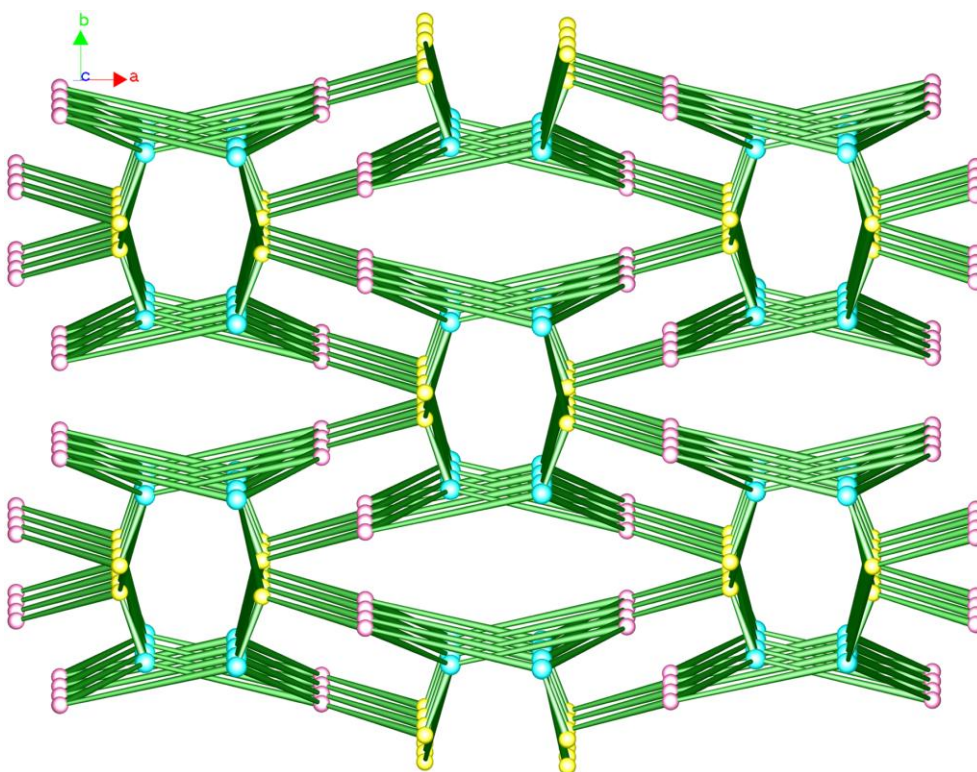


Fig. S16 Perspective view of the hydrogen bonding interactions ($N3 \cdots O3$ 2.861 Å) in the interdigitated array of 2.



(a)



(b)

Fig. S17 (a) Perspective (left) and simplified (right) views of the four-connected Zn center and two types of three-connected nodes (the Htpim and sdba ligands) in **2**. The hydrogen bonds $O(3)\cdots N(3)$ are highlighted by purple dashed lines. (b) Schematic representation of the trinodal (3,4)-connected 3D network of $(4.6.8)(6.8.10)(4.6.8^3.10)$ topology that is formed when hydrogen bonds are taken into account in **2**.

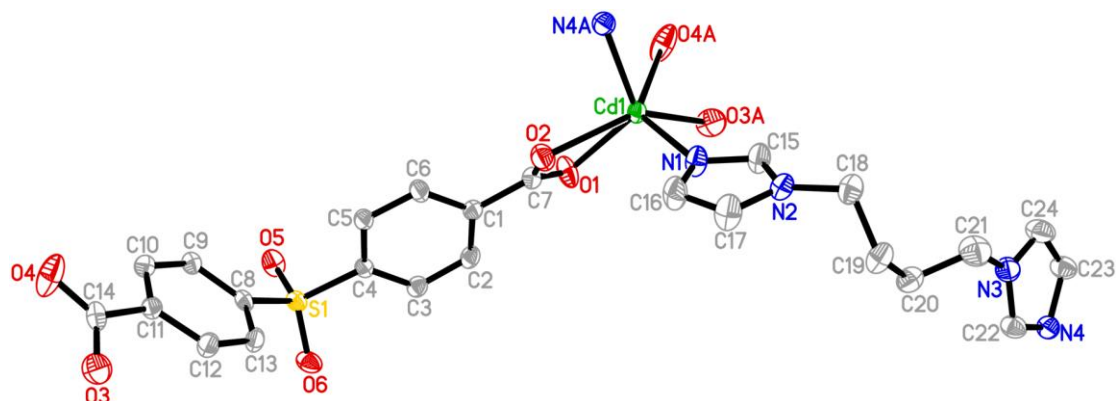


Fig. S18 ORTEP drawing of compound **3** with thermal ellipsoids at 30% probability. The hydrogen atoms are omitted for clarity.

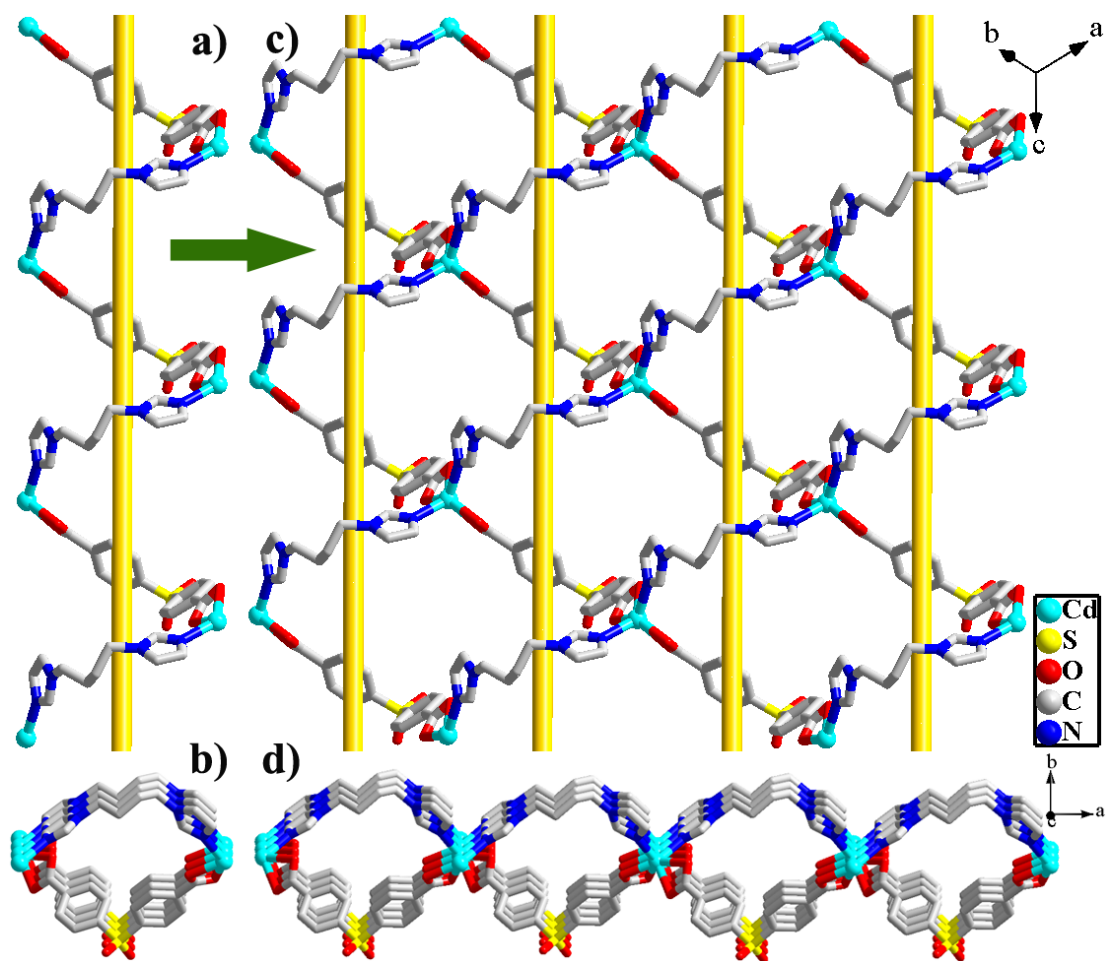


Fig. S19 Perspective views of (a, b) the right-handed helix and (c, d) the right-handed layer in 3.

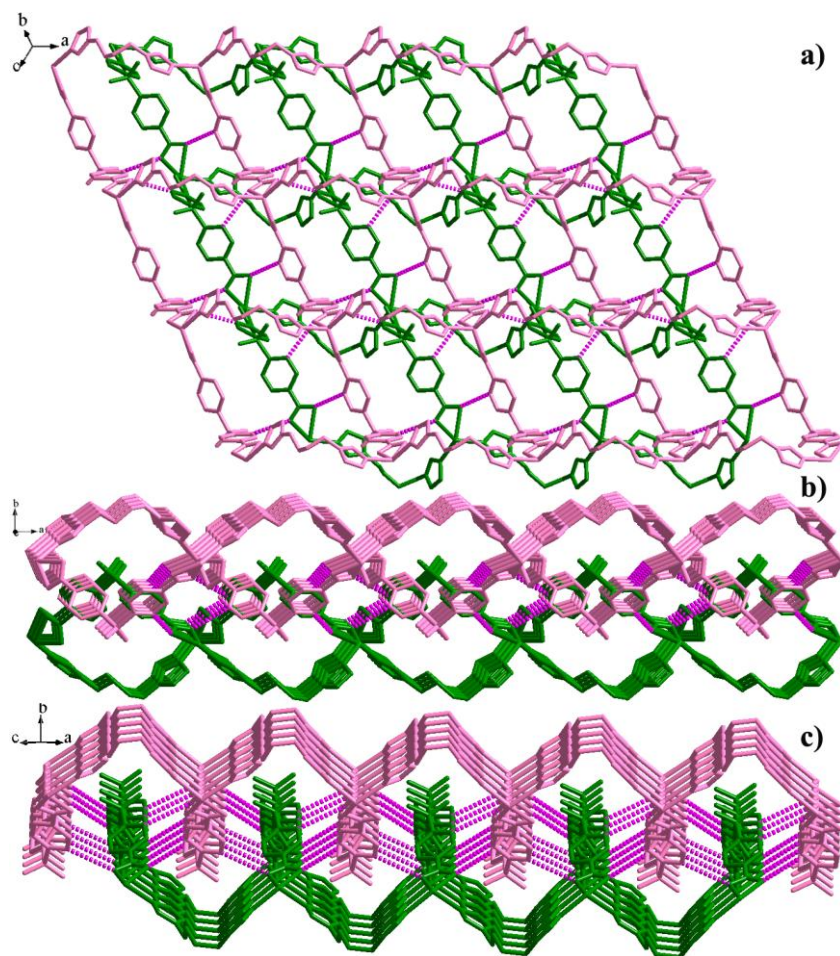


Fig. S20 Perspective views of the hydrogen-bonded bilayer motif of **3** along three different directions. The C-H...O hydrogen bonds (C2...O4 3.241 Å and C9...O3 3.460 Å) are highlighted by purple dashed lines.

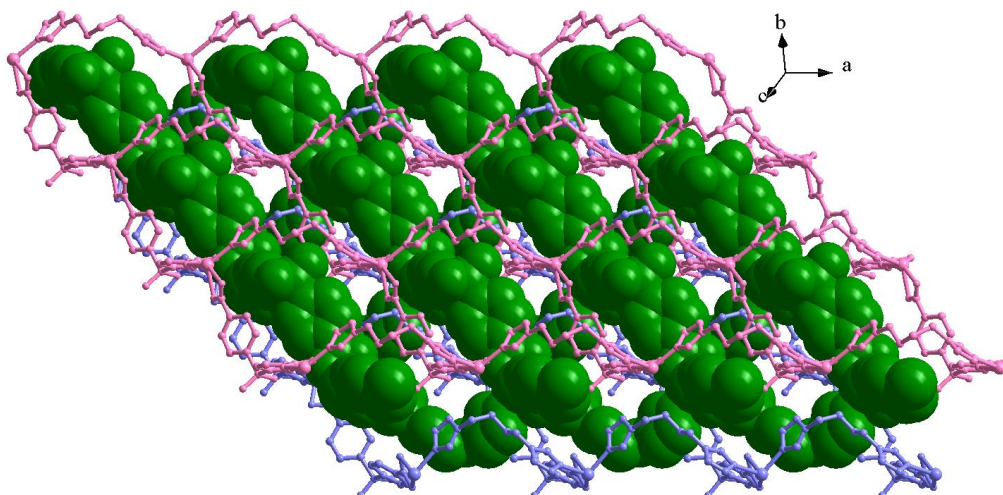


Fig. S21 Perspective and space-filling views of the detail interdigitation of two right-handed (pink and dull purple) and one left-handed (green) 2D layers in **3** along [1 1 2] direction.

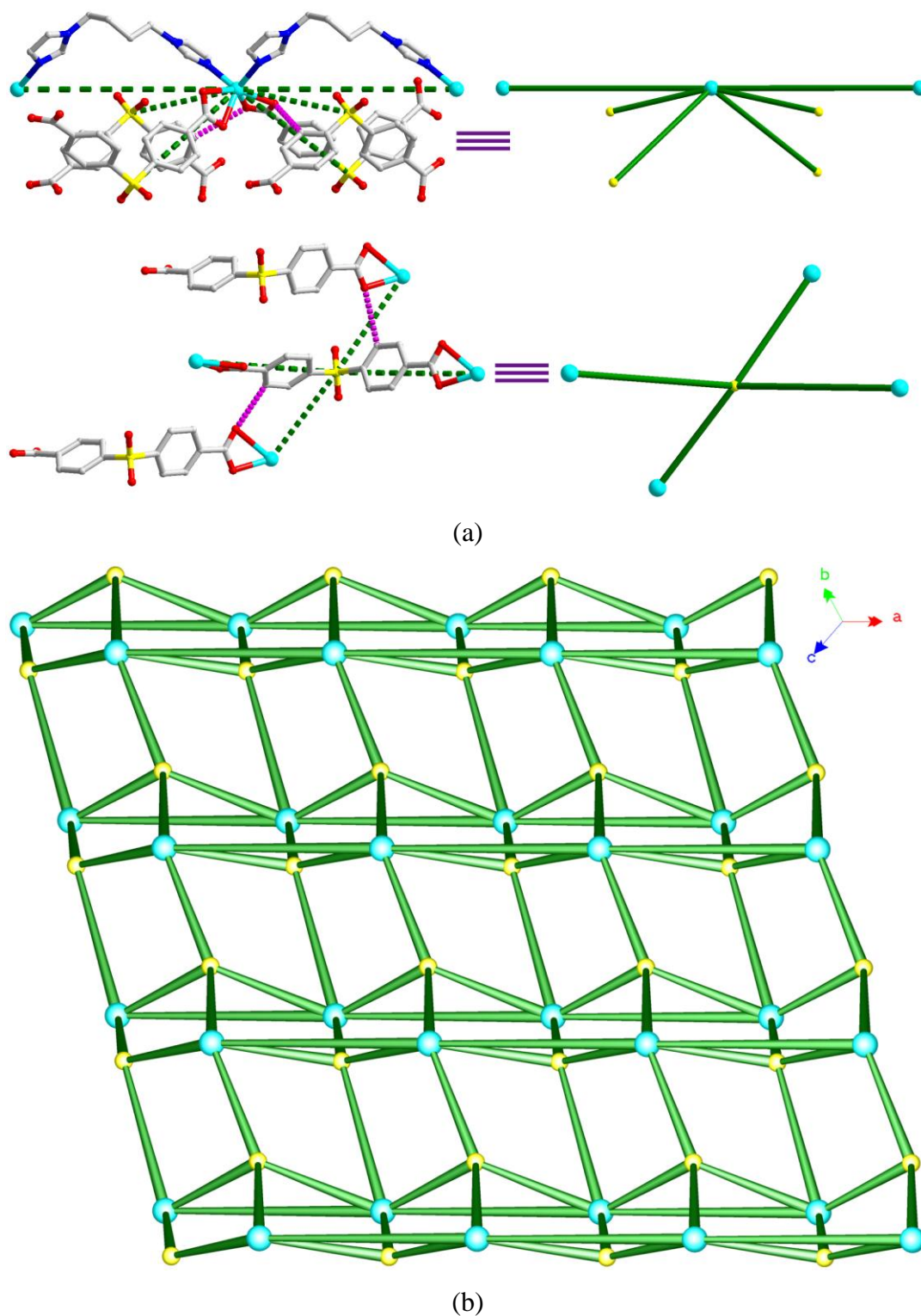


Fig. S22 (a) Perspective (left) and simplified (right) views of the six-connected node (the Cd center) and four-connected nodes (the sdba ligand) in **3**. The C-H...O hydrogen bonds are highlighted by purple dashed lines. (b) Schematic representation of the binodal (4,6)-connected 2D network of $(3.4^4.6)(3^2.4^4.5^5.6^3.7)$ topology that is formed when hydrogen bonds are taken into account in **3**.

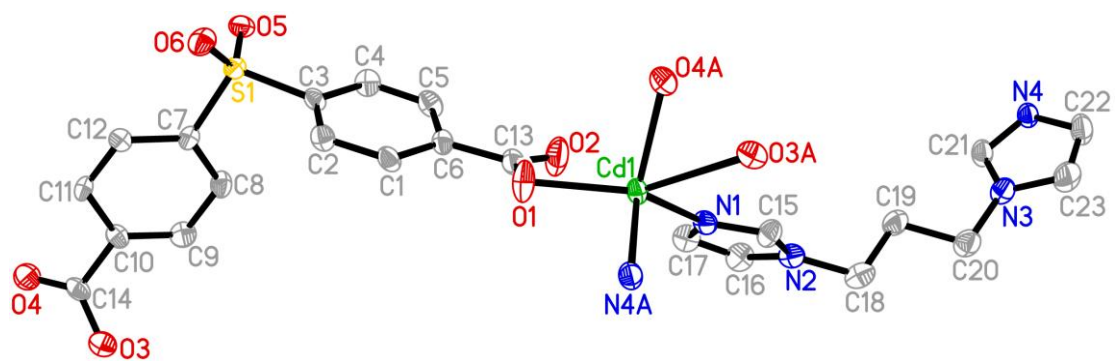


Fig. S23 ORTEP drawing of compound **4** with thermal ellipsoids at 30% probability. The hydrogen atoms are omitted for clarity.

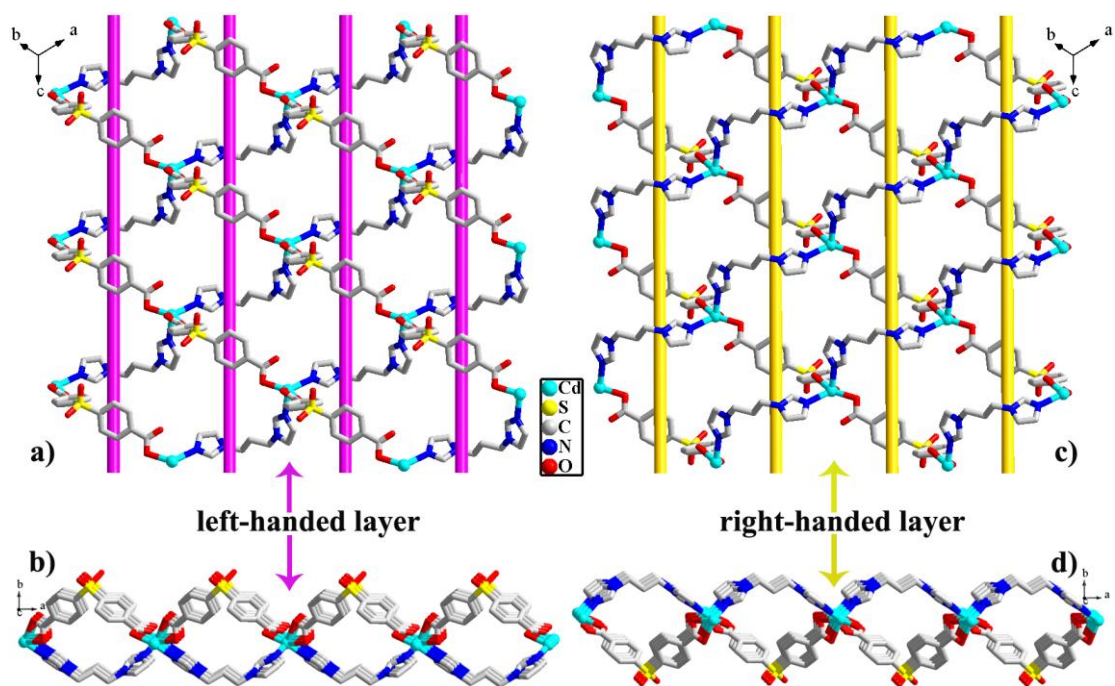


Fig. S24 Perspective view of the (a, b) left-handed and (c, d) right-handed 2D layers of **4**.

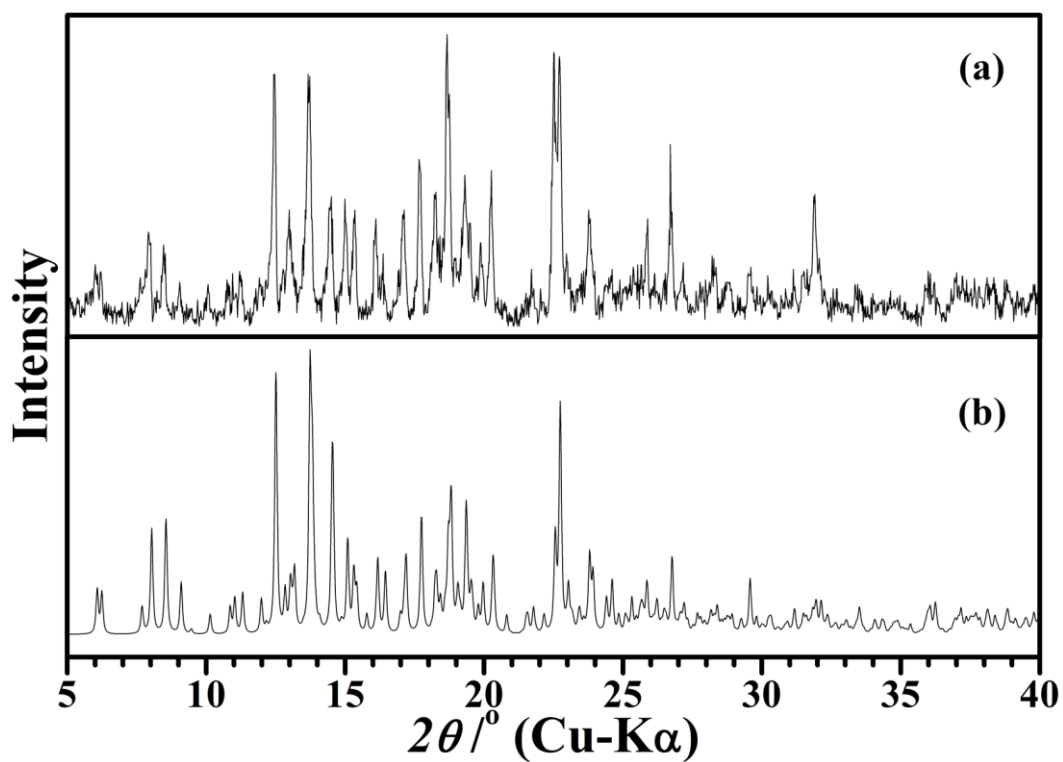


Fig. S25 The XRPD patterns for: (a) as-synthesized samples of **1**, and (b) simulated one based on the single-crystal structure of **1**.

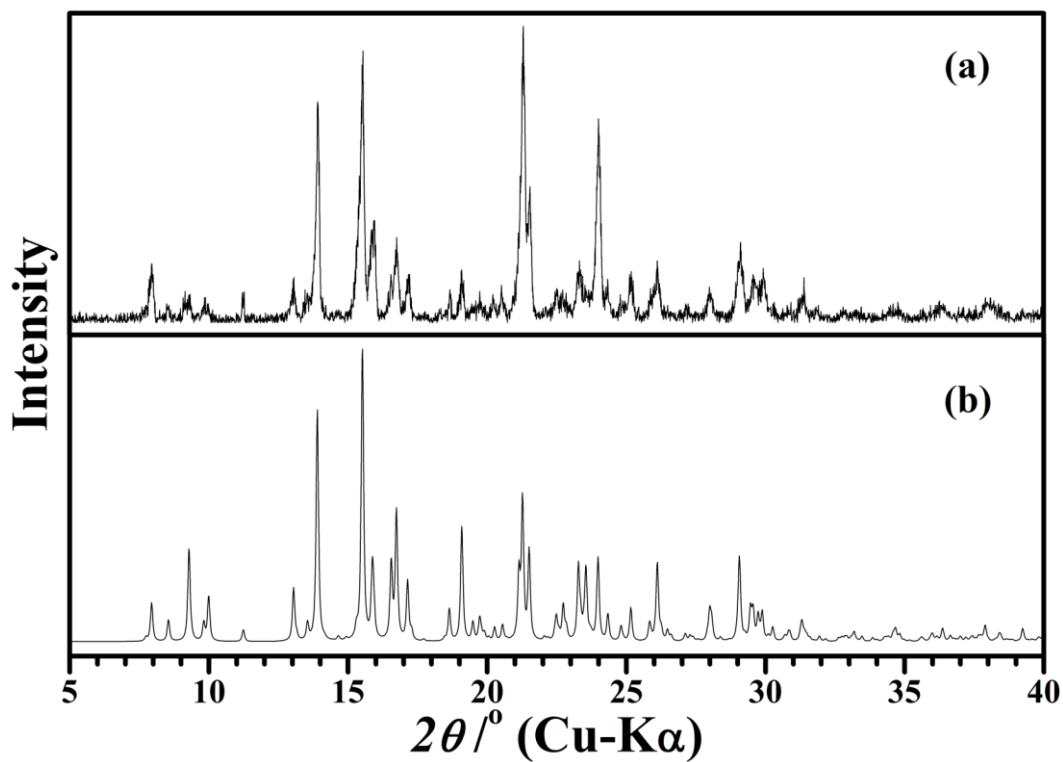


Fig. S26 The XRPD patterns for: (a) as-synthesized samples of **2**, and (b) simulated one based on the single-crystal structure of **2**.

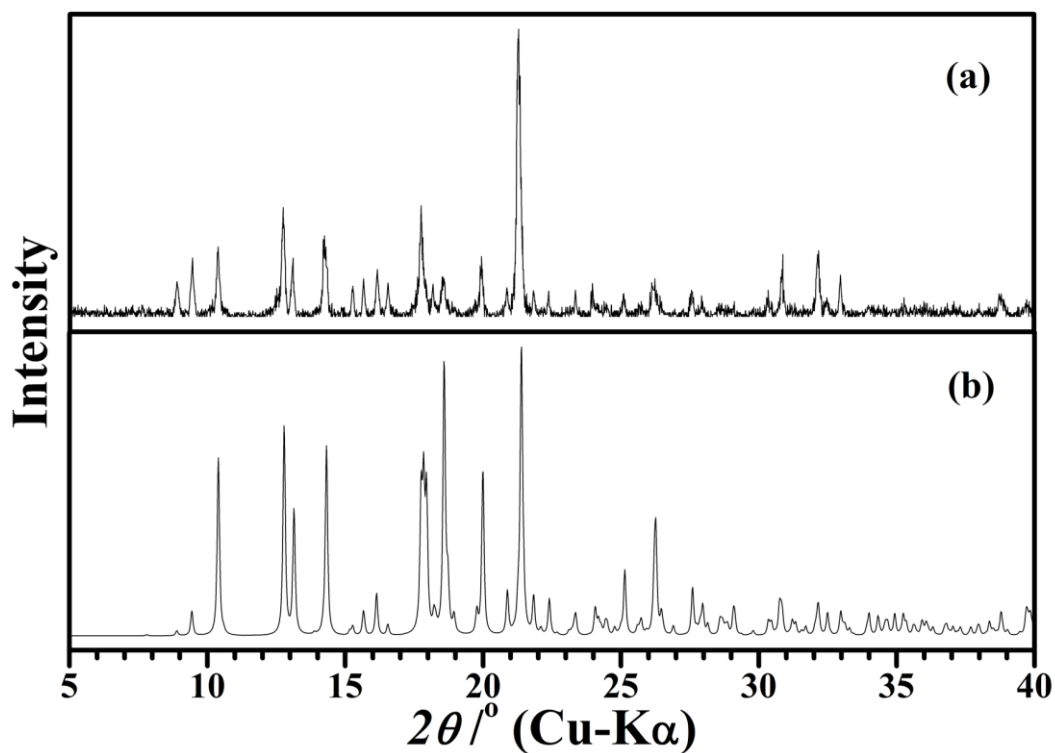
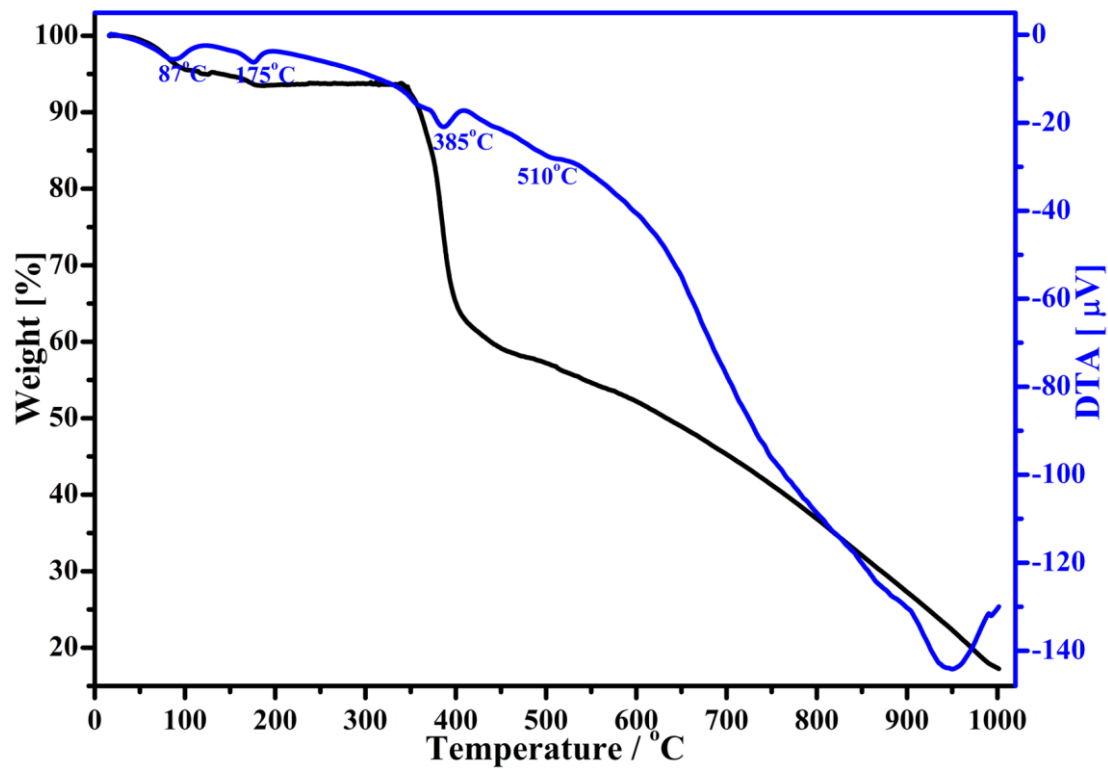
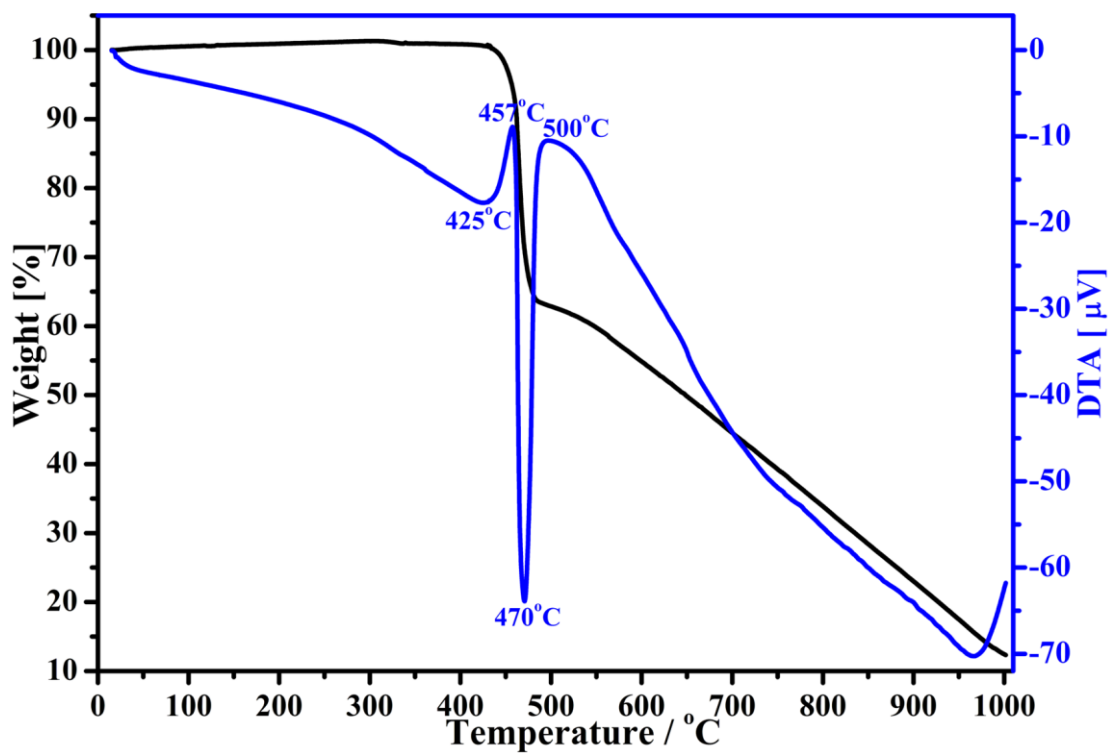


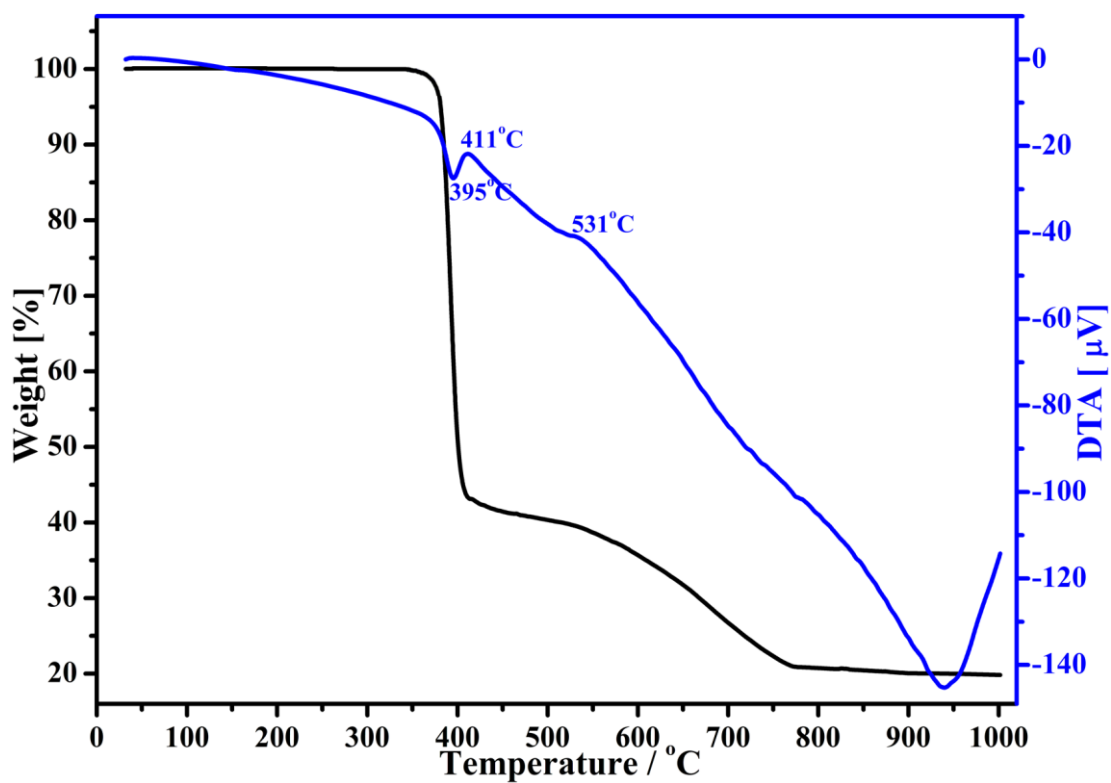
Fig. S27 The XRPD patterns for: (a) as-synthesized samples of **3**, and (b) simulated one based on the single-crystal structure of **3**.



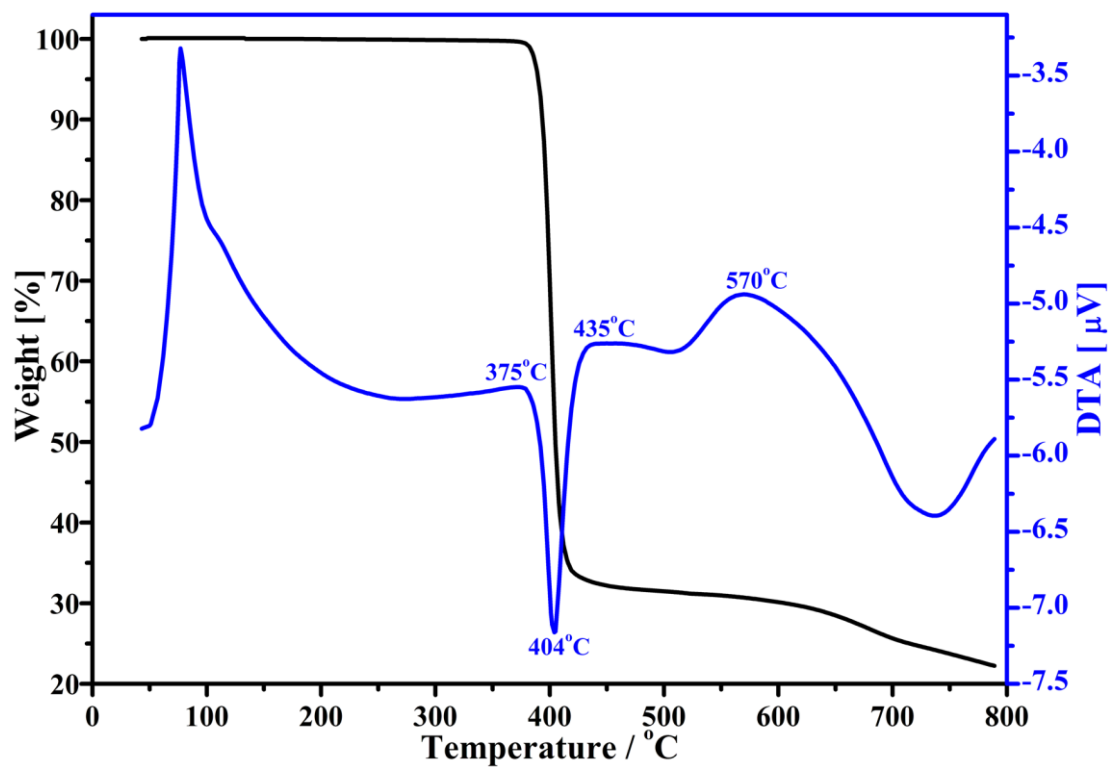
(a)



(b)



(c)



(d)

Fig. S28 The TG-DTA curves of compounds 1(a), 2(b), 3(c), 4(d).

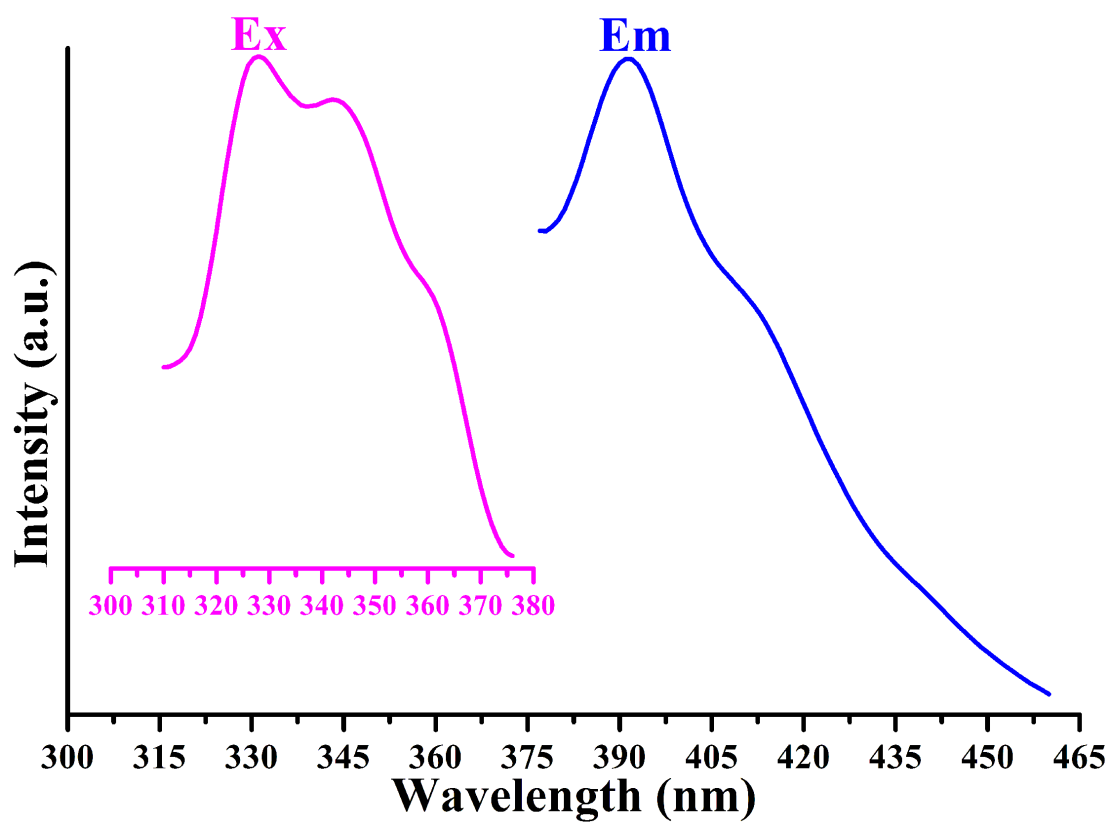
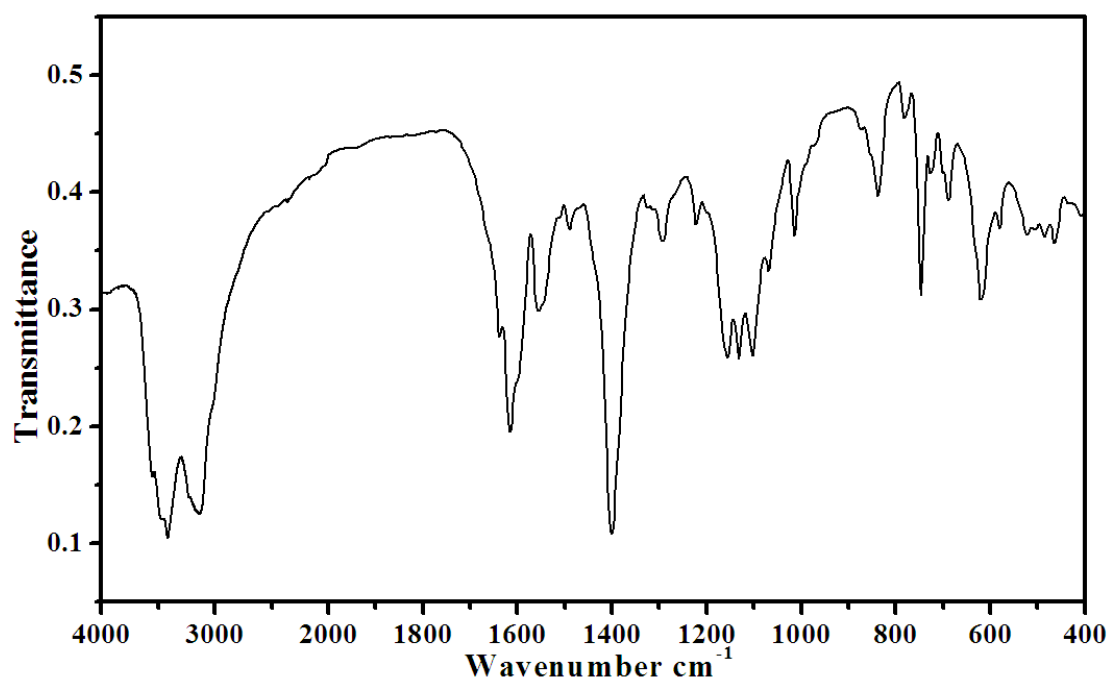
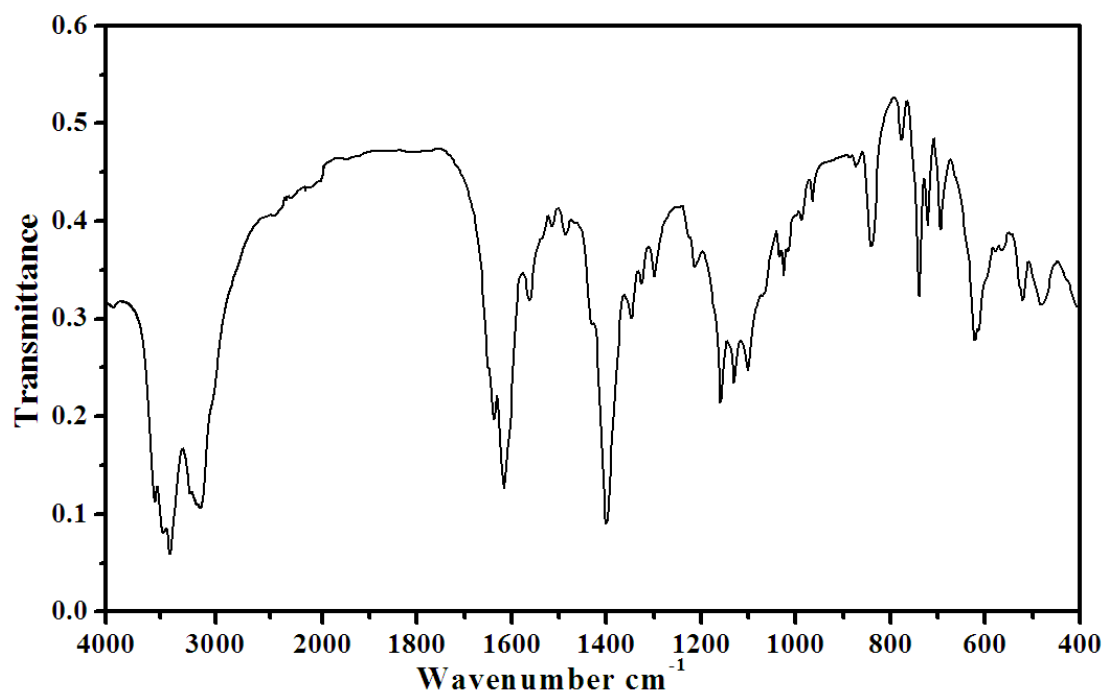


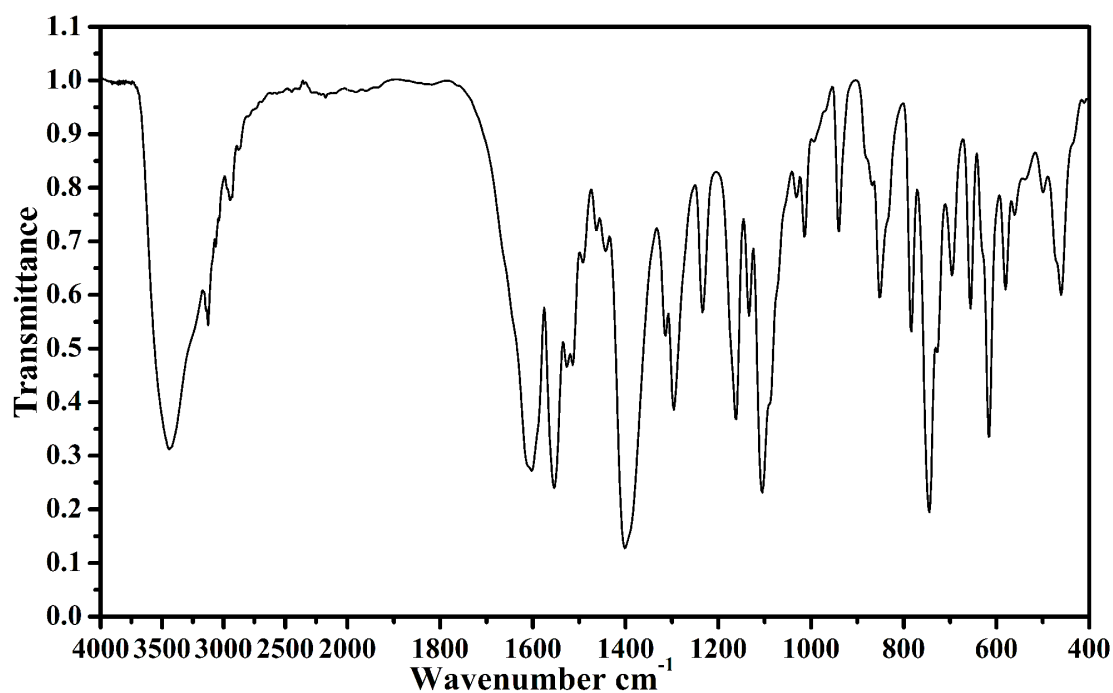
Fig. S29 Solid-state emission spectra of H_2sdba ligand at room temperature.



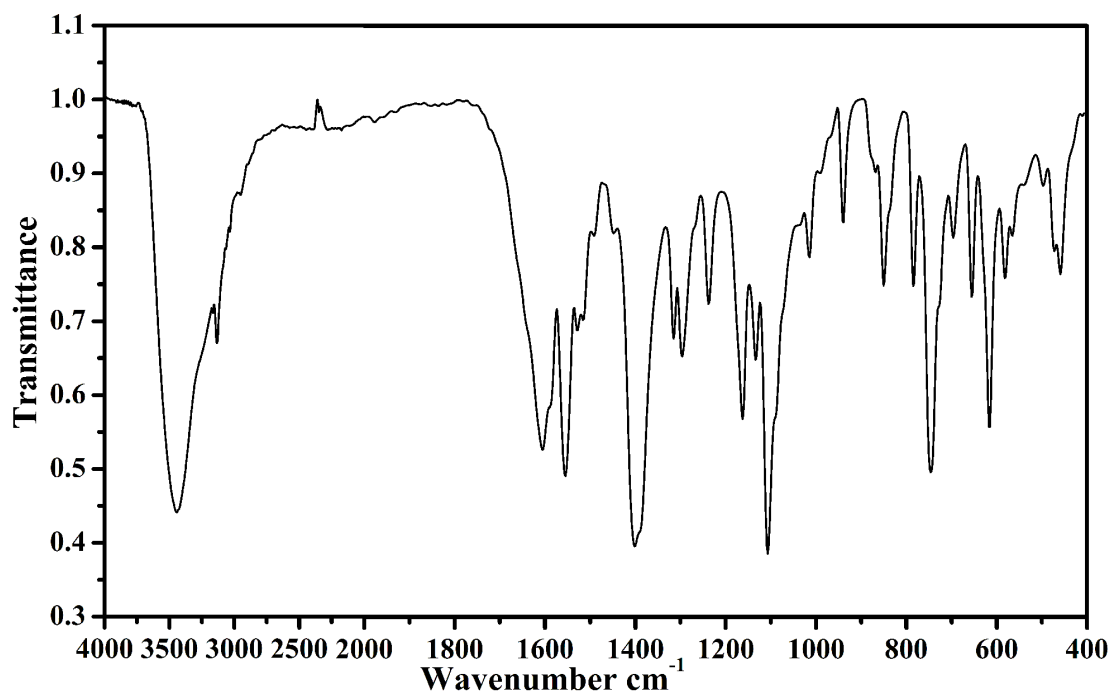
(a)



(b)



(c)



(d)

Fig. S30 The IR spectra for compounds **1**(a), **2**(b), **3**(c), **4**(d).

Additional details for single-crystal structural refinements

In the process of structure refinement of **1**, two carboxylate oxygen atoms (O9, O10) and two sulfonyl oxygen atoms (O11, O12) of sdba ligands were disordered over two

positions. These disordered atoms were modeled by application of distance restraints for chemically equivalent bonding interactions (C-O and S-O distances). The relative occupancies for the disordered components were refined with a total occupancy of 1. The N-H distances within the imidazole rings of Htpim ligands were also refined with the restrained comment "DFIX" for giving a more reasonable chemically equivalent bond distance. The $U_{\text{iso}}/U_{\text{ij}}$ restraints are used to give a more reasonable model of the aqua hydrogen atoms—that is, the aqua hydrogen atoms located from difference Fourier maps were refined with isotropic thermal parameters, 1.2 times those of their carrier atoms [i.e. $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{OW})$]. The restrained refinement comment "ISOR" is used during the refinement to restraint the Non-H atoms with the ADP problems, these atoms are as follows: C28, O9A, O10, O10A, S2, O11, O11A, O12, O12A, OW4, OW5, OW6, OW7, OW8 and OW9 in **1**.

During the refinement of compound **2**, the N-H distances within the imidazole rings of Htpim ligands were refined with a restrained comment "DFIX" for giving a more reasonable chemically equivalent bond distance.