

**Fig. S1** The parallel arrangement of 2D networks along a axis and connected through Cd– $N_{pyridyl}$  bonds to form a 3D framework in **2**.

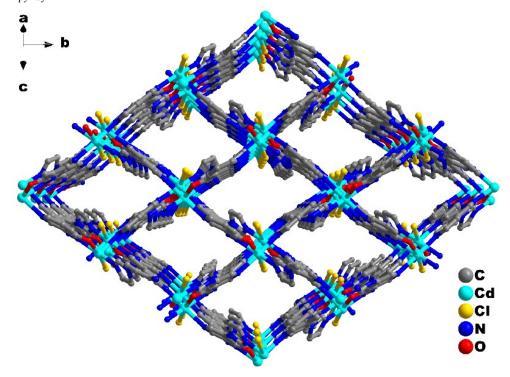
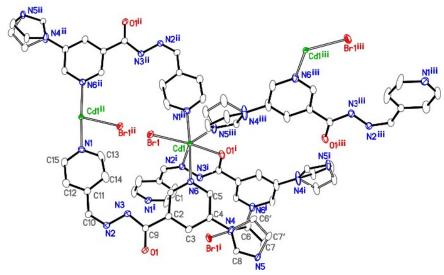
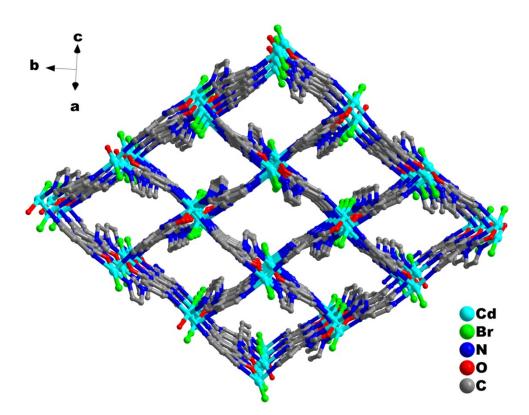


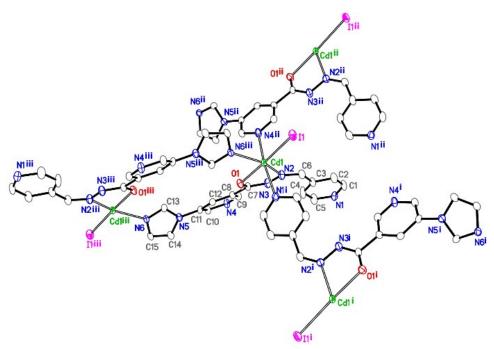
Fig. S2 The 3D framework of 2, and the rhombic channels view along the crystallographic [101] direction.



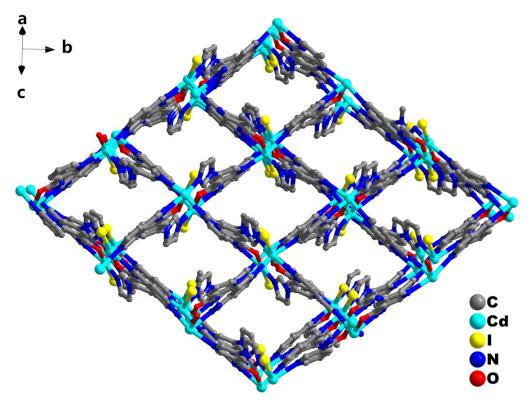
**Fig. S3** The coordination environment of Cd(II) centers in **3**, with displacement ellipsoids drawn at the 50% probability level.



**Fig. S4** The 3D framework of **3**, and the rhombic channels view along the crystallographic [101] direction.



**Fig. S5** The coordination environment of Cd(II) centers in **4**, with displacement ellipsoids drawn at the 50% probability level.



**Fig. S6** The 3D framework of **4**, and the rhombic channels view along the crystallographic [101] direction.

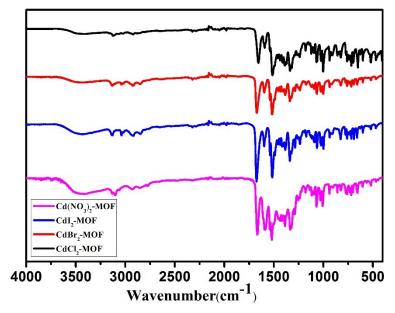


Fig. S7 IR spectra of 1-4.



**Fig. S8** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing the existence of *N*,*N*-Dimethylformamide guest molecules in the channels. The Cd(II) MOFs are not soluble in normal solvents, so the <sup>1</sup>H NMR measurement was performed on the CDCl<sub>3</sub> extract of the as-synthesized MOF crystals.

5.0 ppm

4.5 4.0 3.5

3.0 2.5

0.5

1.0

1.5

6.5 6.0 5.5

00.

7.5

7.0

9.0 8.5 8.0

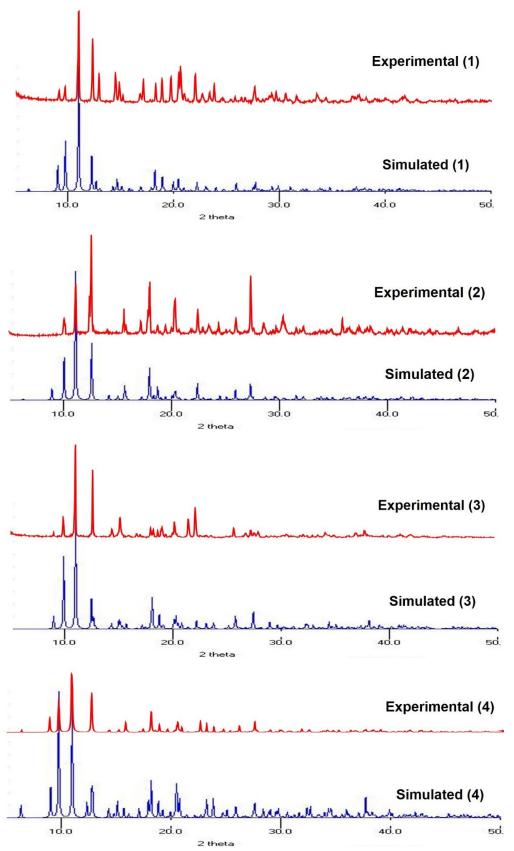


Fig. S9 PXRD patterns of 1-4.