

Supplementary Material

**Reversible Single-Crystal to Single-Crystal Transformation
upon Anion Exchange Induced Cu^{2+} ...I⁻ Weak Interactions and
Modification of Structures and Properties**

Junhong Fu, Huijun Li, Yajuan Mu, Hongwei Hou*, Yaoting Fan

Department of Chemistry, Zhengzhou University, Henan 450052, P. R. China

E-mail: houhongw@zzu.edu.cn

Experimental Section

Materials and Methods

All chemicals were commercially available and used as purchased. Ligand =1,3,5-tris(triazol-1-ylmethyl)- 2,4,6-trimethylbenzene (TTTMB) was prepared according to the literature.^[1] IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the region of 400–4000 cm⁻¹. Elemental analyses (C, H and N) were carried out on a Flash EA 1112 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded using Cu K α 1 radiation on a Philips X'Pert PRO diffractometer. X-ray diffraction (XRF) was tested on Bruker S4 Pioneer. Variable-temperature magnetic susceptibilities were measured using a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms. The surface morphology of the thin films was observed by atomic force microscope (AFM), Veeco Digital Instruments, Nanoscope IIIId in tapping mode at a scan rate of 1.0 Hz with commercial silicon micro-cantiliver probe under ambient conditions (24 \pm 2 °C). Energy-dispersive X-ray spectrometry (EDS) was conducted on a Burker ISMNM 761 scanning electron microscope.

[1]. Du, J. L.; Hu, T. L.; Zhang, S. M.; Zeng, Y. F.; Bu, X. H. *CrystEngComm*, **2008**, *10*, 1866–1874

Synthesis of complex $\{[\text{Cu}_6(\text{TTTMB})_8(\text{OH})_4(\text{H}_2\text{O})_6] \cdot 8(\text{NO}_3) \cdot 34.5\text{H}_2\text{O}\}_n$ (**1**)

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.0216 g, 0.090 mmol), TTTMB (0.0216 g, 0.060 mmol), tris (2-carboxyethyl) isocyanurate (0.0204 g, 0.060 mmol) and H_2O (3 mL) were placed in a Teflon-lined autoclave, and the mixture was sealed and heated to 80 °C for 72 h. The reaction system was cooled to room temperature. Big blue block crystals of $\{[\text{Cu}_6(\text{TTTMB})_8(\text{OH})_4(\text{H}_2\text{O})_6] \cdot 8(\text{NO}_3) \cdot 34.5\text{H}_2\text{O}\}_n$ **1** were obtained. Yield: 85%. Anal. Calcd. For $\text{Cu}_6\text{C}_{144}\text{N}_{80}\text{O}_{68.5}\text{H}_{253}$: C, 37.72%, N, 24.45%, H, 5.56%. Found: C, 37.74%, N, 24.51%, H, 5.12%

Note: only four NO_3^- anions were found in the framework, the presence of the required other NO_3^- anions are determined by elemental analysis. Two oxygen atoms coordinate to Cu_2 , one of them is designated as OH^- in consideration of charge balance. Another possibility is the OH^- exists in the porous framework. [1, 2]

Synthesis of complex $\{[\text{Cu}_6(\text{TTTMB})_8\text{I}_3] \cdot 9\text{I} \cdot 26\text{H}_2\text{O}\}_n$ (**2**)

Complex **2** $\{[\text{Cu}_6(\text{TTTMB})_8\text{I}_3] \cdot 9\text{I} \cdot 26\text{H}_2\text{O}\}_n$ was obtained through suspending Complex **1** in KI aqueous solution for 5 h. The crystals color changes in sequence: blue, cyan, dark-blue. The yield is 100%. Anal. Calcd. For $\text{Cu}_6\text{I}_{12}\text{C}_{144}\text{N}_{72}\text{O}_{23}\text{H}_{45}$: C, 32.75%, N, 19.10%, H, 4.20%. Found: C, 33.05%, N, 18.95%, H, 4.08%.

Synthesis of complex $\{[\text{Cu}_6\text{L}_8(\text{OH})_4(\text{H}_2\text{O})_6] \cdot 8(\text{NO}_3) \cdot x\text{H}_2\text{O}\}_n$ (**1'**)

Complex **1'** was obtained by immersing **2** in saturated KNO_3 or NaNO_3 aqueous solution for five days. Anal. Calcd. For $\text{Cu}_6\text{C}_{144}\text{N}_{80}\text{O}_{68.5}\text{H}_{253}$: C, 37.72%, N, 24.45%, H, 5.56%. Found: C, 37.83%, N, 24.10%, H, 4.50%

Reference:

- [1]. Yang, G.; Raptis, R. G. *Chem. Comm.*, 2004, 2058.
- [2]. Goulding, H. V.; Hulse, S. E.; Clegg, W.; Harrington, R. W.; Playford, H. Y.; Walton, R. I.; Fogg, A. M. *J. Am. Chem. Soc.* 2010, **132**, 13618.

Crystal structure determination

Diffraction intensity data for single crystal of **1**, **2** and **1'** were collected at room temperature on a Oxford Diffraction equipped with graphite monochromated Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The structures were solved by the direct method and refined by the full-matrix least-squares method on F with anisotropic thermal parameters for all non-hydrogen atoms. [1, 2] Hydrogen atoms were located geometrically and refined isotropically. For **1**, **2** and **1'**, SQUEEZE was used to remove the contributions of disordered water molecules. See the CIF file for details.

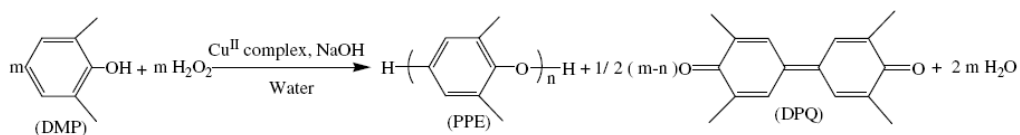
[1] Sheldrick, G. M. *SHELXS 97, Program for the Solution of Crystal Structures*; University of Göttingen: Germany, **1997**.

[2] Sheldrick, G. M. *SHELXL 97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, **1997**.

Experiment procedure for the catalytic oxidative coupling of DMP:

1 mmol DMP (122 mg) was dissolved in 3 mL water containing 1 mmol NaOH (40 mg) and 0.1 mmol sodium *n*-dodecyl sulfate (SDS) (29 mg). The 0.002 mmol complex with appropriate size was added to the above solution, and the mixture was stirred at 50 °C. Then, 10 μ L H₂O₂ (30% aqueous solution) was slowly added into the mixture using a microinjector every 15 min (2 times in all). After 8 h, the reaction was stopped and 1.17 g NaCl was added. Then the mixture was transferred into a separatory funnel, the organic materials were extracted by CHCl₃ for 3 times. The combined organic extracts were dried by anhydrous MgSO₄ and the filtrate was evaporated in vacuo. The products were separated by preparative TLC performed on dry silica gel plates with ethylether–petroleum ether (1:3 v/v) as the developing solvents. The main product poly (1,4-phenylene ether) (PPE) and by-product di-phenoquinone (DPQ) were collected and dried in vacuo, respectively.

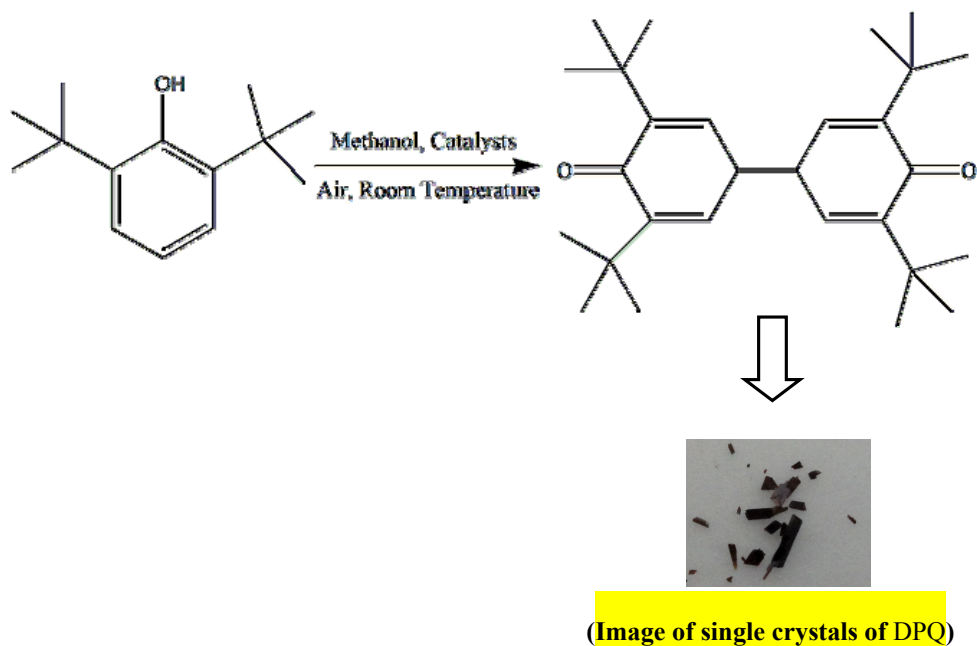
PPE: ¹H NMR (400 MHz, CDCl₃) δ : 2.10 (s, 6H), 6.44 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ : 16.3–16.8, 114.1, 114.5, 124.4, 124.9, 128.6, 129.0, 131.6, 132.7, 145.6, 146.4, 151.4, 152.2, 154.5, 154.7. IR (cm⁻¹, KBr): 3428m, 1609s, 1470s, 1308s, 1188s, 1022s, 858m.



Scheme S1. The oxidative coupling reaction process of 2,6-dimethylphenol in water.

Experiment procedure for the catalytic Oxidative self-coupling reaction:

The oxidative self-coupling reaction was carried out via using 0.010 g (0.05 mmol) 2,6-di-*tert*-butylphenol substrate and a small quantity of complexes **1** and **2** in 1 ml methanol for ten days at room temperature under air atmosphere. The dosages of complexes **1** and **2** were 0.1 μmol . After ten days, transparent red crystals of 3, 3', 5, 5'-tetra-*tert*-butyl-4, 4'-diphenoquinone (DPQ) could be obtained when the substrates were catalyzed by complex **1**, while when using complex **2** as catalysts they could not be obtained. The single crystal parameters are $a = 6.12 \text{ \AA}$, $b = 10.33 \text{ \AA}$, $c = 10.34 \text{ \AA}$, $\alpha = 82.83 \text{ deg}$, $\beta = 82.49 \text{ deg}$, $\gamma = 77.03 \text{ deg}$, $V = 628 \text{ \AA}^3$, which are consistent with the reported ones. ^[1]



Scheme S2. The catalytic oxidative self-coupling reaction.

[1]. Zhao, J. A.; Mi, L. W.; Hu, J. Y.; Hou, H. W.; Fan, Y. T. *J. Am. Chem. Soc.* **2008**, *130*, 15222–15223.

Table S1. Main crystal parameters of **1**, **2** and **1'**

Complex	1	2	1'
Formula	C ₁₄₄ H ₂₅₃ Cu ₆ N ₈₀ O _{68.5}	C ₁₄₄ H ₂₂₀ Cu ₆ N ₇₂ O ₂₆ I ₁₂	C ₁₄₄ H ₂₅₃ Cu ₆ N ₈₀ O _{68.5}
Fw	4582.32	5279.89	4582.32
crystal system	Tetragonal	Tetragonal	Tetragonal
space group	I4/m	I4/m	I4/m
<i>a</i> (Å)	23.2603(5)	23.178(3)	23.0648(13)
<i>b</i> (Å)	23.2603(5)	23.178(3)	23.0648(13)
<i>c</i> (Å)	20.2085(7)	20.105(4)	19.9962(18)
<i>α</i> (deg)	90	90	90
<i>β</i> (deg)	90	90	90
<i>γ</i> (deg)	90	90	90
<i>V</i> (Å ³)	10933.6(5)	10801(5)	10637.7(13)
<i>Z</i>	2	2	2
goodness-of-fit on <i>F</i> ²	1.017	1.028	1.069
Final R1	0.0701	0.0814	0.0910

Table S2. Selected bond lengths and bond angles

1			
Cu1-N7	2.0000(2)	Cu2-N1	1.9973(2)
Cu2-N4	2.0134(2)	Cu2-O2	2.3923(4)
Cu1-O8	2.472	Cu2-O1	2.467
N(7)#1-Cu(1)-N(7)#3	89.900(1)	N(7)#3-Cu(1)-N(7)	175.222(15)
N(1)-Cu(2)-N(1)#4	90.965(14)	N(1)-Cu(2)-N(4)	89.862(9)
N(4)#4-Cu(2)-N(4)	89.267(12)	N(1)-Cu(2)-O(2)	89.592(11)

2			
Cu1-N4	1.9948(4)	Cu2 – N1	1.9777(4)
Cu2-N9	2.0043(4)	Cd(1)-N(4)	2.298(4)
Cu1-I1	3.296	Cu1-I2	3.213
N(1)#1-Cu(2)-N(9)#2	89.834(19)	N(4)#4-Cu(1)-N(4)#5	89.986(1)
N(9)#2-Cu(2)-N(9)#3	89.07(2)	N(1)#1-Cu(2)-N(1)	91.24(3)
N(4)#5-Cu(1)-N(4)#6	90.0	N(4)#6-Cu(1)-N(4)	90.0

1'			
Cu(1)-N(1)#1	1.9902(14)	Cu(2)-N(7)#4	1.982(2)
Cu(2)-N(4)	2.0071(18)	Cu1-O9	2.649
Cu2-O5	2.474	Cu2-O4	2.457
N(4)#6-Cu(2)-N(4)	90.45(10)	N(1)#1-Cu(1)-N(1)#2	89.870(5)
N(7)#4-Cu(2)-N(7)#5	90.57(13)	N(7)#4-Cu(2)-N(4)	89.49(8)

Table 3: Catalytic activities of complexes 1 and 2 for oxidative polymerization of DMP^[a]

Catalyst	Conversion of DMP (%)	Yield (%) ^[b]		Selectivity ^[c] of PPE (%)
		PPE	DPQ	
1	81	57	10	56
2	39	15	6	63

[a] Reaction conditions: DMP (1 mmol), NaOH (1 mmol), H₂O₂ (20 μL) and catalyst (0.002 mmol) in 3 mL of water for 8 h at 50 °C.

[b] Conversions and isolated yields based on the DMP, average of two runs.

[c] Selectivity = ([PPE]×100)/([PPE] + [DPQ]).

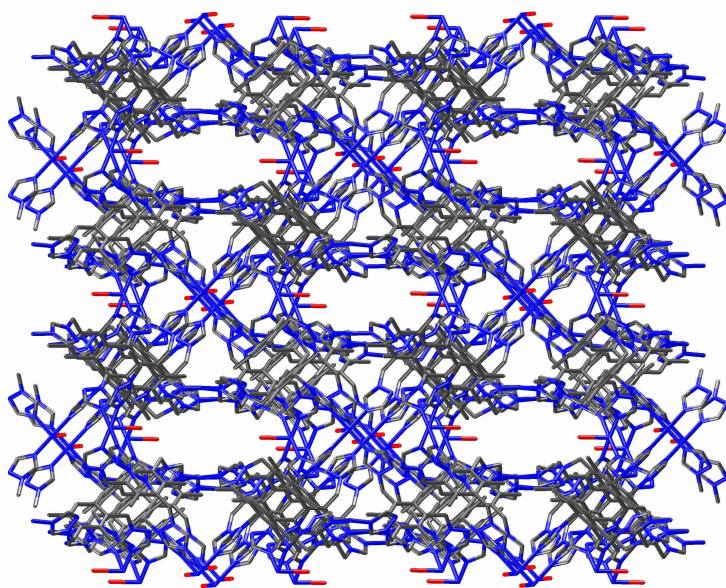
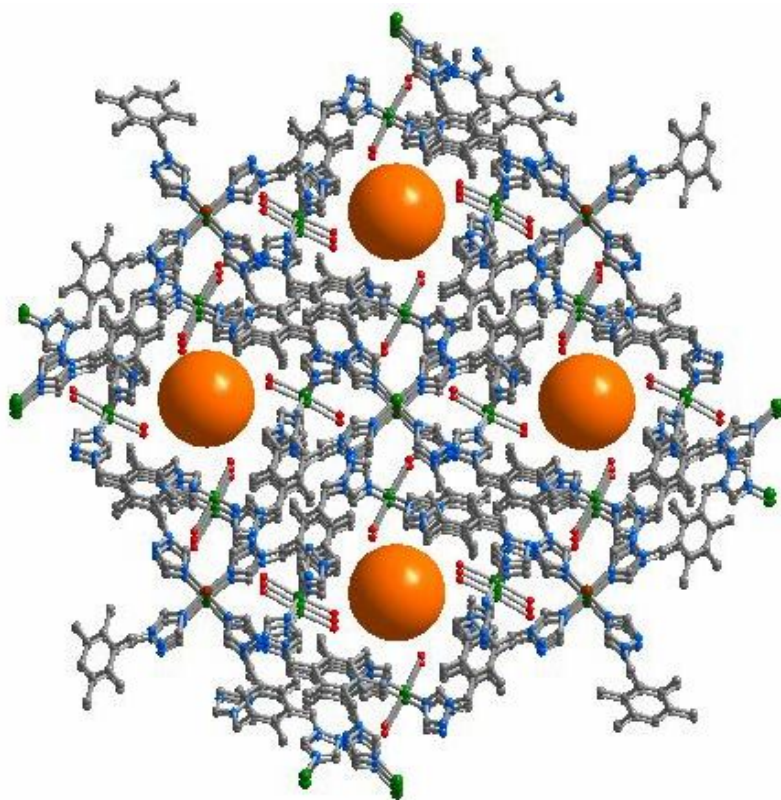


Figure S1: 3D structure of **1** from c axis with 1D channel (top), 3D structure of **1** from b axis (bottom).

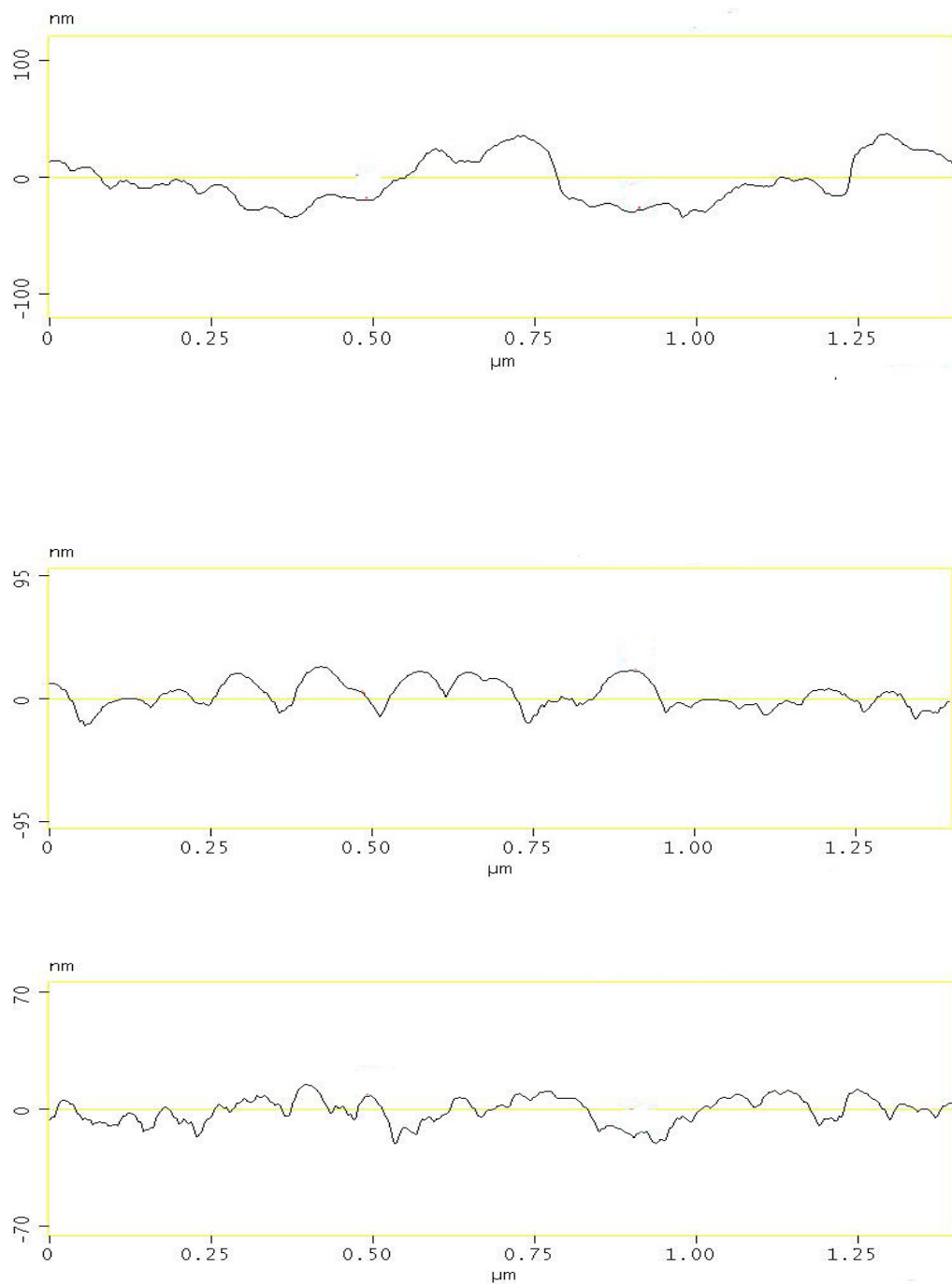


Figure S2: (AFM) Profiles of the single crystal surface of **1**: (top) before anion exchange; (middle) 2 h after suspending in KI solution; (bottom) 5 h after suspending in KI solution.

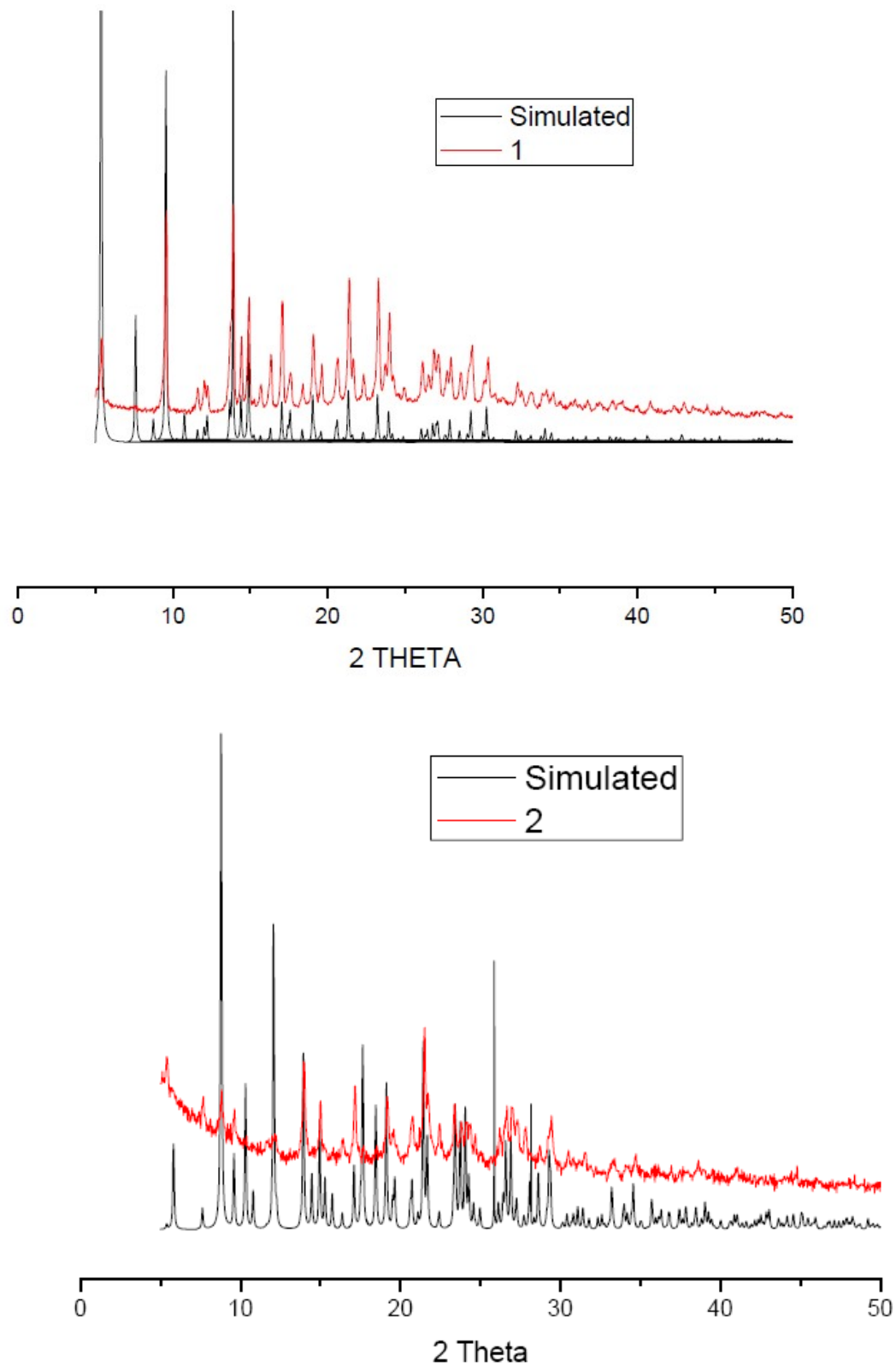


Figure S3: PXRD pattern of complex **1** (top) and **2** (bottom).

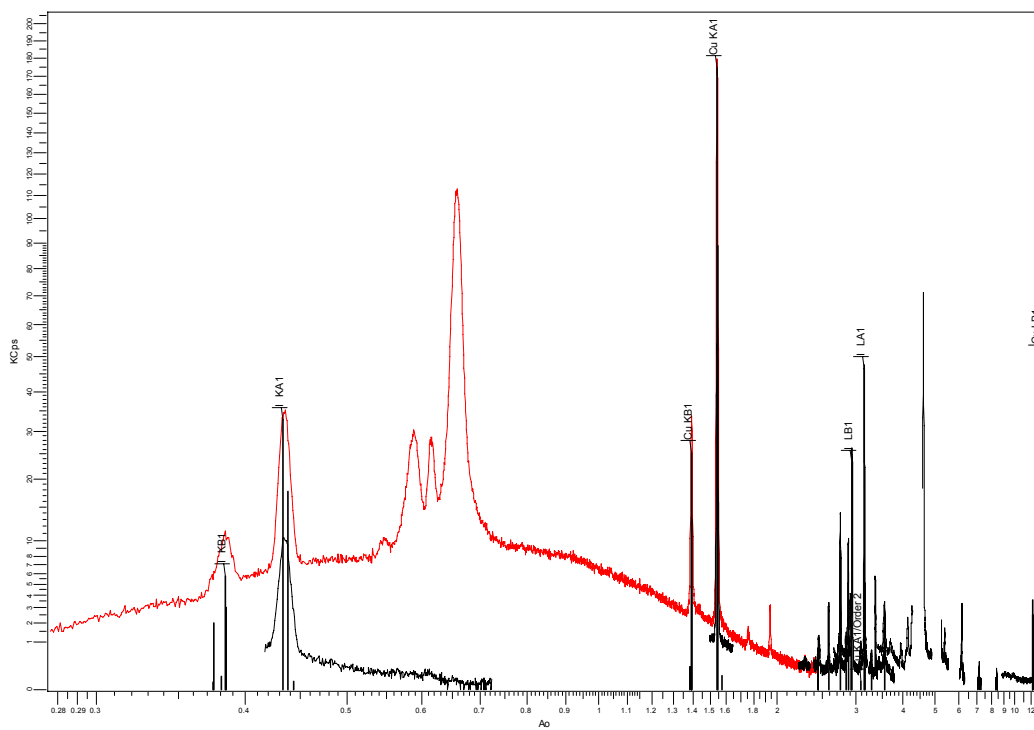
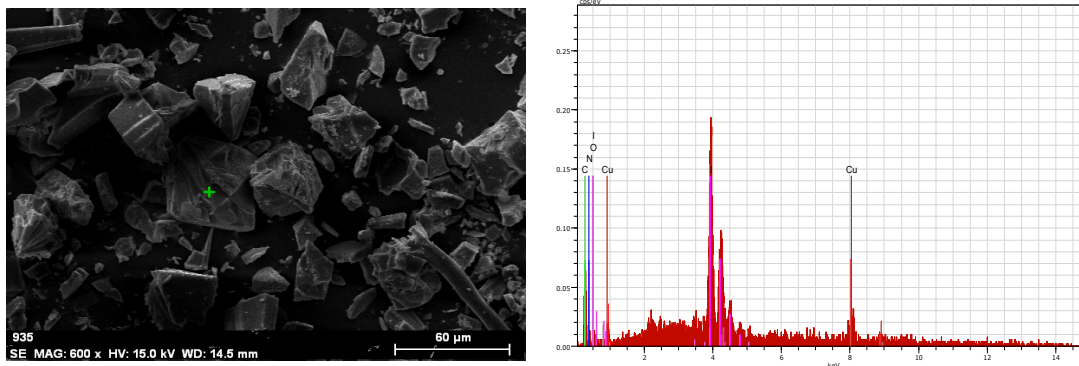


Figure S4: XRF data of **2**. Red curves are the background peaks.



Spectrum: ISMNM 770

El AN Series un. C norm. C Atom. C Error
[wt.%) [wt.%) [at.%) [%]

C	6	K-series	10.13	13.26	39.19 3.1
N	7	K-series	8.55	11.20	28.37 5.2
O	8	K-series	1.71	2.24	4.96 1.4
Cu	29	K-series	19.09	25.01	13.97 1.2
I	53	L-series	36.86	48.29	13.51 1.3

Figure S5: EDS of product 2.

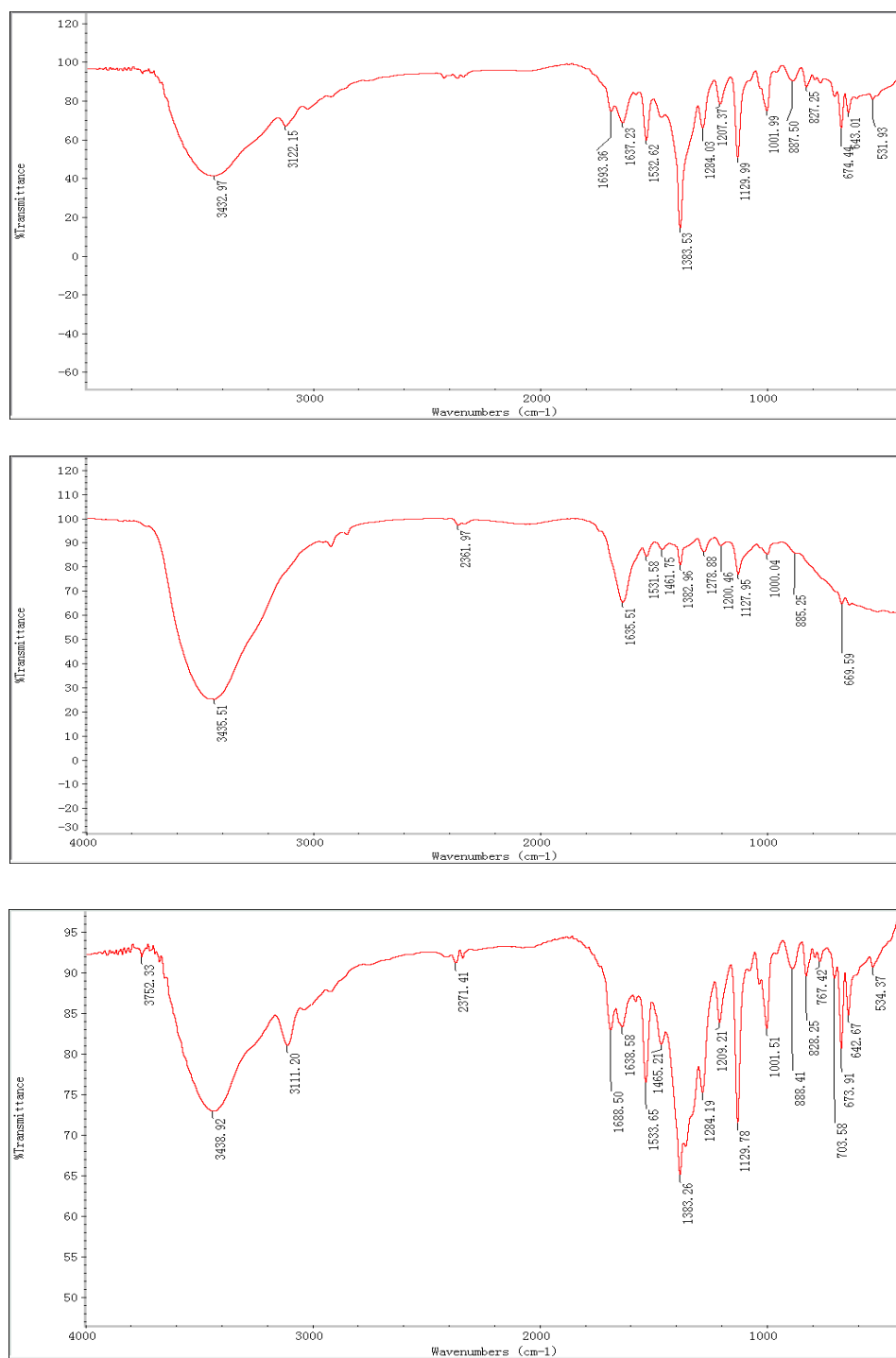


Figure S6: IR Spectrum of 1(top), 2(middle) and 1'(bottom).

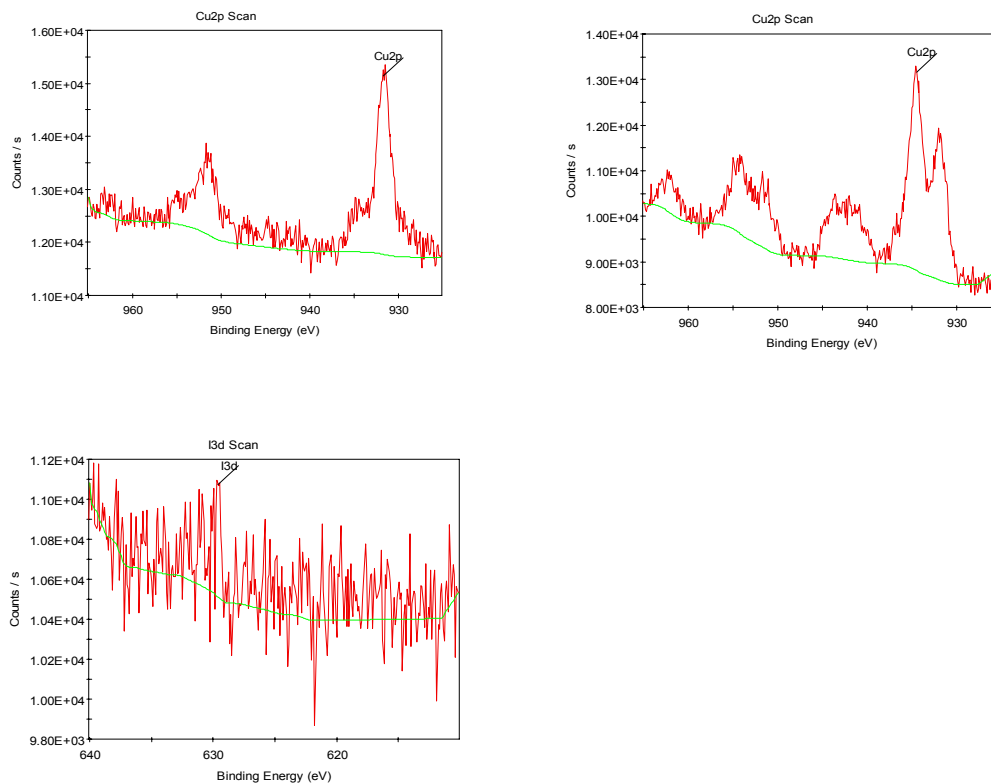


Figure S7: (a) XPS spectra of Cu 2p of **1**, (b) XPS spectra of Cu 2p of **2**, (c) XPS spectra of I 3d of **2**.

The satellite peak in b was probably caused by the occurrence of redox reaction when **2** was exposed to the x-ray environment. ^[1]

[1]. Klein, J.C.; Li, C.P.; Hercules, D. M.; Black, J. F. *Appl. Spectrosc.* 1984, **38**, 729.

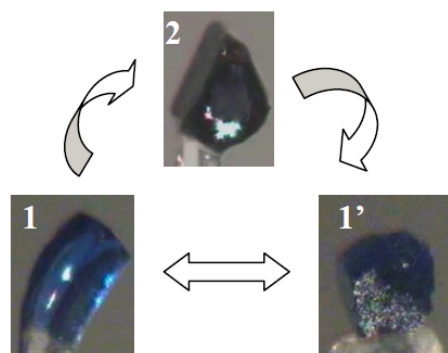


Fig.S8 Images of the single-crystals of **1**, **2** and **1'**

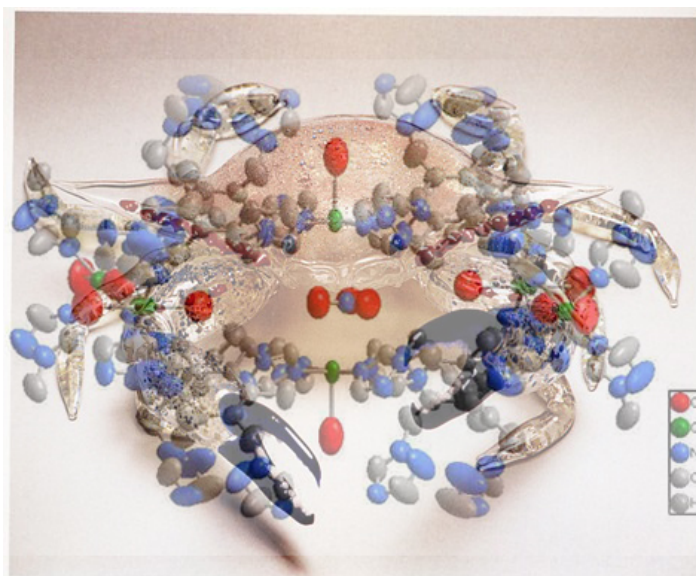


Figure S9: “Crab-shaped” hexa-copper unit in the single crystal of **1**’ with thermal ellipsoids, hydrogen atoms and water molecules are omitted for clarity.

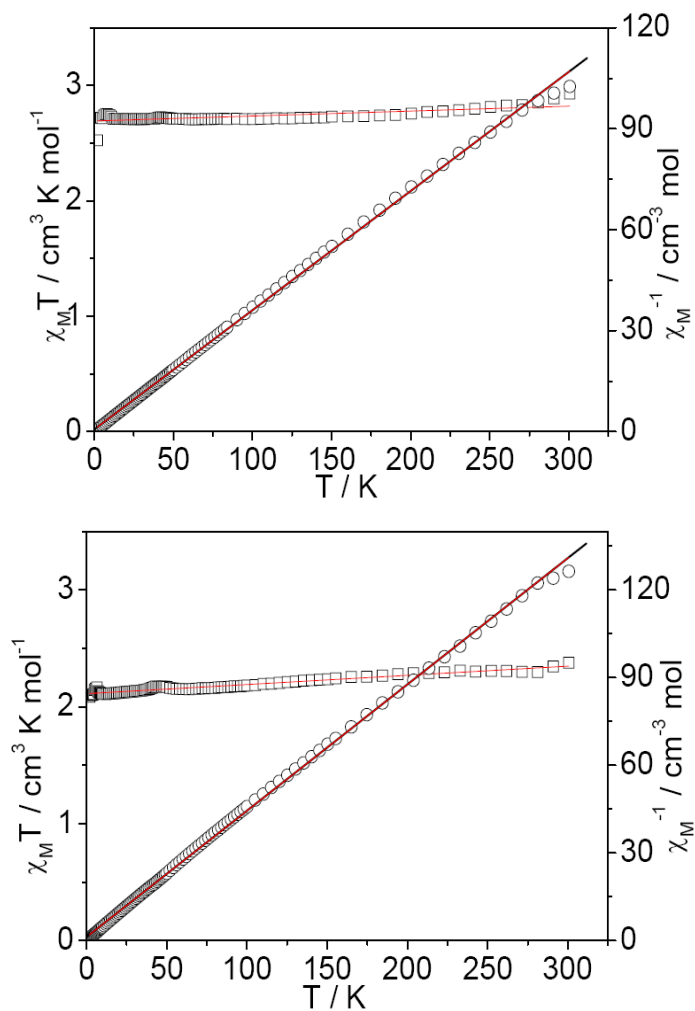


Figure S10. Plots of $\chi_M T$ (\square) and χ_M^{-1} (\circ) vs. T for **1** (above) and **2** (below). The solid lines represent the theoretical curve with the best-fit parameters.