Electronic Supplementary Information (ESI)

Sulfate encapsulation in a metal-assisted capsule based on a mono-pyridylurea ligand

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Experimental

General

Elemental analyses were performed on a VarioEL instrument from Elementar Analysensysteme GmbH. IR spectra were measured using a Nicolet AVATAR 360 FT-IR spectrometer as KBr disks. X-ray powder diffraction data were recorded with an X'Pert PRO instrument. TGA/DSC measurements were carried out between 25 and 900 °C in a nitrogen atmosphere using a Pyris diamond instrument (Perkin Elmer) with a heating rate of 10 °C/min. Fluorescence spectra were measured at room temperature (Hitachi F-7000 spectrophotometer).

Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for the data. The structure was solved by the PATT method for the heavy atoms and TEXP method for other atoms using the SHELXS-97 program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the SHELXL-97 program, and hydrogen atoms were included in idealized positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached.

Crystal data for **1** (low temperature dataset): $C_{228}H_{240}Cu_4N_{48}O_{40}S_4$, Fw = 4675.08, green block, trigonal, space group $R-3$, a = 37.5437(15) Å, b = 37.5437(15) Å, c = 13.5170(11) Å, V = 16500.0(16) Å^3, Z = 3, D_{calc} = 1.411 g cm^{-3}, $F(000)$ = 7332, μ = 0.507 mm^{-1}, T = 150(2) K, 39,685 reflections collected, 7196 independent (R_{int} = 0.0280), R_1 = 0.0416, wR_2 = 0.0658 [$I > 2\sigma(I)$].

Synthesis

The ligand N-(1-naphthyl)-N'-(3-pyridyl)urea (**L**) was prepared as reported previously. Synthesis of **1**: **L** (26.3 mg, 0.10 mmol) and $CuSO_4 \cdot 5H_2O$ (8.2 mg, 0.033 mmol) were dissolved in 5 mL DMF and the

mixture was allowed to evaporate slowly for several weeks to give green crystals (23.4 mg, 60%); M.p.: 141 °C. Anal. Calc. for $C_{228}H_{240}Cu_4N_{48}O_{40}S_4$ (4675.08): C, 58.58; H, 5.17; N, 14.38; Found: C, 58.52; H, 5.29; N, 14.58. IR (KBr, ν/cm^{-1}): 3257 (N−H), 3218 (N−H), 3048, 1701 (C=O), 1653 (C=O), 1543, 1468, 1251, 1209, 1125 (S−O), 1103 (S−O), 793.

Table S1. Hydrogen bond parameters (Å, °) for SO_4^{2-} binding in **1**.

N−H···O	H···O	N···O	∠N−H···O
[Cu^1]			
N2−H2A···O5	2.36	3.149(3)	153
N3−H3A···O6	2.00	2.857(4)	172
N2^i−H2A···O6	2.45	3.120(5)	136
N2^i−H2A···O6^{ii}	2.32	3.171(5)	169
N3^i−H3A···O6	2.53	3.162(5)	131
[Cu^2]			
N5−H5A···O7	2.10	2.885(4)	152
N5^{iii}−H5A···O9	2.19	3.038(4)	169
N6−H6A···O10	2.05	2.896(4)	168
N6^{iii}−H6A···O8	2.28	3.027(4)	146
N5^{iii}−H5A···O8	2.58	3.257(4)	137
C34−H34C···O1	2.45	3.120(3)	127
C37−H37C···O1	2.17	3.047(4)	152

Symmetry codes: i) −x, −y, 1−z; ii) x−y, x, 1−z; iii) −x+1/3, −y+2/3, −z+5/3.

Table S2. The parameters (Å, °) of the π−π stacking interactions in **1**.

dihedral angle (°)	centroid −centroid separation (Å)	vertical displacements between ring centroids (Å)
13.5	3.95	0.66/1.56

Table S3. The parameters (Å, °) of the C−H···π interactions in **1**.

C−H···π	D(H···Cg*)	D(C···Cg)	D(H···plane)	∠C−H···Cg
C5−H5···π$_{py}$	2.85	3.44	2.39	122.2
C(35)−H(35A)···π$_{nap}$	3.15	3.59	2.81	109.7

* Cg represents the centroid of the aryl ring.

Table S4.   Selected bond lengths (Å) and angles (°) for **1**.

Cu1−N1	2.043(2)	Cu2−N4	2.025(2)
Cu2−O3	2.333(2)	Cu2−O4	2.610(1)
N1−Cu1−N1'	97.20(9)	N1−Cu1−N1"	82.80(9)
N1−Cu1−N1'''	180.00(7)	N4−Cu2−N4'	180.0
O3−Cu2−O4	103.28(6)	O3−Cu2−O3'	180.0
O4−Cu2−O4'	180.0		
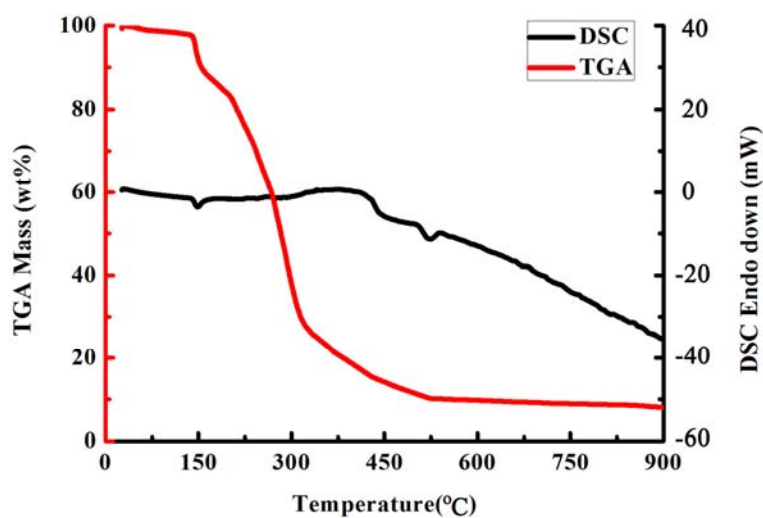
Fig. S1. TGA (red) and DSC (black) curves of **1** at a heating rate of 10 °C/min.
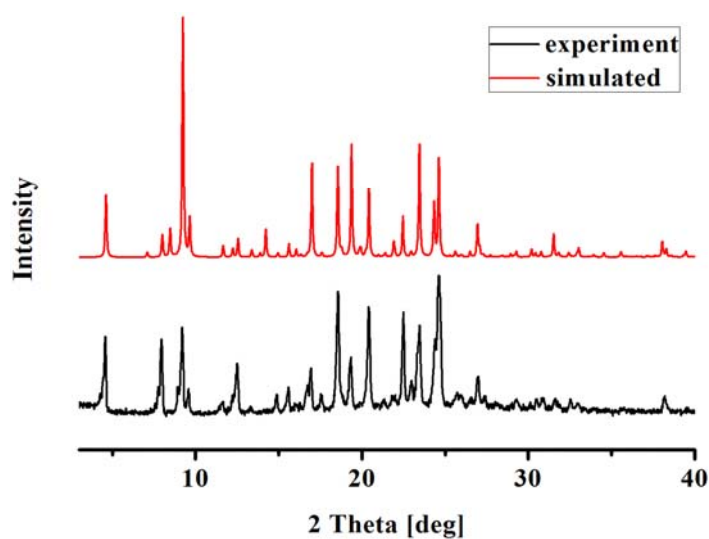
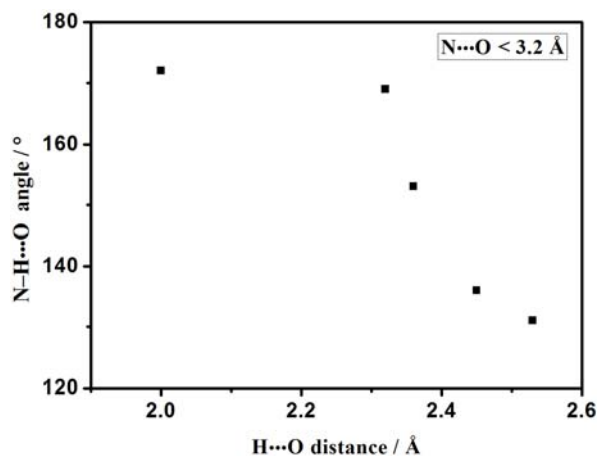**Fig. S2.** PXRD patterns for complex **1** (black: experimental; red: simulated).

Fig. S3. The scatterplot of N−H···O angle vs. H···O distance of the hydrogen bonds in **[Cu^1]** moiety of **1**.
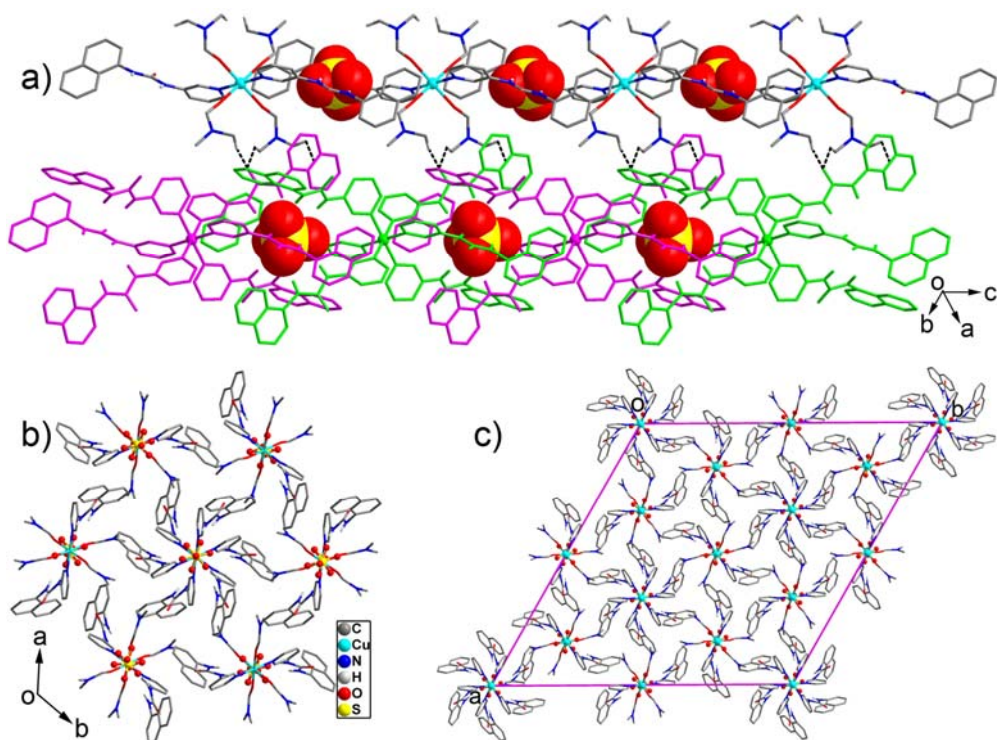

Fig. S4. Packing diagram of **1**. (a) Chain structure along the *c* axis assembled from **[Cu^1]** and **[Cu^2]** units through C−H···O weak hydrogen bonds and C−H···π interaction (dashed lines). (b) A "pinwheel" structure viewed from the *c* axis consisting of one **[Cu^1]** chain and six **[Cu^2]** chains around the **[Cu^1]** chain. (c) Schematic representation of the extended structure of **1** viewed from the *c* axis.
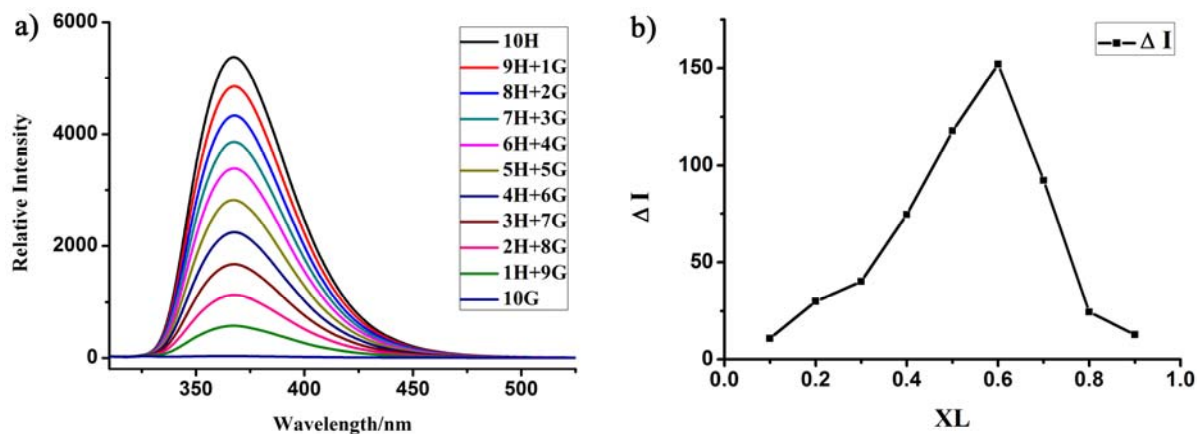
Solution binding studies.

Fig. S5. a) Fluorescence spectra of complexation of $[\mathbf{L}Cu]^{2+}$ with SO_4^{2-} in DMF at room temperature, H = $[\mathbf{L}Cu]^{2+}$ (in the form of equal molar $\mathbf{L}$ and $Cu(ClO_4)_2$), G = SO_4^{2-} (in the form of $(TBA)_2SO_4$), [10H] = [10G] = $7.5*10^{-6}$ M. b) Job's plot of molar fraction *XL* of $[\mathbf{L}Cu]^{2+}$ versus the fluorescence intensity change (*ΔI*) at 367 nm, *XL* is the molar fraction of $[\mathbf{L}Cu]^{2+}$.
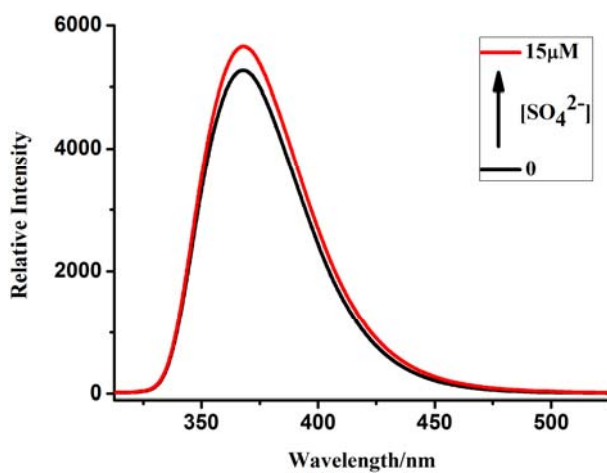

Fig. S6. The change in the emission spectra of $[\mathbf{L}Cu]^{2+}$ upon titration with SO_4^{2-} in DMF at room temperature. H = $[\mathbf{L}Cu]^{2+}$ (in the form of equal molar $\mathbf{L}$ and $Cu(ClO_4)_2$), G = SO_4^{2-} (in the form of $(TBA)_2SO_4$), [H] = $7.5*10^{-6}$ M, [G] = 0 to 15 μM.