Supporting Information of

"Crystal-to-Crystal Transformation from a Chain Compound to a Layered Coordination Polymer"

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Synthetic procedures:

200.8 mg of $CuBr_2 \cdot 2H_2O$ was dissolved in 3.0 ml of CH_3OH, then 2.0 ml of 1,4-dioxane and 0.5 ml of H_2O was added and the solution was allowed to stand at room temperature. Green crystals of compound **1** were obtained after seven days, in a yield of 68.3%. Elemental analysis (%): calc. for $C_8H_{20}O_6Br_2Cu$ (435.57): C 22.06, H 4.59; found: C 22.27, H 4.66.

There are two ways to obtain compound **2**. The first way : 224.8 mg of $CuBr_2 \cdot 2H_2O$ was dissolved in 3.0 ml of CH_3OH, then 2.0 ml of 1,4-dioxane was added and the solution was allowed to stand at room temperature. Brown crystals were obtained after seven days, in a yield of 82.6 %. Another way to obtain **2** : blue crystals of **1** were heated at 70 °C for 30 minutes under vacuum or exposed to dry air and brown crystals of **2** were obtain with a yield of 100%. Elemental analysis (%): calc. for $C_8H_{16}O_4Br_6Cu_3$ (846.27): C 11.35, H 1.91; found: C 11.54, H 2.01. The phase purity of crystals was proved by their powder X-ray diffraction pattern.

Physical Characterizations

Thermogravimetric analysis was carried out on a Shimadzu DTG-60 analyzer at a 5 °C min^{-1} heating rate from room-temperature to 800 °C (Figure S1). There were three dominant mass losses in **1**: 35 % from 20 —70°C, in which **1** transformed into **2**, 30 % from 130— 210 °C, and 15 % from 450—540 °C. There were two dominant mass losses in 2: 47 % loss in 130 —210°C, 29 % loss in 450—540 °C.

The single crystal X-ray diffraction data was collected at 173 K on Rigaku diffractometer with confused monochromated Mo Kα (λ = 0.71073 Å) radiation.[1] The structure was solved by direct method and refined by full-matrix least-squares on F^2 using SHELX program, with anisotropic thermal parameters for all non-hydrogen atoms.[2] Hydrogen atoms of H_2O and 1, 4-dioxane were located by different Fourier map and refined with constrains for the ideal geometry.

The powder X-ray diffraction pattern was obtained on a Rigaku RINT2000 diffractometer at room temperature with Cu Kα (λ = 1.54056 Å) radiation in a flat-plate geometry.

UV-Vis absorption spectra of the solid $(CuBr_2)_3(1,4\text{-dioxane})_2$ (**2**) were measured on a Shimadzu UV-2600 spectrophotometer in the range of 220–900 nm at ambient temperatures.

Magnetization measurements were performed against tightly packed polycrystalline sample in capsule on a Quantum Design MPMS 7XL SQUID system. Susceptibility data were corrected for diamagnetism of sample by Pascal constants (-2.19×10^{-4} cm^3 mol^{-1} for **1**; -1.18×10^{-4} cm^3 mol^{-1} for **2**) and background by experimental measurement on the sample holder.

References

1. *Rigaku CrystalClear*（2007）. Version 1.4.0. Rigaku Inc., Tokyo, Japan.

2. Sheldrick, G. M. (2008). *Acta Cryst*. A64, 112-122.

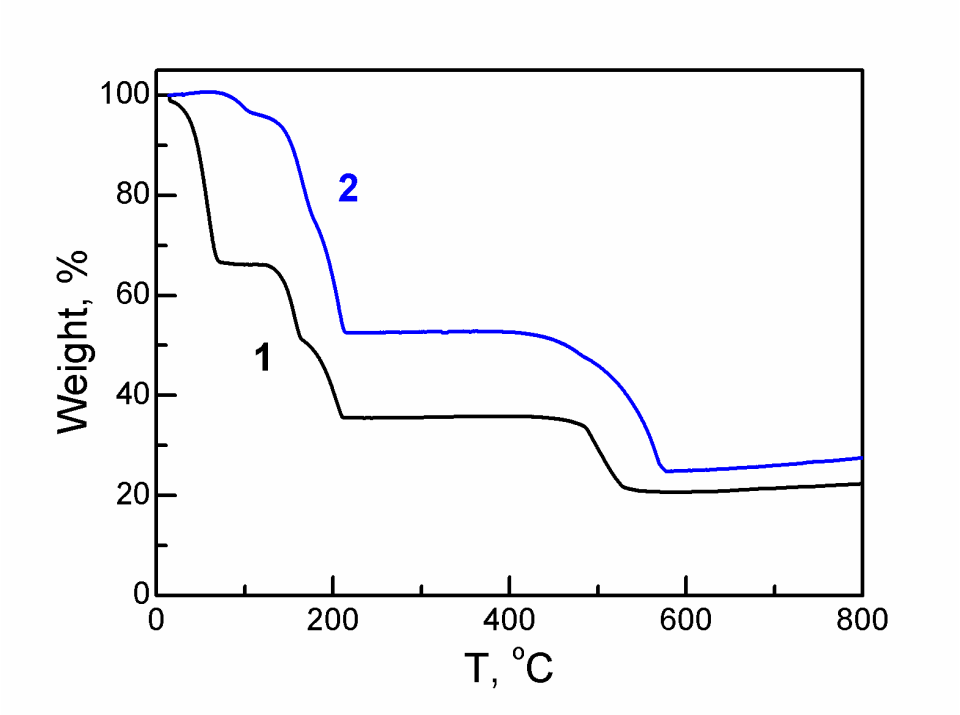

Figure S1. Thermogravimetric analysis plot of $CuBr_2(1,4\text{-dioxane})_2(H_2O)_2$ (**1**) and $(CuBr_2)_3(1,4\text{-dioxane})_2$ (**2**) at a heating rate of 5 °C / min..

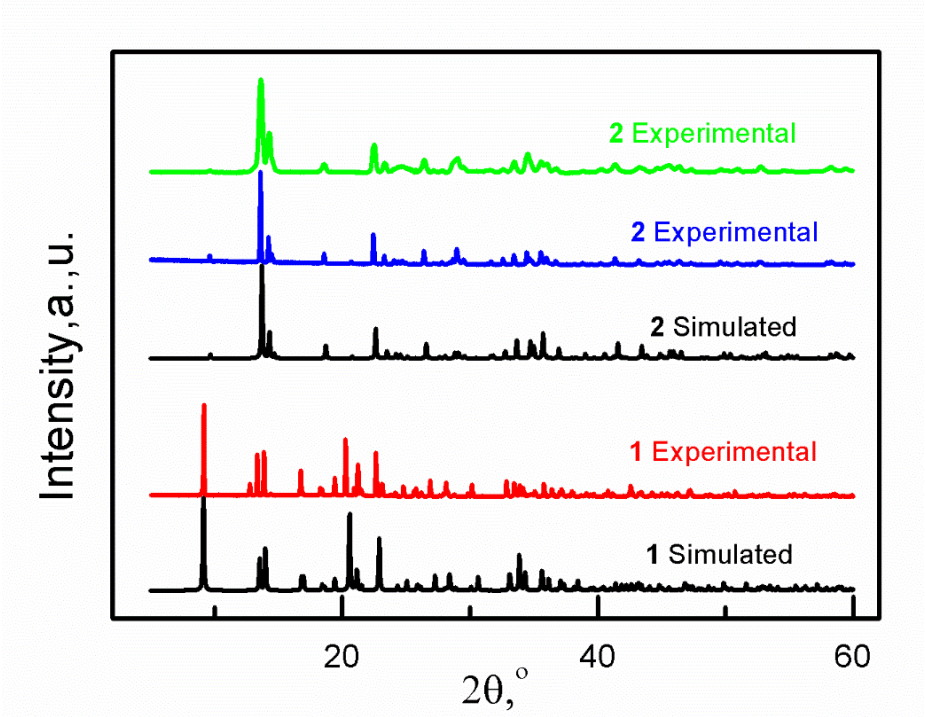

Figure S2. X-ray powder diffraction patterns of $CuBr_2(1,4\text{-dioxane})_2(H_2O)_2$ (**1**) and $(CuBr_2)_3(1,4\text{-dioxane})_2$ (**2**). Bottom: black line is the simulated one based on the single crystal structure of **1**; red line is the experiment data from polycrystal. Top: black line is the simulated one based on the single crystal structure of **2**; blue line is the experiment data from polycrystal obtained by direct synthesize; green line is the experiment data from polycrystal obtained by transformation from **1** to **2**.

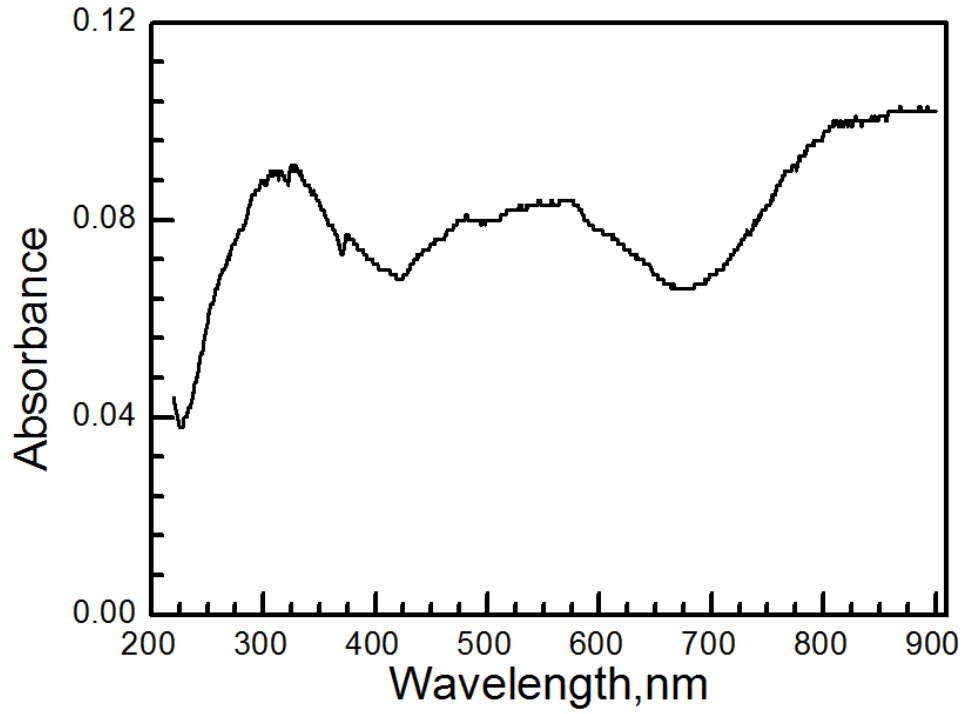

Figure S3. UV-Vis spectra of $(CuBr_2)_3(1,4\text{-dioxane})_2$ (**2**).