

Supplementary Material (ESI) for CrystEngComm.

**Tuning the void volume in a series of isomorphous porous metal-organic frameworks by varying solvent size and length of organic ligand**

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**Materials and General Methods**

Powder X-ray diffractions were conducted on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) at  $2\theta$  ranging from 5 to 50°. The C, H and N elemental analyses were measured on a Perkin–Elmer 2400 elemental analyzer. IR-spectra were carried out on a Mattson Alpha-Centauri spectrometer at the range of 4000–400 cm<sup>-1</sup>. The photoluminescent properties of compounds were measured on an FLSP920 Edinburgh Fluorescence Spectrometer at room temperature.

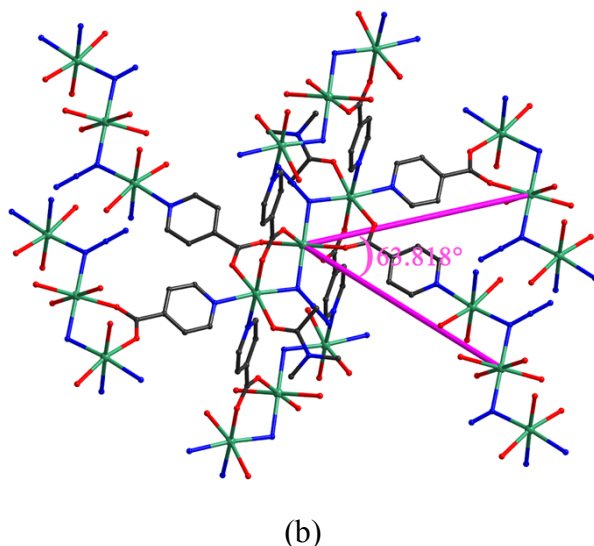
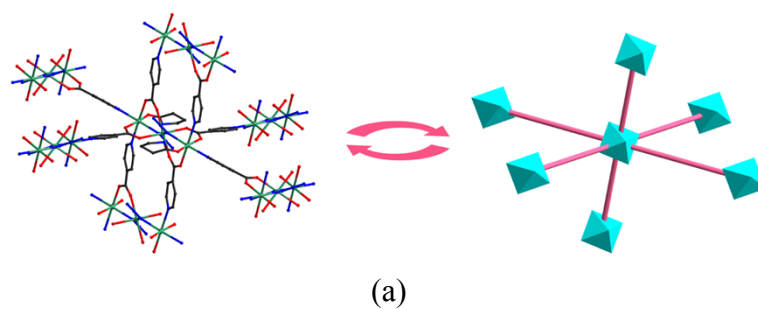
**X-ray crystallography**

Single-crystal X-ray diffraction data for **1–6** were recorded on an Oxford Gemini R Ultra diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293 K. All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program within WINGX.<sup>1</sup> Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at their calculated positions. The disordered atoms in compounds **1** (C13, C17, N6, and N7), **2** (C17, NC1, and NC2), and **5** (C14, C18, C22, N14, N15, and N16) were refined using C and N atoms split over two sites, with a total occupancy of 1. Some solvent hydrogen atoms in compounds **1** and **5** were not included in the model.

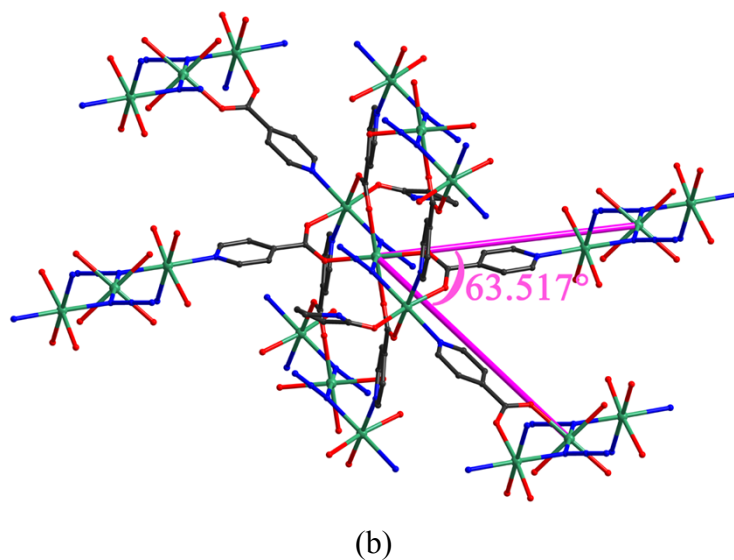
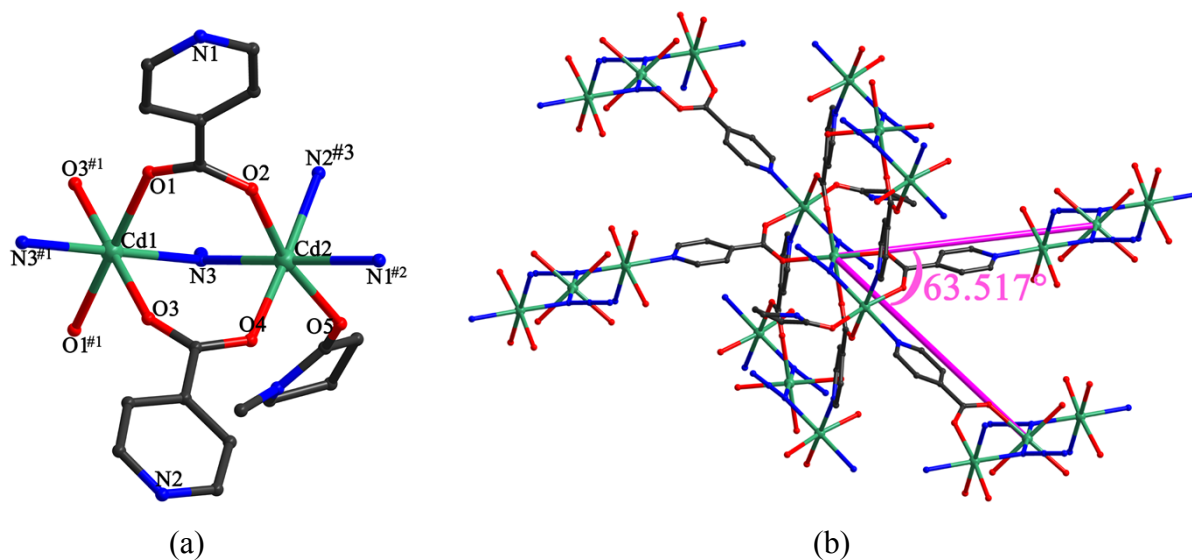
**References**

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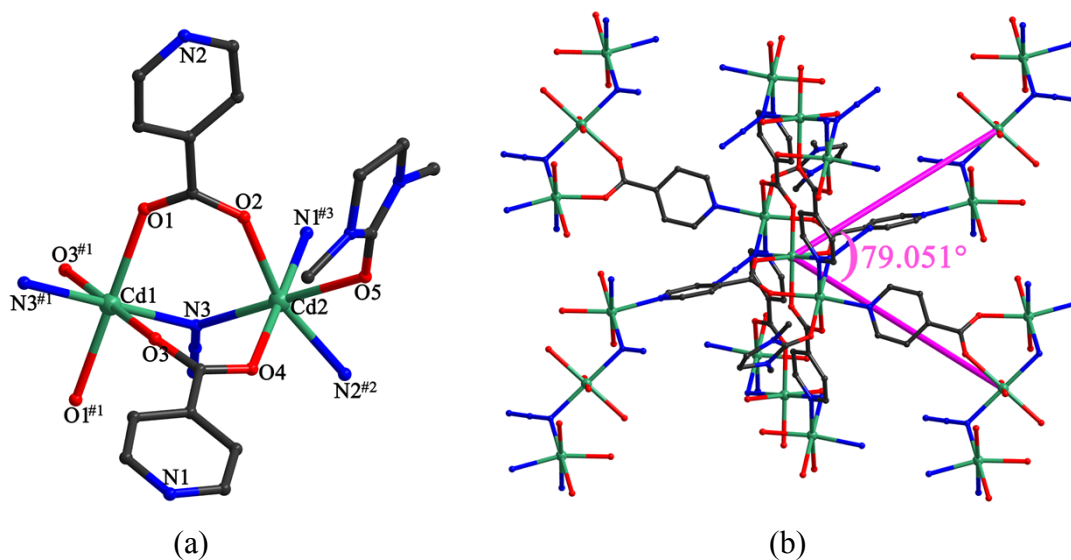
Glasgow, UK, 1988.



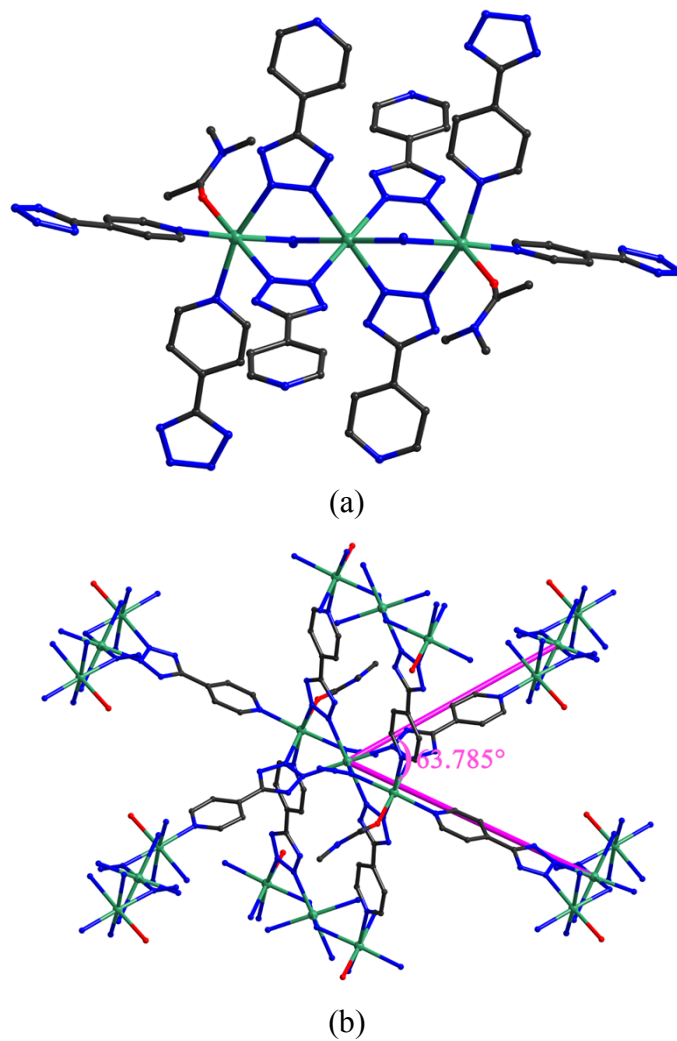
**Fig. S1** (a) View of the 6-connected node. (b) View of the angle  $\eta$  between two adjacent single bridges.



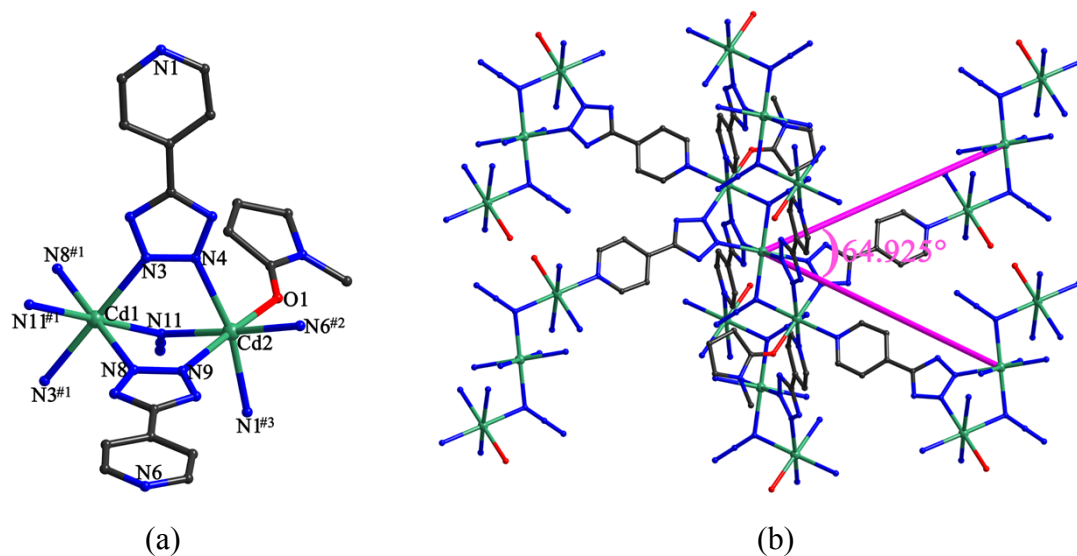
**Fig. S2** (a) Coordination environments of Cd(II) cations in 2. (b) View of angle  $\eta$  between two adjacent single bridges.



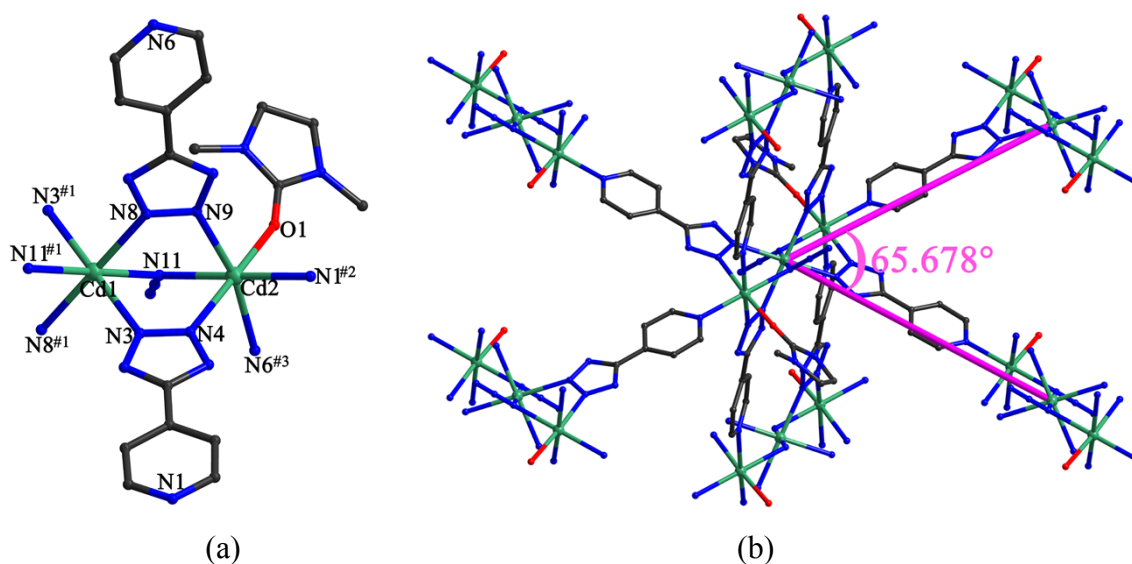
**Fig. S3** (a) Coordination environments of Cd(II) cations in **3**. (b) View of angle  $\eta$  between two adjacent single bridges.



**Fig. S4** (a) View of 6-connected node in **4**. (b) View of angle  $\eta$  with corresponding value.



**Fig. S5** (a) Coordination environments of Cd(II) cations in **5**. (b) View of angle  $\eta$  with corresponding value.



**Fig. S6** (a) Coordination environments of Cd(II) cations in **6**. (b) View of angle  $\eta$  with corresponding value.

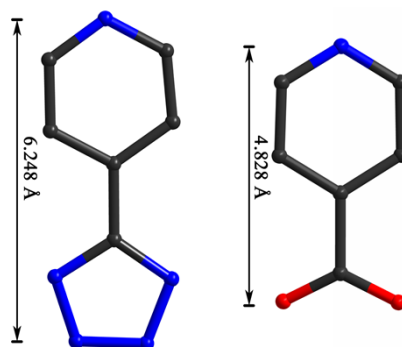
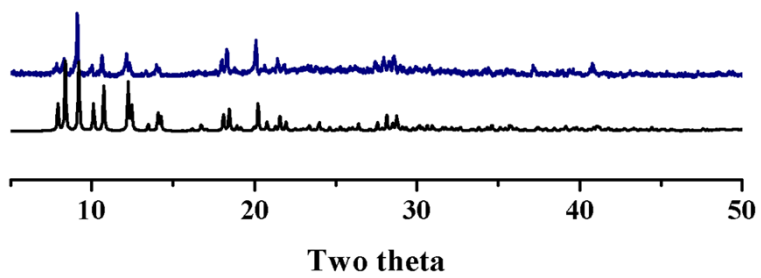
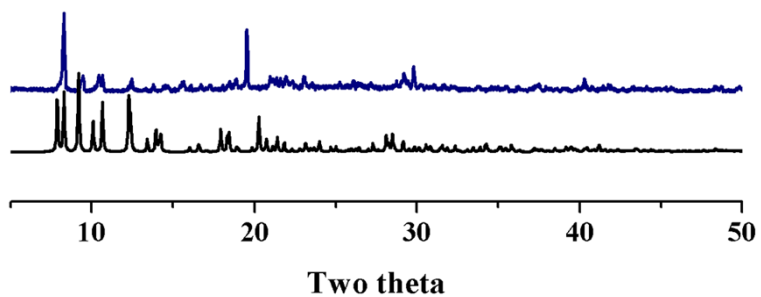


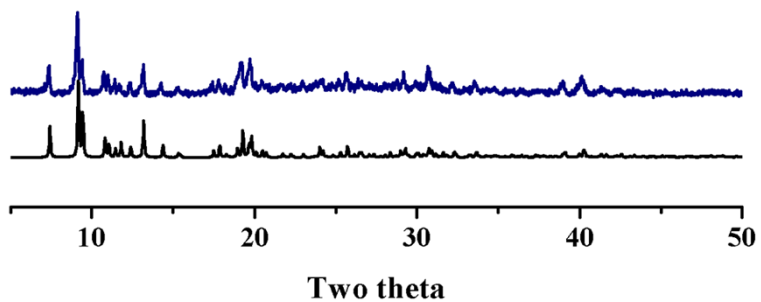
Fig. S7 The lengths of TP anion and HIN anion.



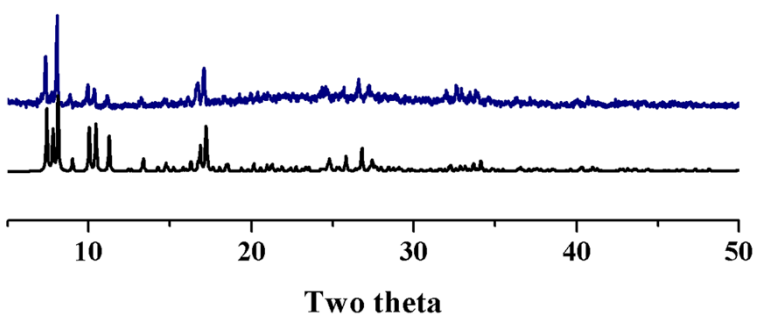
(1)



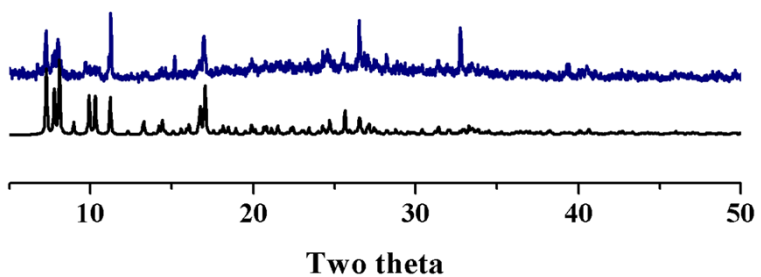
(2)

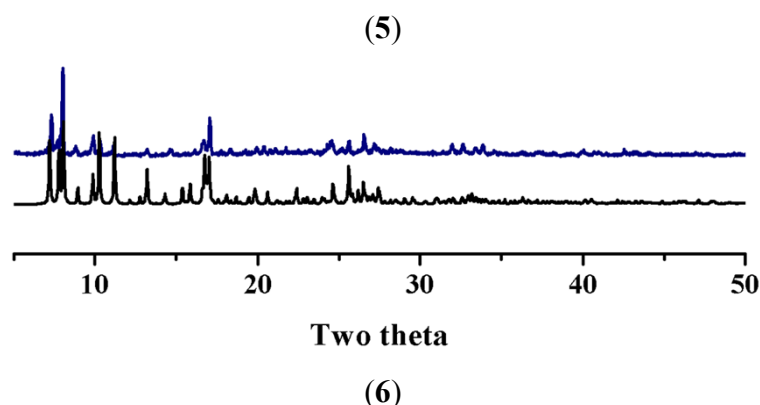


(3)



(4)





**Fig. S8** The simulated (black) and experimental (blue) PXRD patterns for compounds **1-6**.

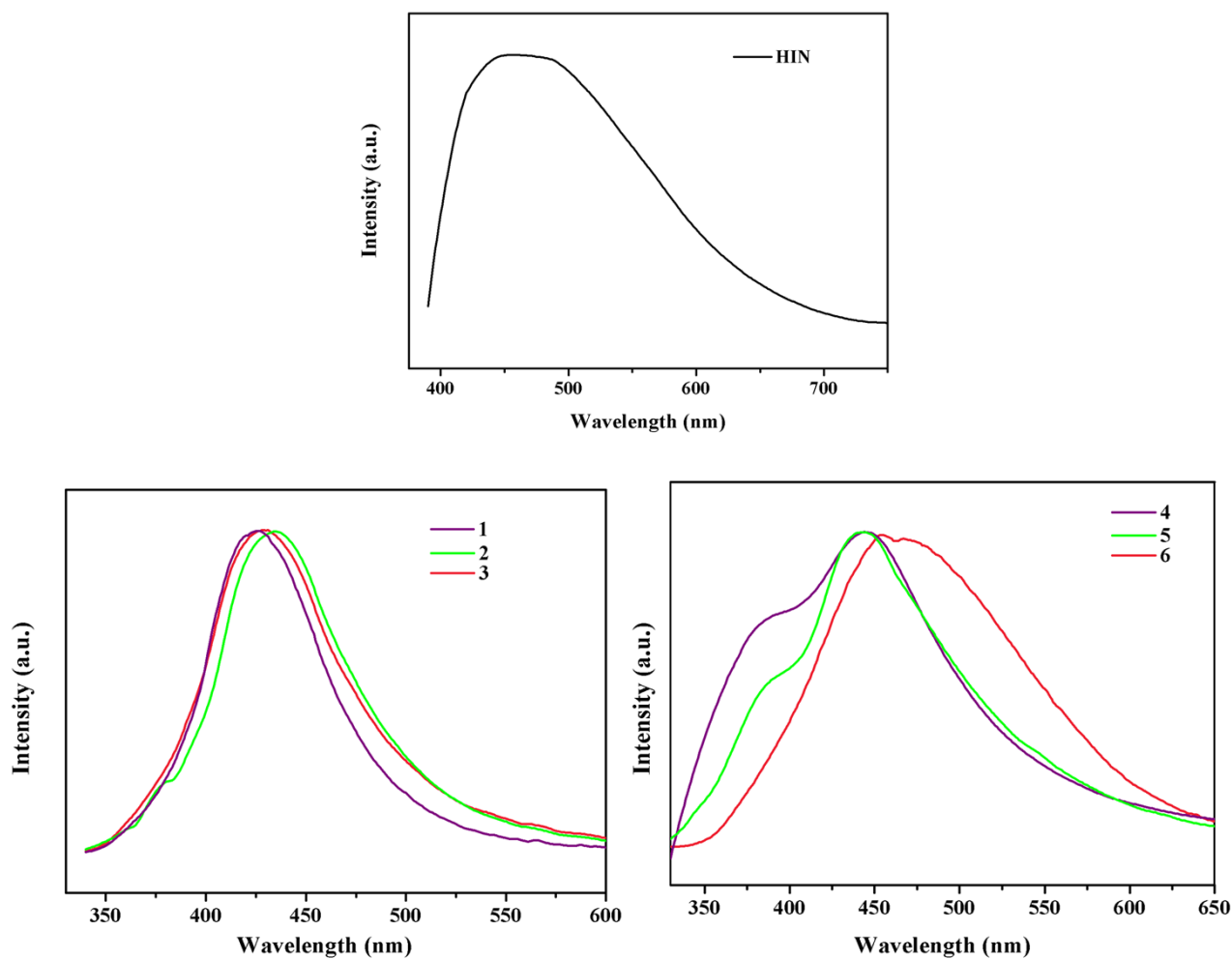
### Luminescent Properties

Luminescent properties of MOFs based Cd(II) cation have attracted much interest because of their potential applications in chemical sensors, electroluminescent display, and photochemistry.<sup>1</sup> The solid-state photoluminescent properties of free HIN and compounds **1-6** were investigated at room temperature (Fig. S9). It can be seen that upon excitation at 322 nm, compounds **1-3** display three strong emission peaks at 425 nm, 435 nm, and 430 nm, respectively, which can probably be attributed to the intraligand fluorescent emissions.<sup>2</sup> There are blue shifts of *ca.* 25 nm, 15 nm, and 20 nm compared with the emission of free HIN ( $\lambda_{em} = 450$  nm), which may be because of the coordination effects of IN anions to Cd(II) cations. The process can increase the ligand conformational rigidity and reduce the nonradiative decay of the intraligand.<sup>3</sup> Upon excitation at 313 nm, compounds **4-6** show emission peaks at 442 nm, 440 nm, and 453 nm, respectively. The emission peaks of these compounds also can be assigned to an intraligand fluorescent emission of TP anion ( $\lambda_{em} = 353$  nm for HTP).<sup>4</sup> However, the emission peaks are red-shifted compared to the free HTP, which may be due to the deprotonation of the HTP ligands after coordinating to Cd(II) ions.<sup>5</sup>

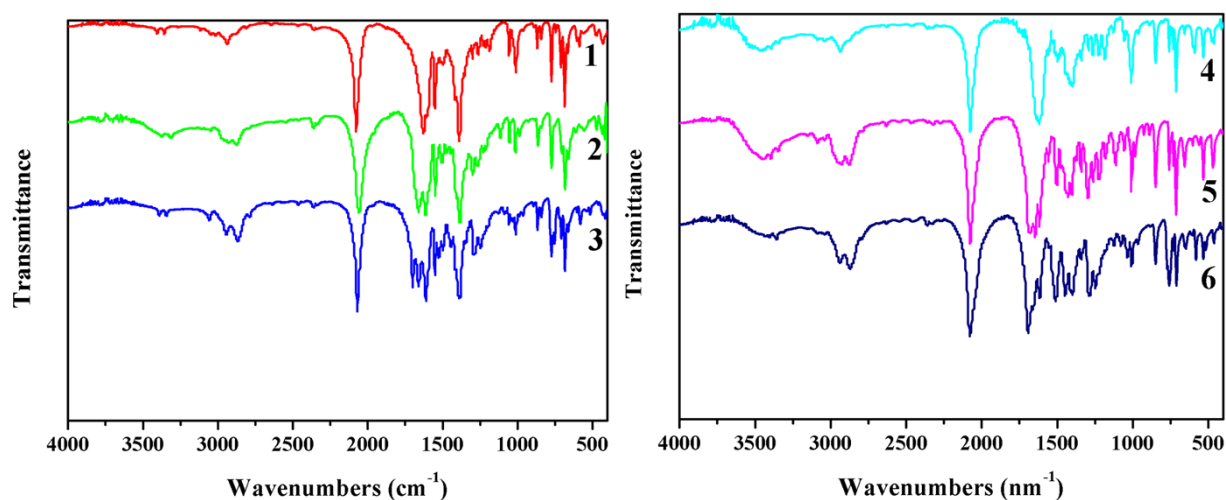
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**Fig. S9** Emission spectra of HIN and compounds 1-6.



**Fig. S10** IR spectra of compounds **1-6**.

**Table S1.** Selected bond distances (Å) and angles (°) for **1**.

Cd(1)-O(3)#1	2.250(5)	Cd(1)-N(3)	2.253(6)
Cd(2)-O(2)	2.241(5)	Cd(1)-O(1)	2.305(5)
Cd(2)-O(4)#1	2.258(5)	Cd(2)-N(3)	2.272(5)
Cd(2)-N(1)#3	2.310(6)	Cd(2)-O(5)	2.327(5)
Cd(2)-N(2)	2.409(6)	O(3)#1-Cd(1)-N(3)	90.8(2)
O(3)#1-Cd(1)-O(1)	88.6(2)	N(3)-Cd(1)-O(1)	94.0(2)
O(3)#1-Cd(1)-O(1)#2	91.4(2)	O(2)-Cd(2)-O(4)#1	91.9(2)
O(2)-Cd(2)-N(3)	98.4(2)	O(4)#1-Cd(2)-N(3)	95.6(2)
O(2)-Cd(2)-N(1)#3	86.31(19)	O(4)#1-Cd(2)-N(1)#3	88.2(2)
N(3)-Cd(2)-N(1)#3	173.8(2)	O(2)-Cd(2)-O(5)	169.0(2)
O(4)#1-Cd(2)-O(5)	95.3(2)	N(3)-Cd(2)-O(5)	89.3(2)
N(1)#3-Cd(2)-O(5)	85.57(19)	O(2)-Cd(2)-N(2)	85.1(2)
O(4)#1-Cd(2)-N(2)	176.9(2)	N(3)-Cd(2)-N(2)	85.1(2)
N(1)#3-Cd(2)-N(2)	91.3(2)	O(5)-Cd(2)-N(2)	87.6(2)

Symmetry transformations used to generate equivalent atoms: #1  $-x+1, -y, -z+1$ ; #2  $-x, -y, -z$ ; #3  $x, -y+1/2, z+1/2$ .

**Table S2.** Selected bond distances (Å) and angles (°) for **2**.

Cd(1)-N(3)	2.249(3)	Cd(1)-O(3)	2.249(3)
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Cd(1)-O(1)	2.306(2)	Cd(2)-O(2)	2.243(2)
Cd(2)-O(4)	2.260(2)	Cd(2)-N(3)	2.263(3)
Cd(2)-O(5)	2.333(2)	Cd(2)-N(2)#3	2.413(3)
N(3)#1-Cd(1)-O(3)	89.27(10)	N(3)#1-Cd(1)-O(1)	85.54(10)
O(3)-Cd(1)-O(1)	86.76(12)	O(2)-Cd(2)-O(4)	91.86(10)
O(2)-Cd(2)-N(3)	98.38(9)	O(4)-Cd(2)-N(3)	95.39(10)
O(2)-Cd(2)-N(1)#2	86.36(9)	O(4)-Cd(2)-N(1)#2	89.24(10)
N(3)-Cd(2)-N(1)#2	173.25(10)	O(2)-Cd(2)-O(5)	168.23(9)
N(1)#2-Cd(2)-O(5)	84.31(9)	O(2)-Cd(2)-N(2)#3	86.49(10)
O(4)-Cd(2)-N(2)#3	177.78(9)	N(3)-Cd(2)-N(2)#3	83.38(10)
N(1)#2-Cd(2)-N(2)#3	92.15(10)	O(5)-Cd(2)-N(2)#3	86.70(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1; #2 x,-y-1/2,z+1/2; #3 x-1,y,z.

**Table S3.** Selected bond distances (Å) and angles (°) for **3**.

Cd(1)-N(3)	2.262(4)	Cd(1)-O(3)	2.270(3)
Cd(1)-O(1)	2.307(3)	Cd(2)-O(2)	2.231(3)
Cd(2)-O(4)	2.291(3)	Cd(2)-N(3)	2.291(4)
Cd(2)-N(2)#2	2.331(4)	Cd(2)-O(5)	2.341(3)
Cd(2)-N(1)#3	2.387(4)	N(3)#1-Cd(1)-O(3)	89.89(14)
N(3)#1-Cd(1)-O(1)	86.97(14)	O(3)-Cd(1)-O(1)	86.51(13)
N(3)#1-Cd(1)-O(1)#1	93.03(14)	O(3)-Cd(1)-O(1)#1	93.49(13)
O(2)-Cd(2)-O(4)	97.46(13)	O(2)-Cd(2)-N(3)	99.23(14)
O(4)-Cd(2)-N(3)	91.29(13)	O(2)-Cd(2)-N(2)#2	162.96(12)
O(4)-Cd(2)-N(2)#2	89.21(13)	N(3)-Cd(2)-N(2)#2	96.26(14)
O(2)-Cd(2)-O(5)	81.19(12)	O(4)-Cd(2)-O(5)	88.18(12)
N(3)-Cd(2)-O(5)	179.36(14)	N(2)#2-Cd(2)-O(5)	83.38(13)
O(2)-Cd(2)-N(1)#3	84.26(14)	O(4)-Cd(2)-N(1)#3	177.33(13)
N(3)-Cd(2)-N(1)#3	86.41(14)	N(2)#2-Cd(2)-N(1)#3	89.69(14)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z; #2 x,-y-1/2,z-1/2; #3 x+1,y,z.

**Table S4.** Selected bond distances (Å) and angles (°) for **4**.

Cd(1)-N(11)	2.293(4)	Cd(1)-N(8)	2.313(5)
Cd(1)-N(3)	2.322(4)	Cd(2)-N(6)#2	2.275(5)

Cd(2)-N(11)	2.276(5)	Cd(2)-O(1)	2.283(4)
Cd(2)-N(1)#3	2.368(4)	Cd(2)-N(9)	2.377(4)
Cd(2)-N(4)	2.402(4)	N(11)#1-Cd(1)-N(8)	92.84(17)
N(11)#1-Cd(1)-N(3)#1	82.80(17)	N(8)-Cd(1)-N(3)#1	94.74(17)
N(11)#1-Cd(1)-N(3)	97.20(17)	N(8)-Cd(1)-N(3)	85.26(17)
N(6)#2-Cd(2)-N(11)	176.87(17)	N(6)#2-Cd(2)-O(1)	87.16(17)
N(11)-Cd(2)-O(1)	92.23(17)	N(6)#2-Cd(2)-N(1)#3	96.18(17)
N(11)-Cd(2)-N(1)#3	86.93(17)	O(1)-Cd(2)-N(1)#3	95.01(18)
N(6)#2-Cd(2)-N(9)	94.47(17)	N(11)-Cd(2)-N(9)	86.21(17)
O(1)-Cd(2)-N(9)	177.98(18)	N(1)#3-Cd(2)-N(9)	83.64(16)
N(6)#2-Cd(2)-N(4)	92.76(16)	N(11)-Cd(2)-N(4)	84.28(16)
N(1)#3-Cd(2)-N(4)	164.57(15)	N(9)-Cd(2)-N(4)	83.14(15)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z; #2 x,-y+1/2,z-1/2; #3 x-1,y,z.

**Table S5.** Selected bond distances (Å) and angles (°) for **5**.

Cd(1)-N(11)	2.294(3)	Cd(1)-N(8)#1	2.333(3)
Cd(1)-N(3)#1	2.341(3)	Cd(2)-O(1)	2.284(3)
Cd(2)-N(6)#2	2.303(3)	Cd(2)-N(11)	2.313(3)
Cd(2)-N(1)#3	2.375(3)	Cd(2)-N(9)	2.392(3)
Cd(2)-N(4)	2.402(3)	N(11)-Cd(1)-N(8)#1	92.99(11)
N(11)-Cd(1)-N(3)#1	96.99(12)	N(8)#1-Cd(1)-N(3)#1	85.58(12)
N(11)-Cd(1)-N(3)	83.01(12)	N(8)#1-Cd(1)-N(3)	94.42(12)
O(1)-Cd(2)-N(6)#2	86.50(11)	O(1)-Cd(2)-N(11)	92.72(12)
N(6)#2-Cd(2)-N(11)	177.46(13)	O(1)-Cd(2)-N(1)#3	92.06(13)
N(6)#2-Cd(2)-N(1)#3	95.86(12)	N(11)-Cd(2)-N(1)#3	86.58(12)
O(1)-Cd(2)-N(9)	176.78(13)	N(6)#2-Cd(2)-N(9)	94.90(11)
N(11)-Cd(2)-N(9)	86.00(11)	N(1)#3-Cd(2)-N(9)	84.91(11)
O(1)-Cd(2)-N(4)	98.43(12)	N(6)#2-Cd(2)-N(4)	93.66(12)
N(11)-Cd(2)-N(4)	84.05(12)	N(9)-Cd(2)-N(4)	84.39(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z; #2 x,-y-1/2,z+1/2; #3 x+1,y,z.

**Table S6.** Selected bond distances (Å) and angles (°) for **6**.

Cd(1)-N(11)	2.283(2)	Cd(1)-N(8)	2.331(2)
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Cd(1)-N(3)	2.358(2)	Cd(2)-N(11)	2.290(2)
Cd(2)-N(1)#2	2.308(2)	Cd(2)-O(1)	2.315(2)
Cd(2)-N(6)#3	2.376(3)	Cd(2)-N(9)	2.414(2)
Cd(2)-N(4)	2.423(2)	N(11)-Cd(1)-N(8)	83.86(9)
N(11)-Cd(1)-N(3)#1	94.07(8)	N(8)-Cd(1)-N(3)#1	95.62(9)
N(11)-Cd(1)-N(3)	85.93(8)	N(8)-Cd(1)-N(3)	84.38(9)
N(11)-Cd(2)-N(1)#2	179.65(9)	N(11)-Cd(2)-O(1)	92.25(8)
N(1)#2-Cd(2)-O(1)	87.58(8)	N(11)-Cd(2)-N(6)#3	86.31(9)
N(1)#2-Cd(2)-N(6)#3	94.00(9)	O(1)-Cd(2)-N(6)#3	91.30(9)
N(11)-Cd(2)-N(9)	85.87(8)	N(1)#2-Cd(2)-N(9)	93.86(9)
O(1)-Cd(2)-N(9)	99.64(9)	N(6)#3-Cd(2)-N(9)	166.78(8)
N(11)-Cd(2)-N(4)	84.88(8)	N(1)#2-Cd(2)-N(4)	95.29(8)
N(6)#3-Cd(2)-N(4)	86.46(9)	N(9)-Cd(2)-N(4)	82.25(8)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z; #2 x,-y-1/2,z+1/2; #3 x+1,y,z.