Electronic Supplementary Information

Sulfate encapsulation in three-fold interpenetrated metal-organic frameworks with bis(pyridylurea) ligands

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Experimental

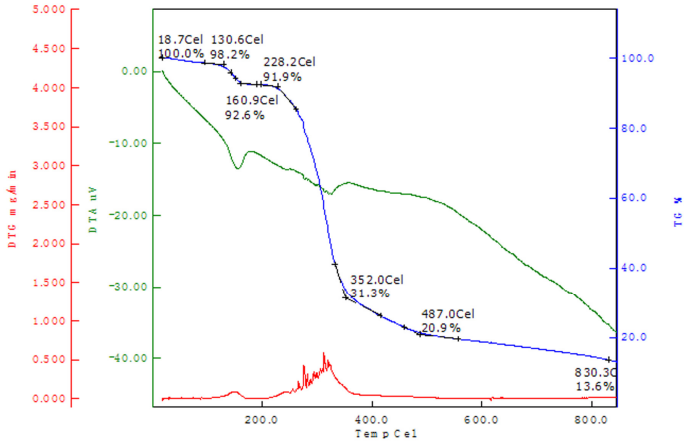

Figure S1. TGA curve of compound **1**.

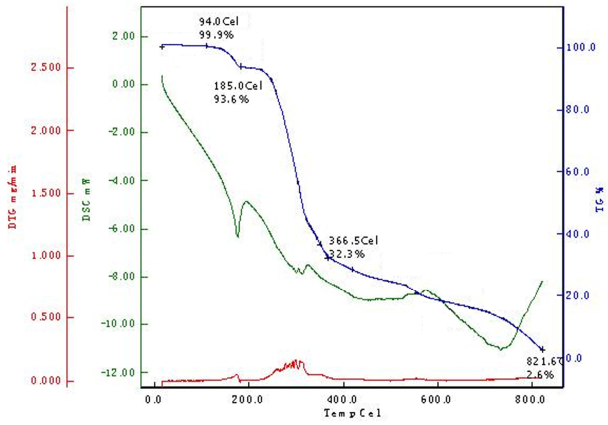

Figure S2. TGA curve of compound **2**.

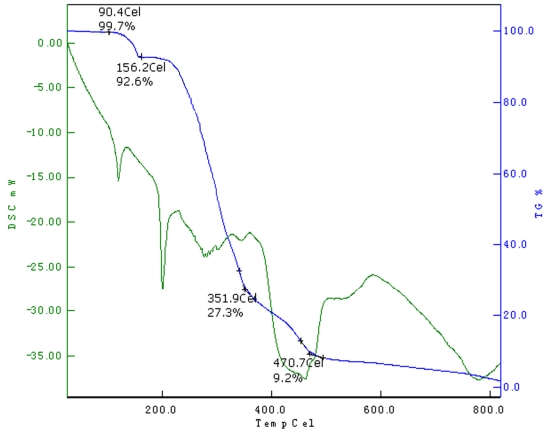

Figure S3. TGA curve of compound **3**.

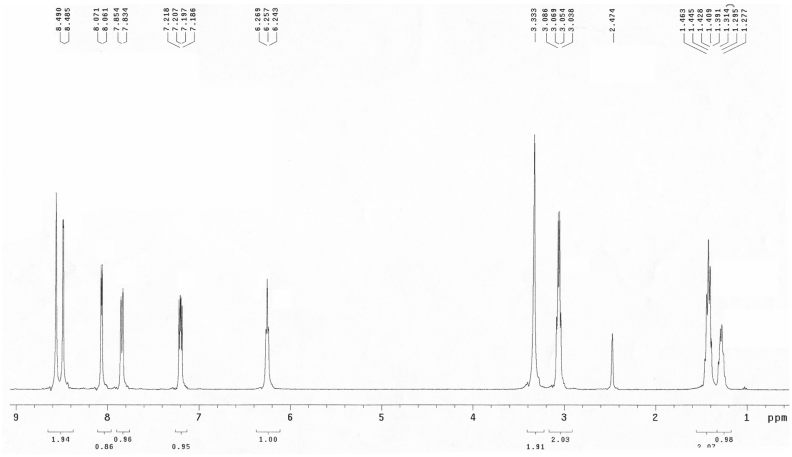

Figure S4. ^{1}H NMR spectrum of $\mathbf{L^5}$.

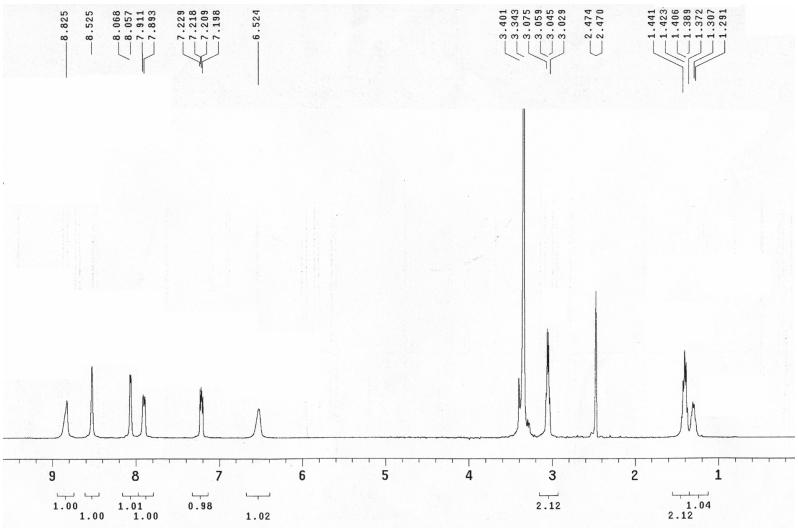

Figure S5. ^{1}H NMR spectrum of **1**.

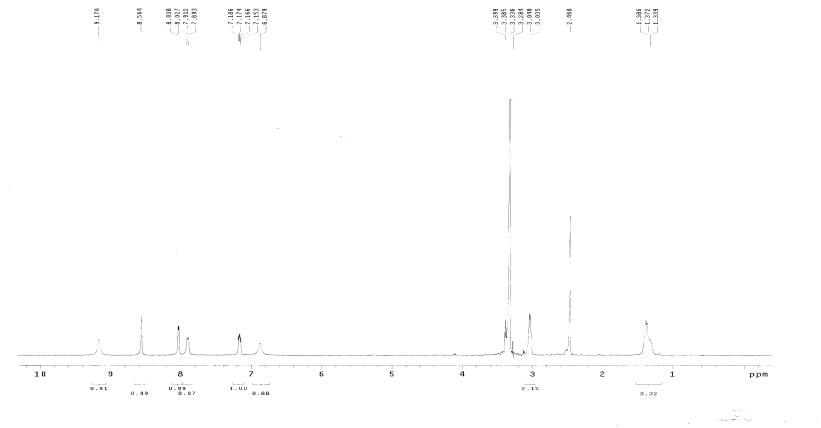

Figure S6. ^{1}H NMR Spectrum of **2**.

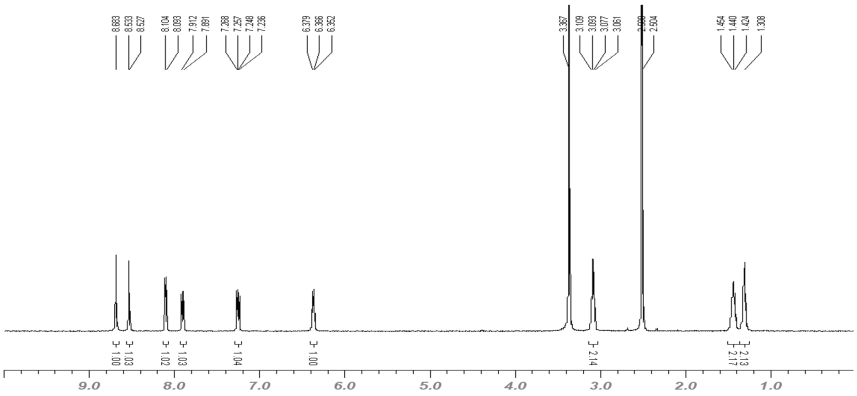

Figure S7. ^{1}H NMR spectrum of **3**.

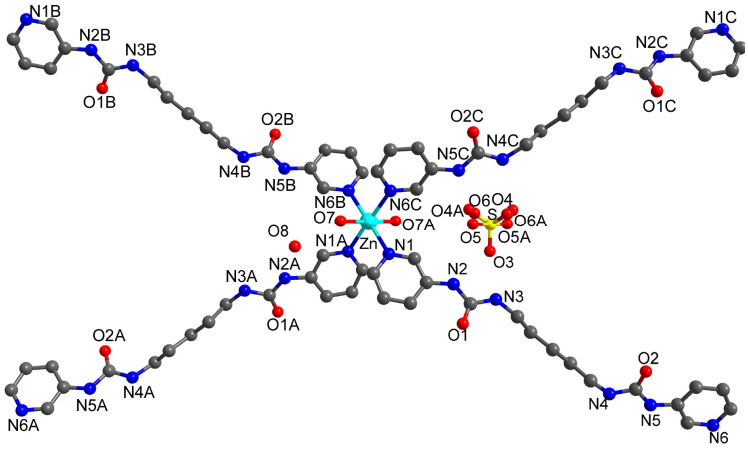

Figure S8. Molecular plot of **1** with atomic labeling. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn–N1, 2.216(1); Zn–N6B,[b] 2.176(1); Zn–O7, 2.127(1); O7–Zn–N1, 88.23(5); N1–Zn–N1A[a], 84.14(8); N6B[b]–Zn–N6C[c], 85.56(7); N6C[c]–Zn–N1 95.16(6); O7–Zn–N1A[a] 92.26(5); N6B[b]–Zn–N1 178.64(5); O7–Zn–N6B[b], 90.63(5); O7–Zn–N6C[c], 88.89(5). Symmetry code: [a] 1–x, y, 0.5–z, [b] 1.5+x, 0.5+y, 0.5–z;. [c] –x–0.5, y+0.5, z.

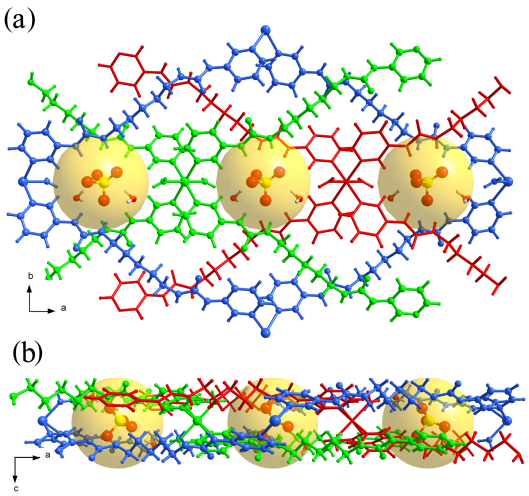

Figure S9. (a) Ellipsoidal cavities in the 3-fold interpenetrated structure of **1** with sulfate ions encapsulated in the cavities; (b) Side view of the interpenetrated bilayer structure of **1**.

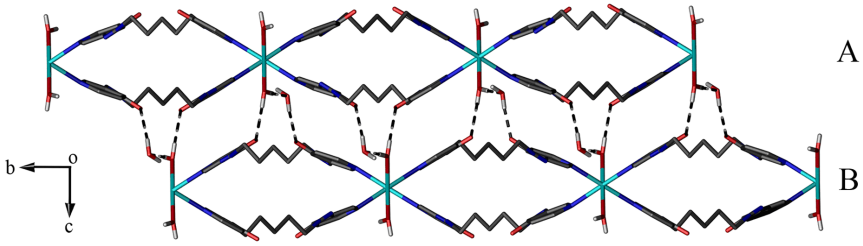

Figure S10. The layered structure of **1** packed in a repeating ABAB sequence.

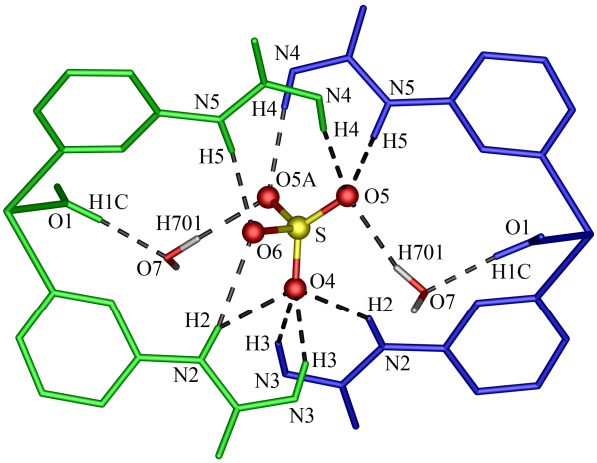

Figure S11. Ellipsoidal cavities in the 3-fold interpenetrated structure of **3**. The ligands are color coded to show that each belongs to a different independent network. Symmetry code of sulfate: 1–x, y, 0.5–z,

Table S1. Hydrogen bonding parameters (Å, °) for SO_4^{2-} binding by the urea groups in **1**.

D–H···A	H···A	D···A	∠D–H···A
N2–H2B···O3	2.11	2.916(2)	156.8
N3–H3B···O3	2.15	2.941(3)	153.6
N4–H4A···O6 [a]	2.14	2.906(7)	148.2
N4–H4A···O4	2.17	3.002(7)	164.2
N5–H5B···O5	2.12	2.869(4)	145.4
N5–H5B···O4 [a]	2.14	2.962(5)	159.7
N2–H2B···O5	2.56	3.221(4)	134.3

[a] symmetry code: x–0.5, y–0.5, 0.5–z.

Table S2. Hydrogen bonding parameters (Å, °) in **2**.

D–H···A	H···A	D···A	∠D–H···A
O7–H7D···O8	1.82(3)	2.651(3)	175(4)
O7–H7C···O2	1.94(3)	2.741(3)	169(4)
O8–H8D···O1	1.87(3)	2.760(3)	174(4)

O8−H8C···O4	1.97(3)	2.884(10)	163(4)
O8−H8C···O6	1.80(3)	2.734(12)	175(4)
N2−H2B···O3	2.09	2.908(3)	157.9
N3−H3B···O3	2.19	2.977(3)	152.3
N4−H4A···O4	2.19	3.036(10)	168.0
N4−H4A···O6	2.11	2.890(11)	150.8
N5−H5B···O5	2.10	2.872(5)	148.3

Table S3. Hydrogen bonding parameters (Å, °) in **3**.

D−H···A	H···A	D···A	∠D−H···A
O1−H1C···O7	1.81(2)	2.646(4)	174.6
O7−H701···O5	2.11(5)	2.926(7)	161.4
O7−H701···O5A	1.89(4)	2.733(12)	173.4
N2−H2···O4	2.31	3.071(4)	147.7
N2−H2···O6	2.32	3.114(7)	153.8
N3−H3···O4	2.11	2.905(5)	153.2
N4−H4···O5	2.08	2.929(7)	170.2
N4−H4···O5A	2.06	2.893(12)	162.9
N5−H5···O5	2.34	3.084(8)	144.7
N5−H5···O6	2.10	2.937(7)	163.5

Anion competitive crystallization experiments

A solution of 68.4 mg (0.2 mmol) of L in 10 mL of MeOH was added to an aqueous solution (5 mL) containing $ZnSO_4$ (0.1 mmol), NaCl (0.2 mmol), $NaNO_3$ (0.2 mmol), and $NaClO_4$ (0.2 mmol). The resulting solution was stirred at room temperature and allowed to evaporate slowly. After one week, colorless crystals were collected and washed with water, ethanol and ether. The FT-IR spectrum and powder X-ray diffraction pattern of the product were identical with those of **1**.

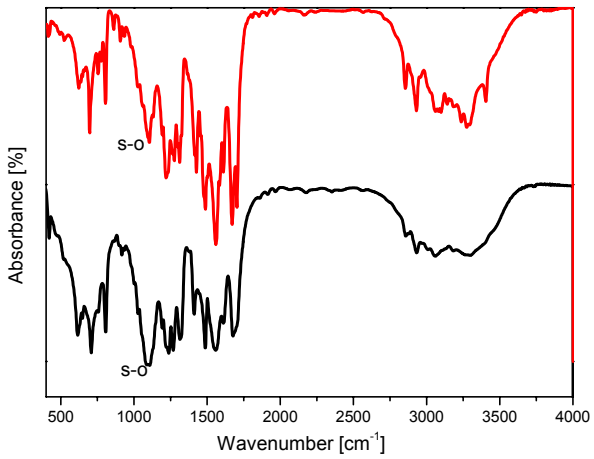

Figure S12. FT-IR spectra of **1** (black) and the solid crystallized in the presence of the anionic mixture (red).

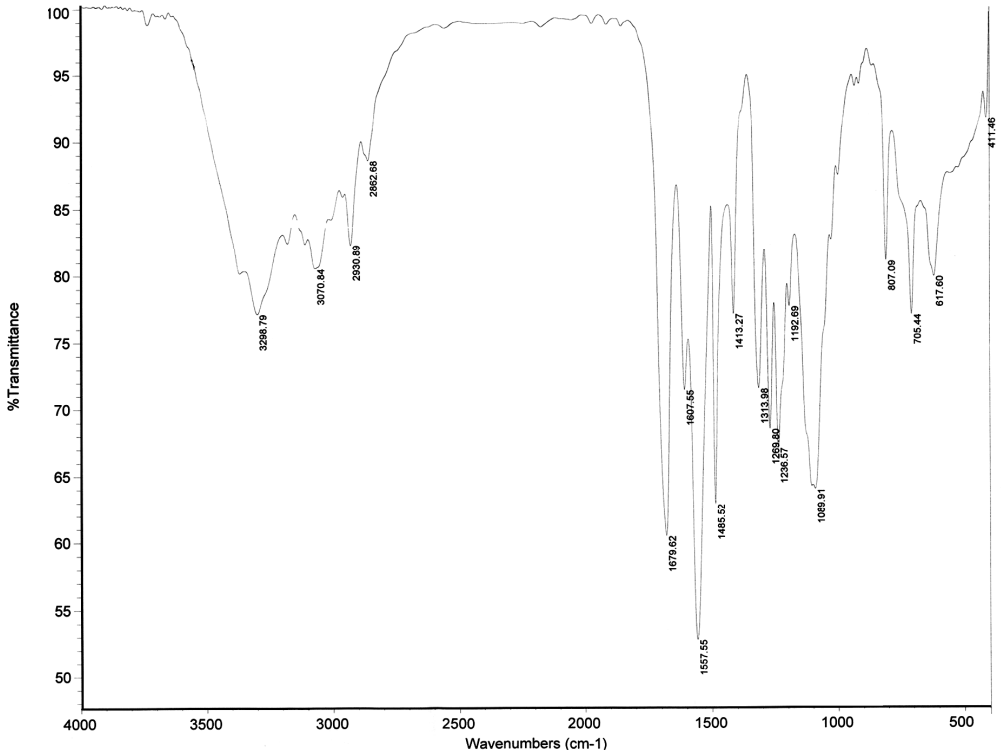

Figure S13. FT-IR spectrum of **2**.

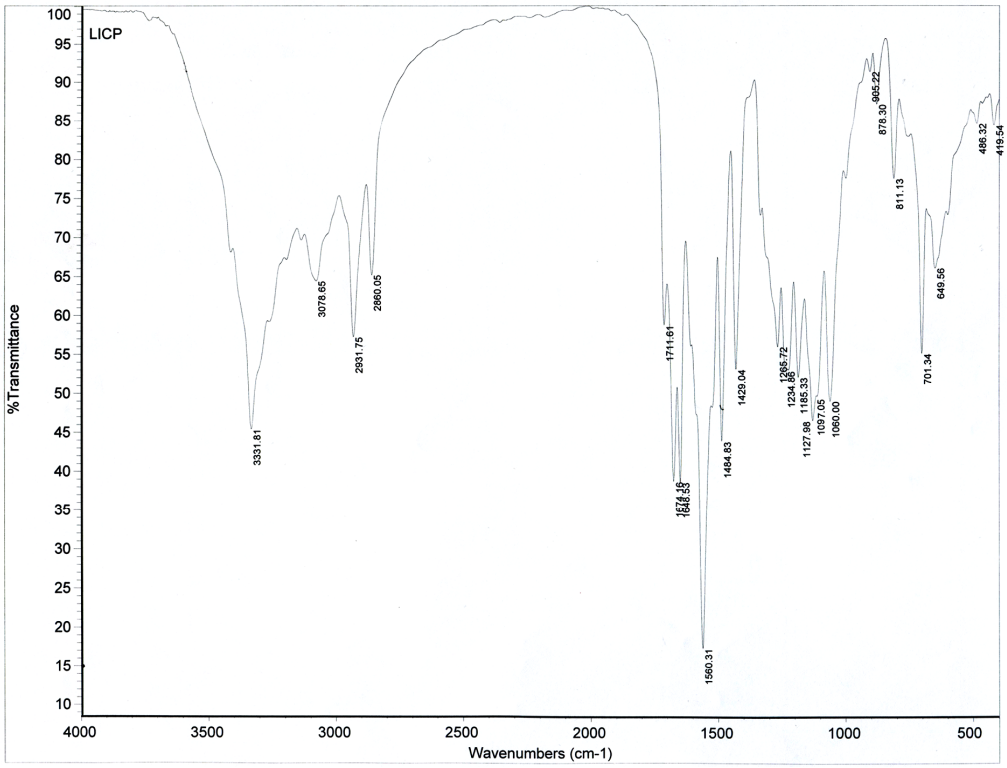

Figure S14. FT-IR spectrum of **3**.