Supporting Information

Enantiomerism, Diastereomerism and Thermochromism in two Cu₇I₄ Cluster-Based Coordination Polymers

Wei-Ming Liao,^{‡a} Xiang-Nan Li,^{‡b} Qi Zeng,^a Yuan-Hui Zhong,^a Ye-Gao

Yin^b and Jun He*a

^aSchool of Chemical Engineering and Light Industry, Guangdong University of

Technology, Guangzhou 510006, China

^bDepartment of Chemistry, Shantou University, Shantou 515063, China

Contents

Experimental section

Figure S1 The imitated and measured powder X-ray diffraction spectra of 1 and 2.

Figure S2 The Cu₇I₄ clusters and PTA ligands in **1***P* and **1***M*, respectively.

Figure S3 Circular dichromic spectra of 1M (a), randomly selected 25 crystals (b) and

six bulk samples (c) of 1 obtained from solvothermal synthesis.

Figure S4 Two kinds of enantiomeric copper iodide clusters present in 2.

Figure S5 The FT-IR spectra of NH₃ molecules and MOF 2.

Figure S6 A $(4^3)(4^{12} \cdot 6^{15} \cdot 8^9)$ net as topological equivalent of **2**.

Figure S7 The TGA curves of **1** and **2**.

Figure S8 Relative emission intensity ratio of I_{HE} : I_{LE} in **2** at various temperatures.

Table S1 A summary of structure determinations of 3 randomly selected crystals of 1.

Table S2 Some selected bond length for 1 and 2.

Table S3 Lifetimes (τ) and corresponding fractional contributions (%) of the solidstate sample excited at 380 nm for HE and LE emission at various temperatures.

Experimental section

Materials and methods

All chemicals and solvents were purchased from commercial sources and used without further purification. HPTA ligand was prepared from a modified method of the references.^{1, 2} Single-crystal X-ray diffraction (SCXRD) data was collected on a Bruker D8 Venture X-ray diffractometer equipped with Cu-K α radiation ($\lambda = 1.54178$ Å). The powder X-ray diffraction (PXRD) data was recorded on a Bruker D8 Advance diffractometer at 40 kV, 40 mA with a Cu-target tube and a graphite monochromator. FT-IR spectra were obtained by using a Nicolet Avatar 360 spectrophotometer. Thermogravimetric analyses (TGA) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (TA-Q600) with a heating rate of 5 °C/min. Excitation and emission spectra were obtained from a FluoroMax-4 spectrometer. Lifetime data were achieved from a Horiba Fluorolog-3 fluorescence spectrometer (equipped with an integrating sphere).

Synthesis of 5-(3'-Pyridyl) tetrazole (HPTA): 26 g (0.25 mol) of 3-Cyanopyridine, 20 g (0.33 mol) of glacial acetic acid and 22 g (0.33 mol) of sodium azide were added into 100 ml of *n*-butyl alcohol and heated under reflux for 4 days. Then 5 g of sodium azide and 10g of glacial acetic acid were added and heating for 2 days. The reaction mixture was diluted with about 300 ml of water and distilled until the *n*-butyl alcohol was removed. The clear aqueous solution was carefully acidified with concentrated hydrochloric acid until the precipitation of the tetrazole was completely achieved. The product was obtained as colorless crystalline solid from water, yield 33.3 g, 91%.

Synthesis of { $[Cu_7I_4(C_6N_5H_4)_3] \cdot 0.5CH_3CN$ }_n (1): A mixture of 0.30 mmol copper(I) iodide, 0.10 mmol 3-HPTA and 5 ml CH₃CN was stirred for 10 min in air and then transferred and sealed in a 15 mL Teflon-lined stainless steel reactor. The reactor was heated in an oven at 160°C for 72 h, and then cooled to room temperature at a rate of 5°C·h⁻¹. Yellowish columnar-like crystals were collected and dried in air (Yield 55% based on copper(I) salts). Elemental analysis (%): calcd for C₁₉H_{13.5}Cu₇I₄N_{15.5}: C, 16.15; H, 0.96; N, 15.37. Found: C, 16.01; H, 1.05; N, 15.48. IR (KBr, cm⁻¹):

3446(s), 2920(w), 2855(w), 1622(m), 1559(w), 1540(w), 1510(w), 1457(m), 1422(s), 1383(w), 1193(w), 1155(w), 1122(w), 1051(w), 1016(w), 820(m), 746(m), 697(s).

Synthesis of {[$Cu_7I_4(C_6N_5H_4)_3(NH_3)$]·9 H_2O }_{*n*} (2): MOF 2 was prepared using the method similar to that of 1 except that CH₃CN (5ml) was replaced by n-butyl alcohol: ammonia water(v:v=5:1). Yellowish block-like crystals were collected and dried in air (Yield 66% based on copper(I) salts). Elemental analysis (%): calcd for C₁₈H₂₃Cu₇I₄N₁₆O₉: C, 13.77; H, 1.47; N, 14.28. Found: C, 13.86; H, 1.43; N, 14.21. IR (KBr pellet, cm⁻¹): 3438(s), 3340(s), 3208(w), 3063(w), 2957(m), 2924(w), 2863(w), 1610(m), 1583(w), 1459(s), 1420(s), 1363(w), 1191(m), 1151(s), 1061(w), 1022(m), 946(w), 816(s), 746(m), 695(s), 648(m).

Crystal data collection and refinement

The single crystals were picked and mounted on the top of the glass fiber with paratone-N oil on the microscope. Single-crystal X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å) at T = 298 K or 100 K using SMART, with the data integrated using SAINT and corrected for absorption and other systematic errors using SADABS.³ The space group of **1** and **2** was assigned using XPREP and the structures were solved by direct method and refined by full-matrix leastsquares procedures on F^2 using SHELXL⁴ on the Olex 2 software package. H atoms attached to carbon and nitrogen atoms were positioned geometrically and constrained to ride on their parent atoms. SQUEEZE command has been used to deal with the disordered solvent molecules with PLATON⁵ program. The electron count of **1** was evaluated to be 4-10 from the refinement data of three crystals, indicative of 0.2-0.6 CH₃CN molecules. And the electron count of **2** was calculated to be 0.5 and 9 by elemental analysis, respectively.



Figure S1 The simulated (a) and experimental (b) powder X-ray diffraction spectra of 1 and 2.



Figure S2 The Cu₇I₄ clusters and PTA ligands (dihedral angle of two aromatic planes is 9.525°) in **1***P* and **1***M*, respectively.





Figure S3 (a) Circular dichromic spectra of 1M, (b) randomly selected 25 crystals and (c) six bulk samples of 1 obtained from solvothermal synthesis.



Figure S4 Two kinds of enantiomeric copper iodide clusters present in 2.



Figure S5 The FT-IR spectra of NH_3 molecules (This data is downloaded from the website of https://www.nist.gov.) and MOF **2**.



Figure S6 A $(4^3)(4^{12} \cdot 6^{15} \cdot 8^9)$ net as topological equivalent of **2**.



Figure S7 The TGA curves of 1 (a) and 2 (b).



Figure S8 Relative emission intensity ratio of I_{HE} : I_{LE} in **2** at various temperatures.

No.	<i>a=b</i> (Å)	<i>c</i> (Å)	α=β	γ	V	<i>R</i> 1	flack	absolute
			(°)	(°)	(Å ³)		parameter	configuration
1 <i>M</i> (293	14.8073(6)	21.8280(18)	90	120	4144.7(6)	0.0463	0.16(15)	1 <i>M</i> ^a
K)								
1 P (100	14.7057(7)	21.8415(19)	90	120	4090.6(5)	0.0498	0.28(9)	1 P ^a
K)								
1 P (293	14.8107(5)	21.9159(15)	90	120	4163.3(4)	0.0384	0.038(9)	1 <i>P</i>
K)								

Table S1 A summary of structure determinations of 3 randomly selected crystals of 1.

^a the main component of in the single crystal.

Table S2 Some selected bond length for 1 and 2.

		U			
1 P (293 K)					
Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Cu1	Cu3	2.8172(12)	Cu2	Cu3	3.2747(5)
1 <i>P</i> (100 K)					
Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Cul	Cu3	2.7567(14)	Cu2	Cu3	3.2741(8)
1 <i>M</i> (293 K)					
Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Cul	Cu3	2.7497(6)	Cu2	Cu3	3.4601(11)
1 <i>М</i> (100 К)					
Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Cul	Cu3	2.7067(10)	Cu2	Cu3	3.4584(10)

Table S3 Lifetimes (τ) and corresponding fractional contributions (%) of the solidstate sample excited at 380 nm for HE and LE emission at various temperatures.

For HE emission:								
Т	100 K	110 K	120 K	130 K	150 K	200 K	250 K	295 K
τ_1 (µs)	0.44	0.34	0.35	0.36	0.52	0.40	0.31	0.26
$\tau_2 (\mu s)$	3.9	5.5	5.0	4.6	3.0	3.3	4.0	4.0
For LE emission:								
Т	100 K	110 K	120 K	130 K	150 K	200 K	250 K	295 K
$\tau_1 (\mu s)$	0.37	0.37	0.36	0.33	0.32	0.40	0.20	0.38
$\tau_{2}\left(\mu s\right)$	4.0	4.1	4.1	4.0	3.8	3.3	4.4	3.4

Table S4 Crystal data and structure refinement parameters for **1***P* and **2**.

Compound	1 <i>P</i>	2
Chemical formula	$C_{18}H_{12}Cu_7I_4N_{15}$	$C_{18}H_{15}Cu_7I_4N_{16}$
CCDC number	1914082	1914083
Formula weight	1390.88	1407.84
Temperature (K)	293(2)	293(2)
Crystal system	Hexagonal	Trigonal
Space group	<i>P</i> 6 ₃ 22	<i>P</i> -3 <i>c</i> 1
<i>a</i> (Å)	14.8107(5)	14.7747(6)
<i>b</i> (Å)	14.8107(5)	14.7747(6)
<i>c</i> (Å)	21.9159(15)	21.6485(1)
α (deg)	90.00	90.00
β (deg)	90.00	90.00
γ (deg)	120.00	120.00
$V(Å^3)$	4163.3(3)	4092.6(3)
Ζ	4	4
ρ_{calcd} (g/cm ³)	2.219	2.285
Goodness of fit on F^2	1.088	1.086
$R_1^a[I \ge 2\sigma(I)]$	0.0384	0.0255
$wR_2^{b}[I \ge 2\sigma(I)]$	0.0841	0.0767
R_1^a [all data]	0.0463	0.0334
wR_2^b [all data]	0.0872	0.0790

 $\overline{{}^{a} R_{1} = \sum (||F_{0}| - |F_{c}||) / \sum |F_{0}|; {}^{b} wR_{2} = [\sum w(F_{0}^{2} - F_{c}^{2})^{2} / \sum w(F_{0}^{2})^{2}]^{1/2}}$

References

- J.-Q. Sha, J.-W. Sun, C. Wang, G.-M. Li, P.-F. Yan and M.-T. Li, *Cryst. Growth Des.*, 2012, 12, 2242-2250.
- 2. Y.-Z. Tang, G.-X. Wang, Q. Ye, R.-G. Xiong and R.-X. Yuan, *Cryst. Growth Des.*, 2007, 7, 2382-2386.
- 3. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3-10.
- 4. G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112-122.
- 5. A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7-13.