

Supporting Information

A New Type of Polyhedron-based Metal-Organic Frameworks with Interpenetrating Cationic and Anionic Nets Demonstrating Ion Exchange, Adsorption and Luminescent Properties

Zhen-Jie Zhang, Wei Shi, Zheng Niu, Huan-Huan Li, Bin Zhao,
Peng Cheng*, Dai-Zheng Liao, and Shi-Ping Yan*

Experiment

Materials and Methods: All reagents were commercially available and were used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. IR spectra were recorded in the range of 400-4000 cm^{-1} on a Bruker TENOR 27 spectrophotometer using a KBr pellet. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu $K\alpha$ radiation. The fluorescent spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. Thermal analyses (N_2 atmosphere, heating rate of 1.5 $^\circ\text{C}/\text{min}$) were carried out in a Labsys NETZSCH TG 209 Setaram apparatus. Atomic Sorption was performed by Polarized Zeeman Atomic Absorption Spectrophotometer (HITACHI-180-80). Energy dispersive X-ray spectroscopy (EDS) was measured on a JEOL-7500F Microscope equipped with an energy-dispersive spectroscopy (EDS) instrument. ICP was measured by ICP-9000(N+M) (USA Thermo Jarrell-Ash Corp).

Synthesis of N-phenyl-N'-phenyl bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarbox-diimide tetracarboxylic acid (L1): A mixture of 20 mmol (3.62 g) of

5-Aminoisophthalic acid and 10 mmol (2.48 g) bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride was added to 100 mL acetic acid. Then the solution was heated to reflux for 12 h. White power was filtrated and washed twice with water. **L1** was used without further purification. IR (KBr) for **L1**: 3460(*s, b*), 1719(*s*), 1609(*w*), 1459(*m*), 1383(*s*), 1308(*w*), 1274(*m*), 1190(*s*), 1118(*w*), 1083(*w*), 1048(*w*), 948(*w*), 793(*m*), 758(*m*), 682(*m*), 622(*w*), 527(*w*), 497(*w*), 442(*w*) cm^{-1} .

Synthesis of N-phenyl-N'-phenyl bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarbox-diimide dicarboxylic acid (L2): A mixture of 20 mmol (2.74 g) of 3-Aminobenzoic acid and 10 mmol (2.48 g) bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride was added in 100 mL acetic acid. Then, the solution was heated to reflux for 12 h. White power was filtrated and washed twice with water. **L2** was used without further purification. IR (KBr) for **L2**: 3470(*s, b*), 2980(*s*), 2676(*s*), 2558(*s*), 1784(*m*), 1717(*s*), 1594(*m*), 1499(*m*), 1456(*s*), 1419(*m*), 1378(*s*), 1308(*s*), 1238(*w*), 1188(*s*), 1083(*m*), 937(*m*), 795(*s*), 757(*s*), 682(*s*), 627(*w*), 592(*w*), 507(*w*), 472(*w*), 422(*w*) cm^{-1} .

Synthesis of 1: A mixture of L1 (0.054 g, 0.1 mmol) and ZnCl_2 (0.044 g, 0.33 mmol) was added into a mixed solution of 5 mL DMF, 6 mL methanol and 0.5 mL water, placed into a 25 mL Teflon-lined Parr, and incubated at room temperature for 1 months. The block-like colorless crystals of **1** were obtained in a 30% yield (based on Zn). Formula, $\text{C}_{3792}\text{H}_{5232}\text{N}_{560}\text{Zn}_{192}\text{O}_{2096}$. Element analysis (%) found (calcd.), C 43.10 (43.47), H 5.23 (5.03), and N 7.55 (7.48). IR (KBr) for **1**: 3478(*s, b*), 2928(*w*), 2359(*s*), 1715(*s*), 1654(*s*), 1574(*m*), 1594(*m*), 1379(*s*), 1456(*s*), 1233(*m*), 1198(*m*), 1103(*w*), 1008(*w*), 918(*w*), 848(*w*), 775(*m*), 723(*w*), 687(*m*), 618(*w*), 527(*w*), 457(*w*) cm^{-1} .

Synthesis of 2: A mixture of L2 (0.049 g, 0.1 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.042 g, 0.25 mmol) was added into a mixed solution of 5 mL DMA, placed a 25 mL Teflon-lined

Parr, heated to 80 °C for 3 days, and then cooled to room temperature for 2 days. The prism-like blue crystals of **2** were obtained in a 50% yield (based on Cu). Formula, C₁₄₄H₁₇₀N₁₈Cu₄O₅₀. Element analysis (%) found (calcd.), C 53.70 (53.93), H 5.14 (5.34), and N 8.09 (7.86). IR (KBr) for **2**: 3462(*s, b*), 2938(*s*), 1775(*m*), 1714(*s*), 1606(*s*), 1510(*m*), 1447(*m*), 1400(*s*), 1196(*s*), 1021(*m*), 763(*s*), 692(*w*), 600(*w*) cm⁻¹.

X-ray Structure Determination: All crystallographic data were collected with a Supernova Single Crystal Diffractometer, which was equipped with graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods with the SHELXTL-97 program and refined by full-matrix least-squares techniques against F^2 with the SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and refined isotropically. The contribution of disordered solvent molecules was treated as a diffuse using the Squeeze procedure in Platon. The resulting new HKL4 files were used to further refine the structures.

Crystal data for 1: $M_r = 71922.72$, cubic, $Fm-3c$, $a = 63.0890(3)$ Å, $V = 251108(2)$ Å³, $Z = 2$, $D_c = 0.951$ g/cm³, $\mu = 0.961$ mm⁻¹, GOF = 1.032, $R_{int} = 0.0310$, final R indicates ($I > 2\sigma(I)$): $R_1 = 0.0582$, $wR_2 = 0.2119$. CCDC: 752311. For **2**, $M_r = 2403.62$, triclinic, $P2_1/c$, $a = 19.9699(19)$ Å, $b = 17.0730(15)$ Å, $c = 30.915(2)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 126.461(4)^\circ$, $V = 8477.2(12)$ Å³, $Z = 2$, $D_c = 0.942$ g/cm³, $\mu = 0.553$ mm⁻¹, GOF = 0.966, $R_{int} = 0.0324$, final R indicates ($I > 2\sigma(I)$): $R_1 = 0.0688$, $wR_2 = 0.1991$. CCDC: 752313. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax 44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk).

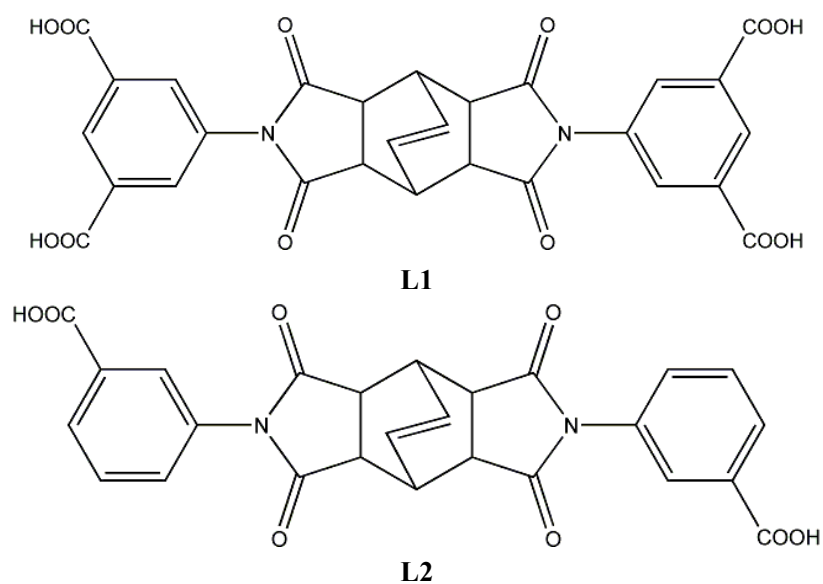
Adsorption and desorption of I₂ experiment: In the adsorption experimental process, the crystals of **1** were initially immersed in 5 mL methanol solution of I₂ (0.1 M/L) in a small sealed flask at room temperature. During the process, the methanol

solution of I₂ was refreshed every 6 h. After 12 and 24 h, respectively, the products were filtered and washed with sufficient methanol for four times. The products of I₂-**1** were finally immersed into fresh methanol for convenient observation and removing surface absorption.

In the desorption experimental process, the dark brown crystals of **2.65I₂-1** were immersed in 5 mL fresh methanol solution in a small sealed flask at room temperature. During the process, the methanol solution was refreshed every 6 h. After 24 and 48 h respectively, the products were filtered and washed with sufficient methanol four times. The products of I₂-**1** were immersed into fresh methanol for convenient observation and removing surface absorption.

BET research: The BET researches of **1** and **Cu-1** were performed on a Quantachrome IQ2 automatic volumetric instrument. The surface area of **1** can not be obtained because the framework of **1** may collapse during the guest-removal process. Fortunately, the surface area (BET) of **Cu-1** was obtained as 373 m²g⁻¹ and the N₂ adsorption isotherm for **Cu-1** at 77 K is shown in Figure S12. This result is significantly lower than the surface area theoretically obtainable, however the TGA and I₂-loaded experiments indicate that the interior is accessible to guest molecules.

Supporting Scheme, Figures and Tables



Scheme S1. Structures of ditopic ligands.

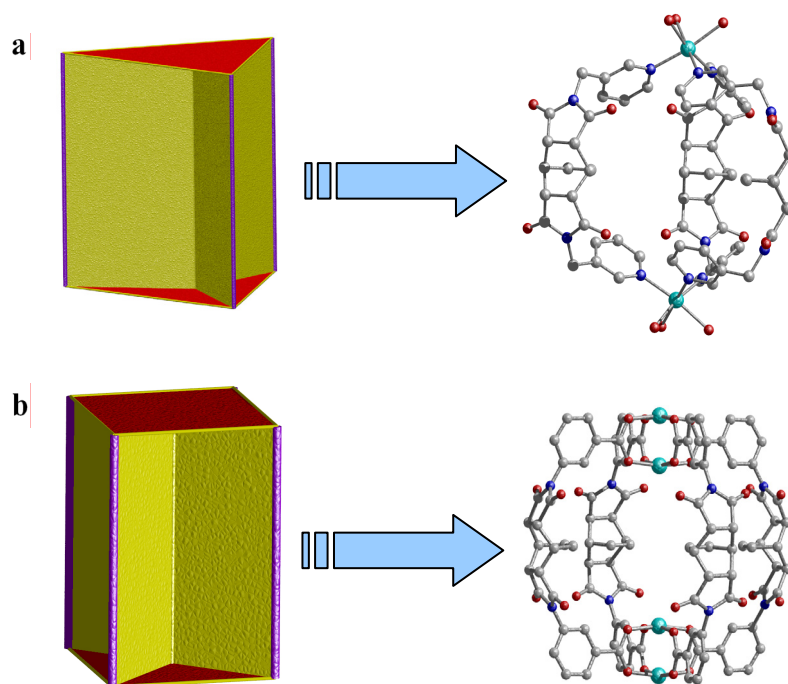


Figure S1. Two types of MOCs, trigonal(a) and tetragonal(b) prisms of regular faces (square or triangle) in red, pillars in purple and open windows in yellow.

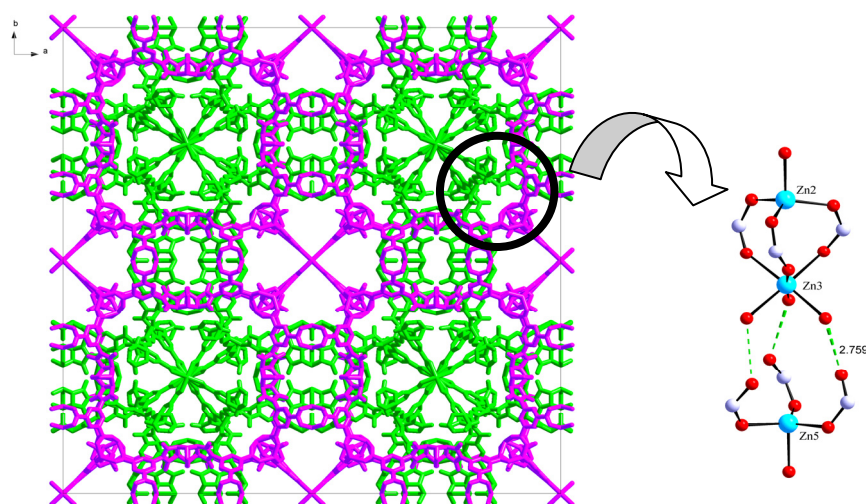


Figure S2. (Left) Composition of one unit cell of **1**; (Right) two kinds of triangle paddlewheels linked with hydrogen-bonding interactions ($[\text{Zn}_2(\text{CO}_2)_3]^+$ for MOP-A⁺ and $[\text{Zn}(\text{CO}_2)_3]$ for MOP-B⁻). The overall structure is neutral and sustained via the hydrogen-bonding interactions (2.759 Å) as well as electrostatic interactions between $[\text{Zn}_2(\text{CO}_2)_3]^+$ and $[\text{Zn}(\text{CO}_2)_3]$.

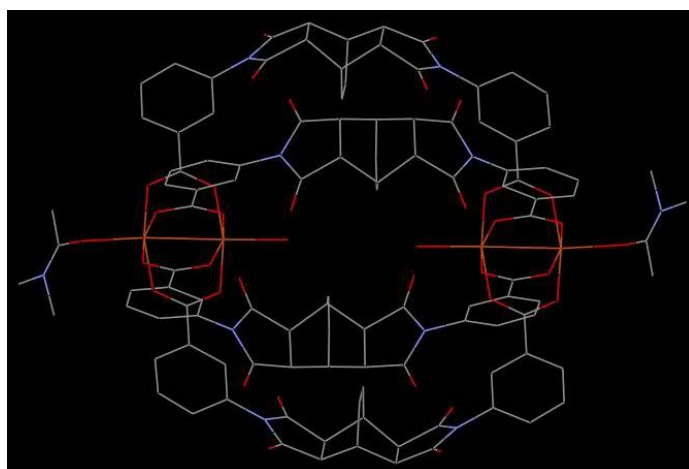


Figure S3. Crystal structure of **2**.

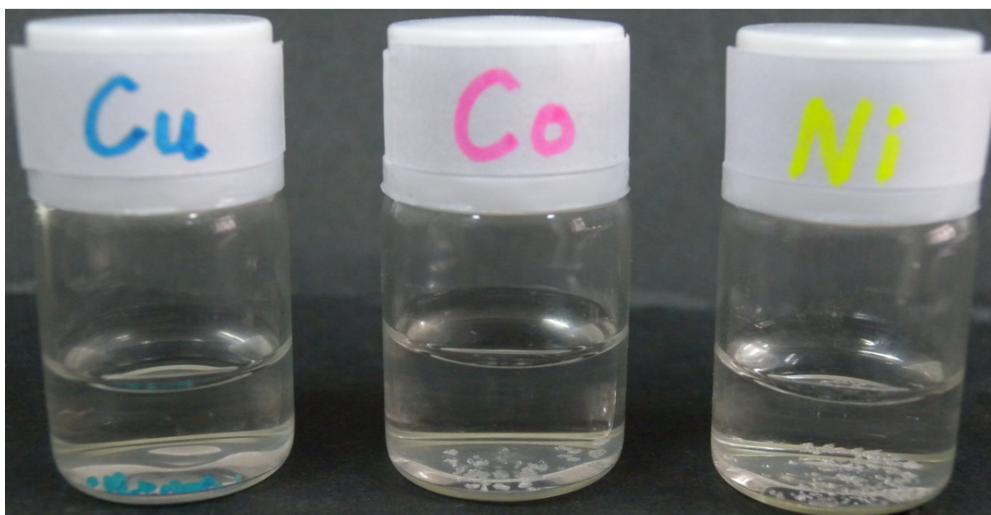


Figure S4. Crystal pictures of Cu^{2+} -exchanged, Co^{2+} -exchanged and Ni^{2+} -exchanged products. Initially, the crystals of **1** were immersed in methanol solutions of CuCl_2 , CoCl_2 and NiCl_2 (0.5 mmol/mL), respectively. During 1 week, the methanol solutions of metal ions were refreshed four times. Then the immersed crystals were filtered and washed with sufficient methanol. **The final ion-exchanged crystals were immersed in fresh methanol for convenient observation and removing surface absorption.**

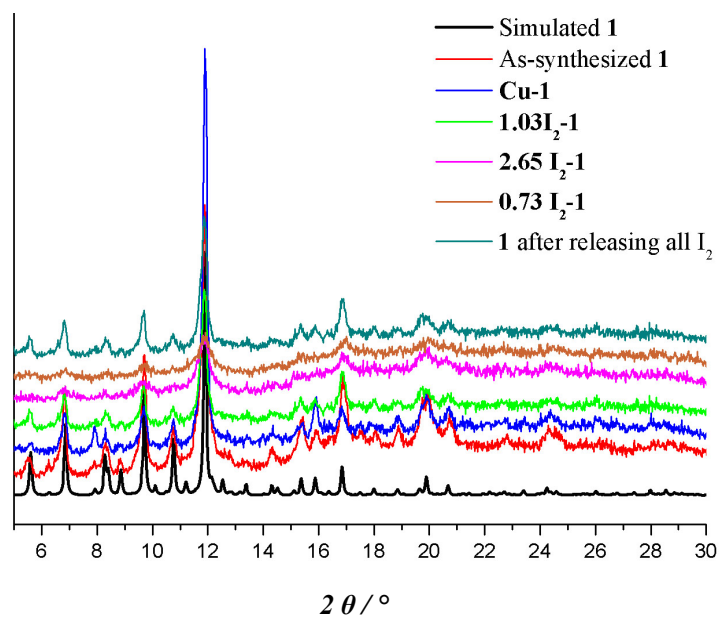


Figure S5. X-Ray powder diffraction patterns of **1** with I₂, Cu-1, as-synthesized and simulated samples.

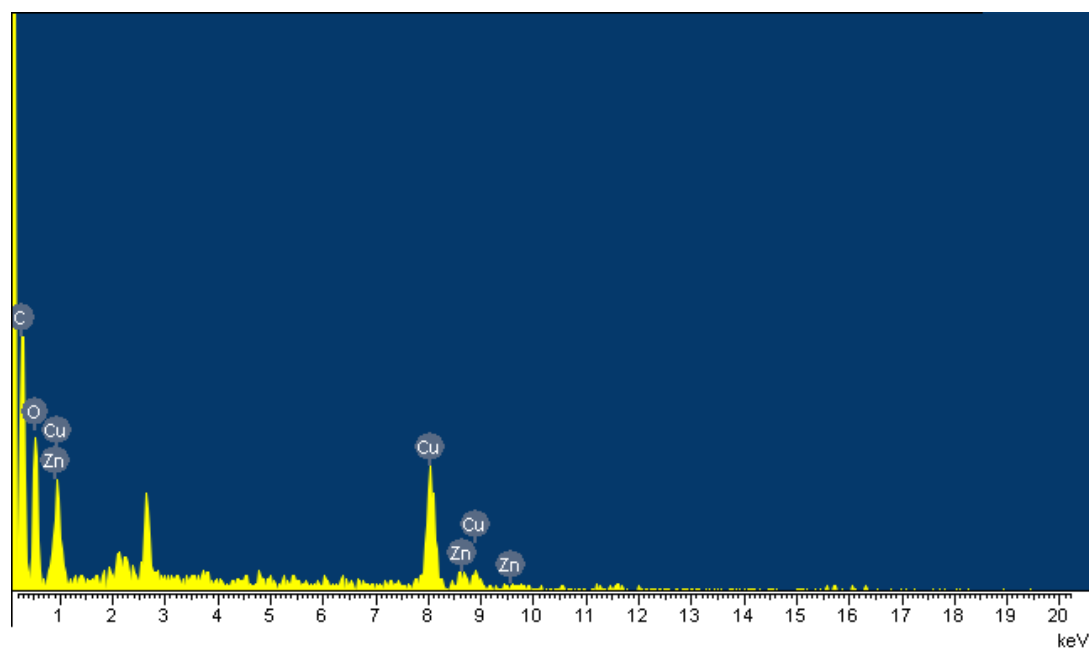


Figure S6. Energy dispersive X-ray spectroscopy. The Peak of 2.641 keV of Cl⁻ has been omitted for calculation.

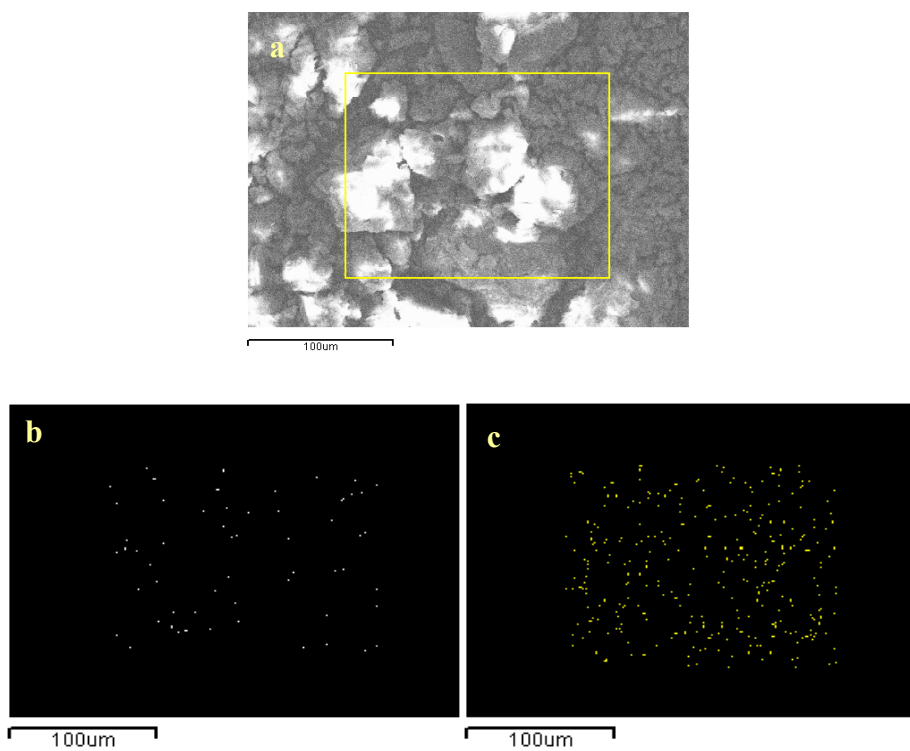


Figure S7. (a) FT-SEM micrograph of Cu (II)-exchanged product; (b) EDS maps for Zn; and (c) EDS maps for Cu.

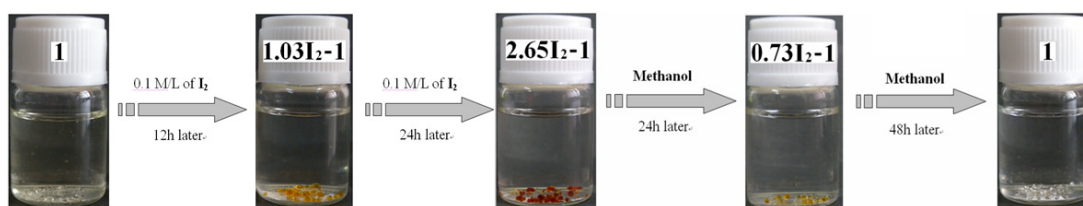


Figure S8. Adsorption and desorption photographs of **1** with I₂.

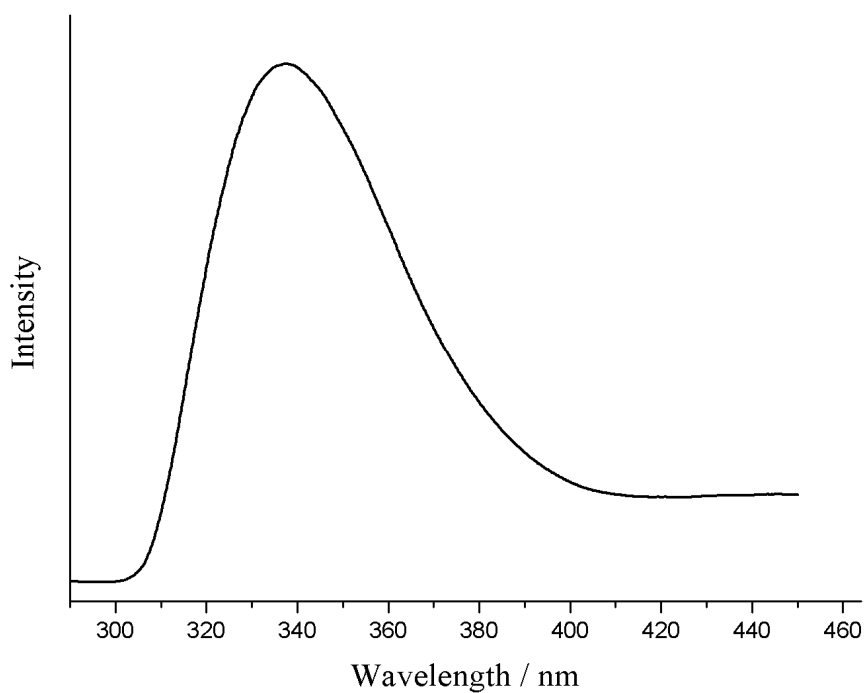


Figure S9. Solid-state fluorescence of ligand **L1** excited at 280 nm.

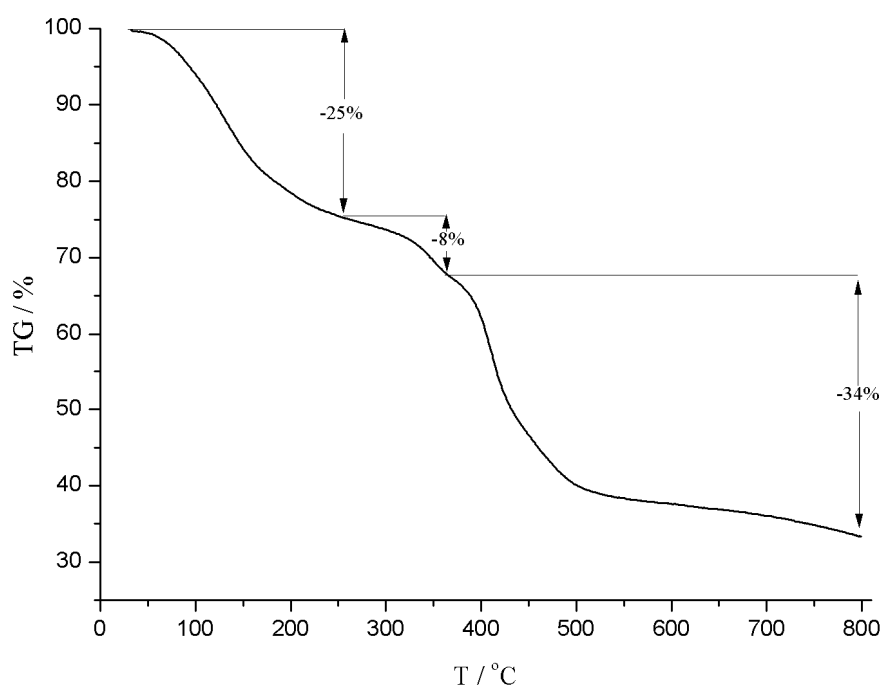


Figure S10. TGA curve for **1**. The sample was heated to 800 °C at a heating rate of 1.5 °C/min.

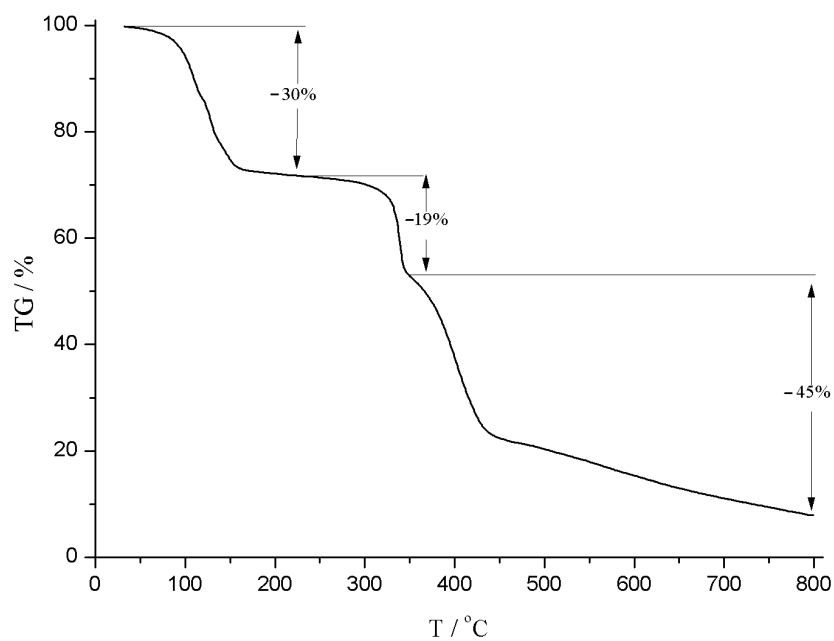


Figure S11. TGA curve for **2**. The sample was heated to 800 °C at a heating rate of 1.5 °C/min.

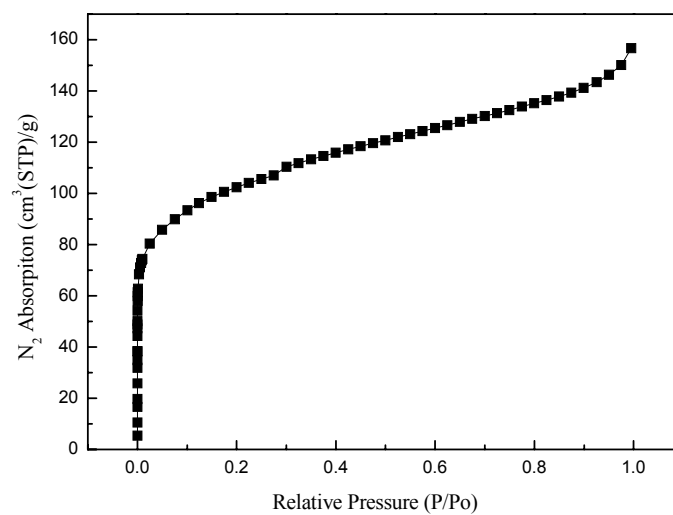


Figure S12. N₂ adsorption isotherm for **Cu-1** at 77 K.

Table S1. Metal ion analysis for compound Cu^{II}-exchanged product.

sample	ICP	EDS	Atomic Sorption
Cu ^{II} -exchanged product	Cu 86.38 % Zn 13.62 %	Cu 86.14 % Zn 13.86 %	Cu 87.52% Zn 12.48 %
Cu ^{II} -exchanged solution ^a	Cu 84.73 % Zn 78.41 %		
Co ^{II} -exchanged product	no Co	no Co	no Co
Ni ^{II} -exchanged product	no Ni	no Ni	no Ni

^a The content of DMF in this solution was measured on Shimadzu GC-9A instrument and ~3.36% DMF was detected.

Table S2. ICP-MS analysis for the products absorbing and releasing I₂.

ICP-MS	1.03 I ₂ -1	2.65 I ₂ -1	0.73I ₂ -1	1-After releasing all I ₂
Concentration of I (mg / L)	0.035	0.124	0.022	no I monitored
Concentration of Zn (mg / L)	3.35	4.65	2.96	