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Single-Crystal-to-Single-Crystal (SCSC) transformation and Dissolution-Recrystallization Structural Transformation (DRST) among Three New Copper(II) Coordination Polymers

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Experiment of Crystalline phase transitions.

Experiment for the transformation of 1 to 2.

By using a reaction of the same initial reactants, complexes 1 and 2 were synthesized at 120 and 90 °C, which showing a 3D coordination framework of 1 and 1D-polymeric chains of 2, respectively. To further understand the relationship of 1 and 2, we either prolonged the reactive time of 1 at 120 °C from 12 h to 48 h, or immersed 1 into deionized water and hearted to 120 °C for 48 h, the green crystals of 1 decreased and light blue crystals of 2 appeared, proved that 1 conversion into 2. The conclusion was further authenticated by X-ray single-crystal diffraction. We reasoned that the transformation from 1 to 2 may be induced by temperature and water. For a better understanding the temperature induced the structural transformation, a process was monitored at a regular interval for 5 °C from 80 °C to 160 °C in a stepwise manner. The results revealed that the mixture of 1 and 2 were generated during 95 °C to 115 °C, while no crystal occur above 130 °C and below 90 °C. All of above-mentioned practice indicate temperature plays a provable role in regulation the syntheses of complexes 1 and 2. Besides, we replaced water to other solvents, there is no corresponding phenomenon observed. It proved that water also plays an important role in regulating the transformation. Therefore, we conclude that water and temperature induced complex 1 converted into complex 2. Moreover, several practices are tried and the original framework structure changes of **1** is not restored.

Experiment for the transformation of 2 to 3.

Compared with the transformation of aforementioned, the transformation of 2 to 3 is simple, which is complete after socked 2 in deionized water for 24 h. This process is different from above due to the retention of single crystals throughout the transformation, and can be assigned as SCSC. The result is further confirmed by X-ray single-crystal diffraction. To further investigate the influence factor for this transformation, a series of additions including metal ions, ligands and solvents were added in. The results show that water induced the process and the additions have no influence for this transformation. No reverse phase change was observed, though several practices are tried.

Experiment for the transformation of 1 to 3.

While the solid crystals of 1 was immersed to deionized water in a beaker at room temperature for two days, micro-meter-sized blue crystals of Compound 3 recrystallized and complex 1 become slowly resolved. That is to say, the 3D coordination framework of 1 can suffer another DRST to form a 2D supramolecular of 3 for the process starts with single crystals and end with single crystals but without retention of single-crystal form. The transformation was completed after one month, when Compound 1 was totally resolved. The structural gradual transformation from 1 to 3 for bulk crystalline materials was further confirmed by PXRD patterns. Also several practices are tried. It is found that this process is specific to water and not responsive to other conventional solvents (eg: CH₃ON, CH₃CH₂OH, CH₃CN, CH₂CI₂, DMF, DMA et), metal ions and ligands. The irreversible process was not achieved up to now.

Cu1—O6 ⁱ	1.921 (6)	Cu2—O2 ⁱⁱⁱ	1.973 (6)
Cu1—O1	1.957 (6)	Cu2—O9 ⁱⁱⁱ	2.332 (9)
Cu1—O11	1.976 (6)	Cu2—O9	2.332 (9)
Cu1—N1A	2.033 (9)	Cu3—O4 ⁱⁱ	1.920 (7)
Cu1—N1	2.072 (9)	Cu3—O8	1.948 (8)
Cu1—O4 ⁱⁱ	2.529 (9)	Cu3—O11	1.950 (7)
Cu1—O9 ⁱⁱⁱ	2.644 (10)	Cu3—N2	2.004 (8)
Cu2—O11	1.948 (6)	O6—Cu1 ^{iv}	1.921 (6)
Cu2—O11 ⁱⁱⁱ	1.948 (6)	O4—Cu3 ^v	1.920 (7)
Cu2—O2	1.973 (6)	O4—Cu1 ^v	2.529 (9)
06 ⁱ —Cu1—O1	172.8 (3)	O11—Cu2—O9 ⁱⁱⁱ	84.8 (3)
O6 ⁱ —Cu1—O11	94.3 (3)	O11 ⁱⁱⁱ —Cu2—O9 ⁱⁱⁱ	95.2 (3)
01—Cu1—O11	92.8 (3)	O2—Cu2—O9 ⁱⁱⁱ	92.4 (3)
O6 ⁱ —Cu1—N1A	87.1 (4)	O2 ⁱⁱⁱ —Cu2—O9 ⁱⁱⁱ	87.6 (3)
O1—Cu1—N1A	85.9 (4)	O11—Cu2—O9	95.2 (3)
O11—Cu1—N1A	178.3 (5)	O11 ⁱⁱⁱ —Cu2—O9	84.8 (3)
O6 ⁱ —Cu1—N1	85.6 (4)	O2—Cu2—O9	87.6 (3)
O1—Cu1—N1	87.7 (4)	O2 ⁱⁱⁱ —Cu2—O9	92.4 (3)
011—Cu1—N1	170.2 (4)	O9 ⁱⁱⁱ —Cu2—O9	180.0
O6 ⁱ —Cu1—O4 ⁱⁱ	102.5 (3)	O4 ⁱⁱ —Cu3—O8	158.6 (4)
O1—Cu1—O4 ⁱⁱ	81.4 (3)	O4 ⁱⁱ —Cu3—O11	86.2 (3)
O11—Cu1—O4 ⁱⁱ	70.7 (2)	O8—Cu3—O11	99.6 (3)
N1A—Cu1—O4 ⁱⁱ	108.0 (4)	O4 ⁱⁱ —Cu3—N2	93.3 (3)
N1—Cu1—O4 ⁱⁱ	99.8 (4)	O8—Cu3—N2	96.7 (3)
O6 ⁱ —Cu1—O9 ⁱⁱⁱ	95.9 (3)	O11—Cu3—N2	135.4 (3)
O1—Cu1—O9 ⁱⁱⁱ	84.1 (3)	Cu2—O11—Cu3	111.0 (3)
O11—Cu1—O9 ⁱⁱⁱ	76.2 (3)	Cu2—O11—Cu1	109.5 (3)
N1A—Cu1—O9 ⁱⁱⁱ	104.7 (4)	Cu3—O11—Cu1	107.9 (3)
N1—Cu1—O9 ⁱⁱⁱ	113.6 (4)	C7—O2—Cu2	128.9 (6)
O4 ⁱⁱ —Cu1—O9 ⁱⁱⁱ	143.0 (2)	C7—O1—Cu1	132.6 (6)
O11—Cu2—O11 ⁱⁱⁱ	180.0	C16—O6—Cu1 ^{iv}	131.9 (6)
O11—Cu2—O2	91.4 (3)	C8—O4—Cu3 ^v	122.1 (8)
O11 ⁱⁱⁱ —Cu2—O2	88.6 (3)	C8—O4—Cu1 ^v	123.9 (8)
O11—Cu2—O2 ⁱⁱⁱ	88.6 (3)	Cu3 ^v —O4—Cu1 ^v	90.0 (3)
O11 ⁱⁱⁱ —Cu2—O2 ⁱⁱⁱ	91.4 (3)	C23—N1—Cu1	122.6 (7)
O2—Cu2—O2 ⁱⁱⁱ	180.0	C19—N1—Cu1	117.2 (7)

Table S1. Selected Bond Lengths (Å) and Angles (°) for complex 1

Symmetry codes for 1: (i) -x+1/2, y-1/2, -z+3/2; (ii) x, -y, z+1/2; (iii) -x+1/2, -y+1/2, -z+1; (iv) -x+1/2, y+1/2, -z+3/2; (v) x, -y, z-1/2; (vi) -x+1/2, -y-1/2, -z+1; (vii) -x, y, -z+1/2; (viii) -x, -y+1, -z+1.

Cu1—O4 ⁱ	1.934 (3)	Cu1—N1	2.012 (4)
Cu1—O1	1.944 (3)	Cu1—06	2.409 (4)
Cu1—O7	1.961 (3)	O4—Cu1 ⁱ	1.934 (3)
O4 ⁱ —Cu1—O1	85.25 (13)	N1—Cu1—O6	94.21 (15)
O4 ⁱ —Cu1—O7	89.89 (14)	C13—O1—Cu1	120.6 (3)
O1—Cu1—O7	172.00 (14)	Cu1—O7—H7A	108.5
O4 ⁱ —Cu1—N1	175.49 (15)	Cu1—O7—H7B	114.7
O1—Cu1—N1	91.41 (14)	$C12$ — $O4$ — $Cu1^i$	133.7 (3)
O7—Cu1—N1	93.09 (14)	Cu1—O6—H6A	110.6
O4 ⁱ —Cu1—O6	89.03 (16)	Cu1—O6—H6B	109.3
01—Cu1—O6	93.59 (15)	C1—N1—Cu1	120.0 (3)
O7—Cu1—O6	92.67 (16)	C5—N1—Cu1	123.6 (3)

Table S2. Selected Bond Lengths (Å) and Angles (°) for complex 2

Symmetry codes for **2**: (i) -x, -y, -z+1; (ii) -x+1, -y+1, -z.

Table S3. Selected Bond Lengths (Å) and Angles (°) for complex $\bf 3$

Cu1—016	1.960 (2)	Cu2—O12	1.980 (2)
Cu1—O7	1.939 (2)	Cu2—O1 ⁱⁱ	1.937 (2)
Cu1—O9 ⁱ	1.948 (2)	Cu2—O11	2.346 (3)
Cu1—N2	2.021 (3)	Cu2—N1	2.001 (3)
Cu1—O12	2.573 (3)	O9—Cu1 ⁱ	1.948 (2)
Cu2—O5	1.955 (2)	O1—Cu2 ⁱⁱ	1.937 (2)
O16—Cu1—N2	92.99 (10)	O1 ⁱⁱ —Cu2—O12	89.47 (10)
O7—Cu1—O16	89.70 (9)	O1 ⁱⁱ —Cu2—O11	88.39 (11)
O7—Cu1—O9 ⁱ	86.10 (9)	O1 ⁱⁱ —Cu2—N1	177.19 (10)
O7—Cu1—N2	176.39 (11)	N1—Cu2—O11	91.35 (10)
O9 ⁱ —Cu1—O16	173.96 (10)	C20—O7—Cu1	131.9 (2)
O9 ⁱ —Cu1—N2	91.03 (10)	C9—O5—Cu2	119.1 (2)
O5—Cu2—O12	159.64 (10)	C27—O9—Cu1 ⁱ	117.9 (2)
O5—Cu2—O11	97.78 (10)	C1—O1—Cu2 ⁱⁱ	132.2 (2)
O5—Cu2—N1	92.37 (10)	C18—N2—Cu1	121.7 (2)
O12—Cu2—O11	101.60 (10)	C17—N2—Cu1	122.6 (2)
O12—Cu2—N1	93.33 (10)	C10—N1—Cu2	124.2 (2)
O1 ⁱⁱ —Cu2—O5	84.89 (9)	C14—N1—Cu2	119.7 (2)

Symmetry codes for **3**: (i) -x-2, -y-1, -z; (ii) -x+1, -y+2, -z+1; (iii) -1+x, -1+y, z.



Fig. S1 (a) The Cu₅ linked by μ_4 - η^1 : η^2 : η^1 -MIPA in 1. (b) The Cu₅ linked by μ_4 - η^1 : η^2 -MIPA in 1. (c) View of 2D layers of 1 formed by Cu₅ and μ_4 - η^1 : η^2 : η^1 -MIPA and μ_4 - η^1 : η^2 : η^1 -MIPA. (d) The four-connected net based on the connectivity between Cu₅ and MIPA units of 1. All hydrogen atoms and guest molecules are omitted for clarity.



Fig. S2 (a) View of 2D layers of 1 formed by Cu_5 and 4,4'-bpy. (b) The four-connected net based on the connectivity between Cu_5 and 4,4'-bpy units in 1. All hydrogen atoms and guest molecules are omitted for clarity.



Fig. S3 Water-mediated SCSC transformation of 2 into 3.



Fig. S4 Infrared spectra of complexes 1-3.



Fig. S5 PXRD patterns of **1** (a), **2** (b) and **3** (c).



(a)

Fig. S6 PXRD patterns of 1 (a) and 2 (b) are soaking in variable solvents at room temperature for one month.



Fig. S7 TGA curves for complexes 1-3.



Fig. S8 Temperature dependence of χ_M for **3**. The open points are the experimental data, and the solid line represents the best fit obtained from the spin Hamiltonian given in the text.

For compound **3**, a modified Bleaney—Bowers expression (2), which was derived from the isotropic spin Hamiltonian (1) with local spin S = 1/2.

$$H = \sum_{i=1}^{N/2} (S_{2i} \cdot S_{2i-1} + \alpha S_{2i} S_{2i+1})$$
(1)
$$\chi = \frac{Ng^2 \beta^2}{kT} \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3}$$
(2)

where α ($0 \le \alpha \le 1$) is the alternation parameter, $x = |J|/k_BT$, and the coefficients A-F are listed below.

$$\begin{aligned} x &= |J| / k_B T \\ A &= 0.25 \\ B &= (-0.068475 + (0.13194^*\alpha)) \\ C &= (0.0042563 - (0.031670^*\alpha) + (0.12278^*(\alpha^2)) - (0.29943^*(\alpha^3)) + (0.21814^*(\alpha^4))) \\ D &= (0.035255 + (0.65210^*\alpha)) \\ E &= (-0.00089418 - (0.10209^*\alpha) + (0.87155^*(\alpha^2)) - (0.18472^*(\alpha^3))) \\ F &= (0.045230 - (0.0081910^*\alpha) + (0.83234^*(\alpha^2)) - (2.6181^*(\alpha^3)) + (1.92813^*(\alpha^4))) \end{aligned}$$