Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Reversible Solid State Hydration and Dehydration Process Involving Anion Transfer in a Self-Assembled Cu2 System

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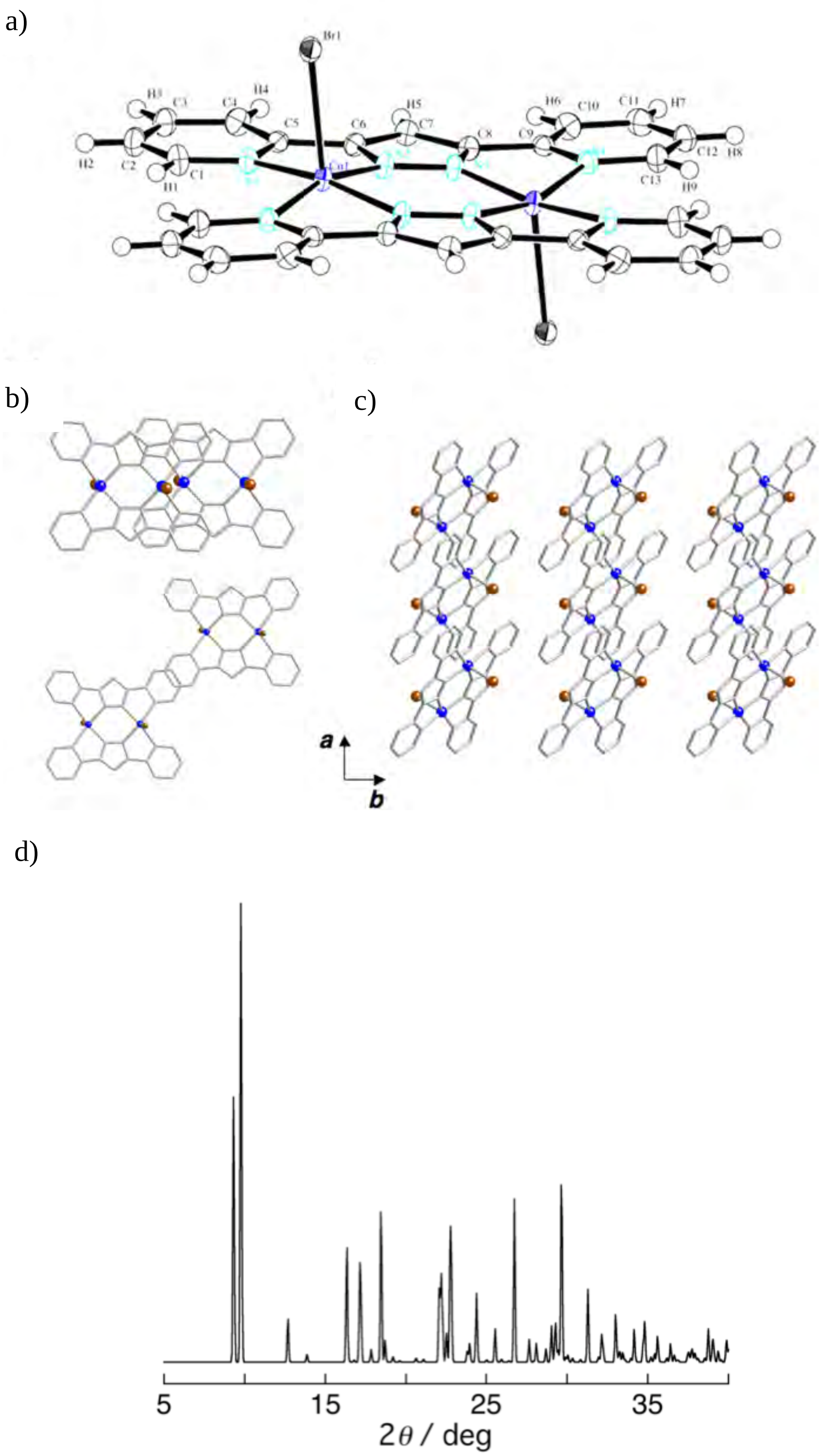


Figure S1 a) ORTEP drawing of the dimer unit in the crystal of **2** with labelling scheme and thermal ellipsoids at the 50% probability level. b) Two type of $\pi\cdots\pi$ stacking interaction between adjacent dimer complexes of **2**. c) Crystal packing of **2** along the 001 direction. Atoms: Cu (blue), Br (brown), C, N (stick model). d) Simulated XRPD pattern of **2**.

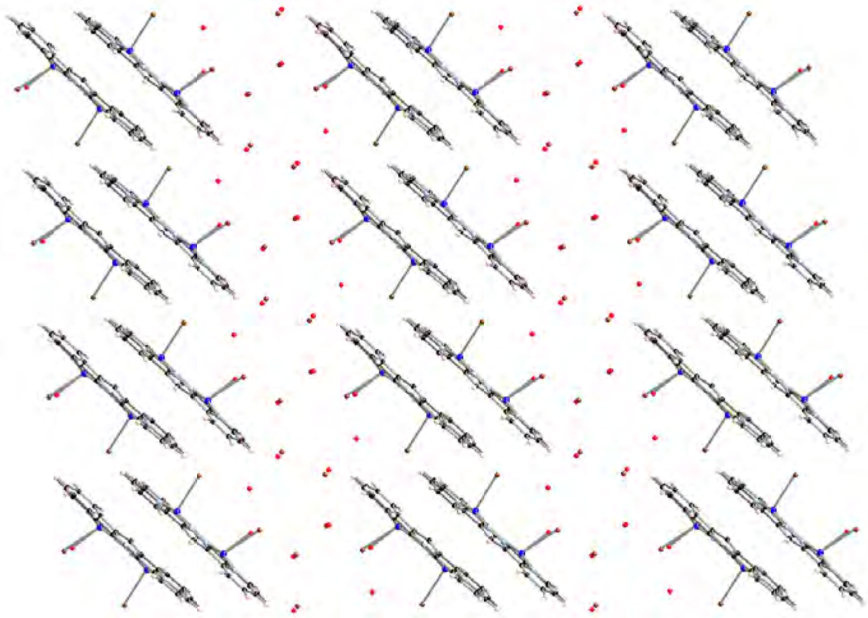
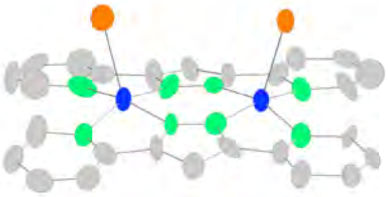


Figure S2. Hydrogen-bonding network of **1** along the *a*-axis. Atoms: Cu (blue), Br (brown), C (black), N (sky blue), O (red).



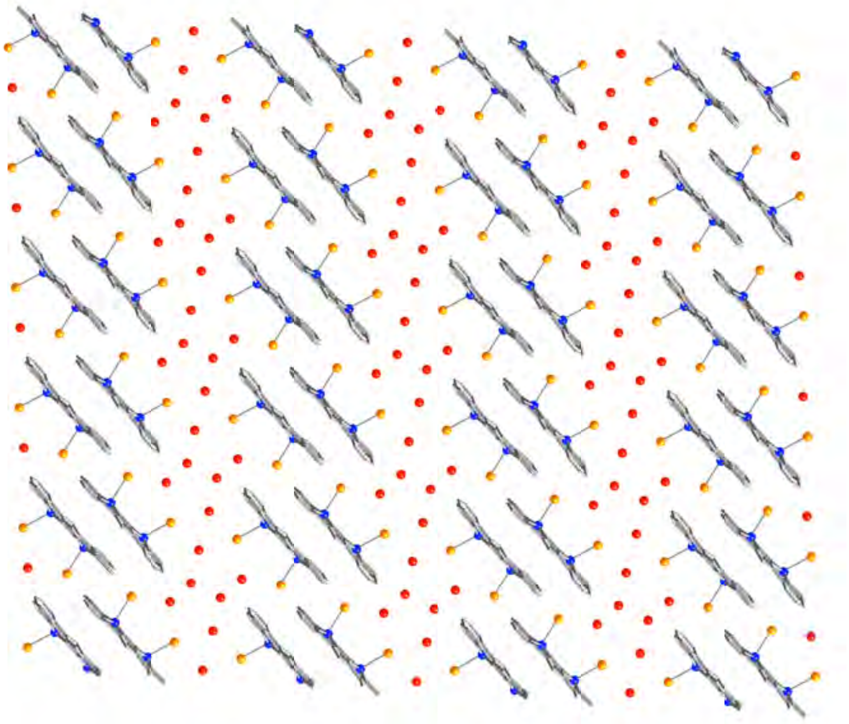


Figure S3. Hydrogen-bonding network of **1a** along the *a*-axis. Atoms: Cu (blue), Br (brown), C (gray), N (green), O (red).

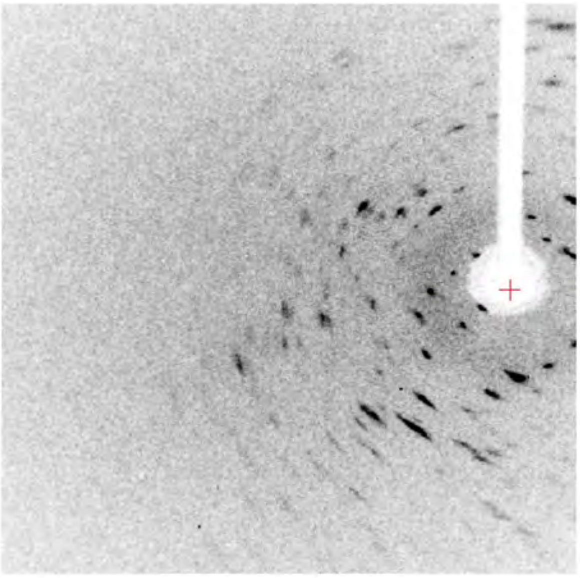


Figure S8. One of the diffraction patterns for **1b**.

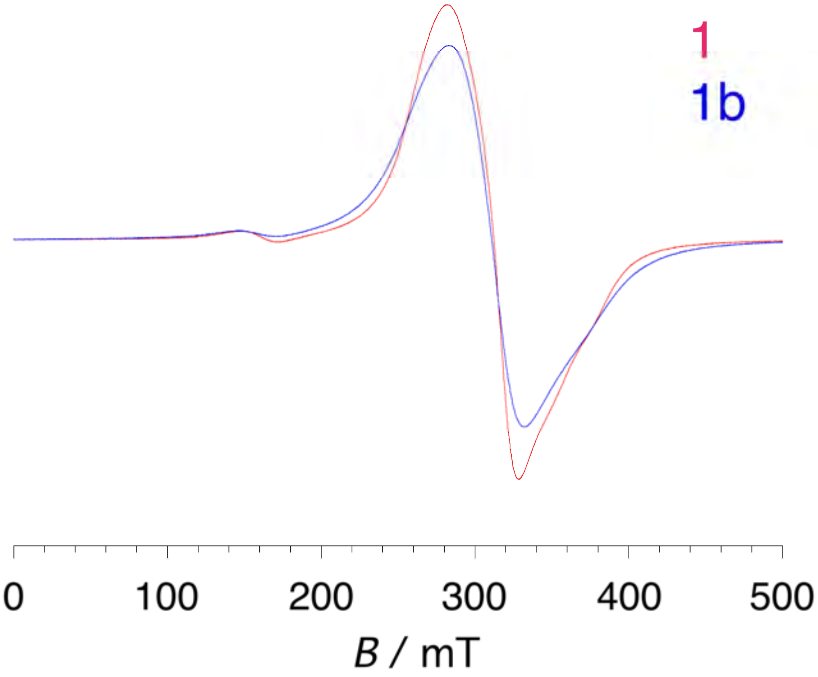


Figure S5. The EPR spectra corroborate the strong antiferromagnetic couplings: the typical *DMs* = 2 bands of the S = 1 states are shown.

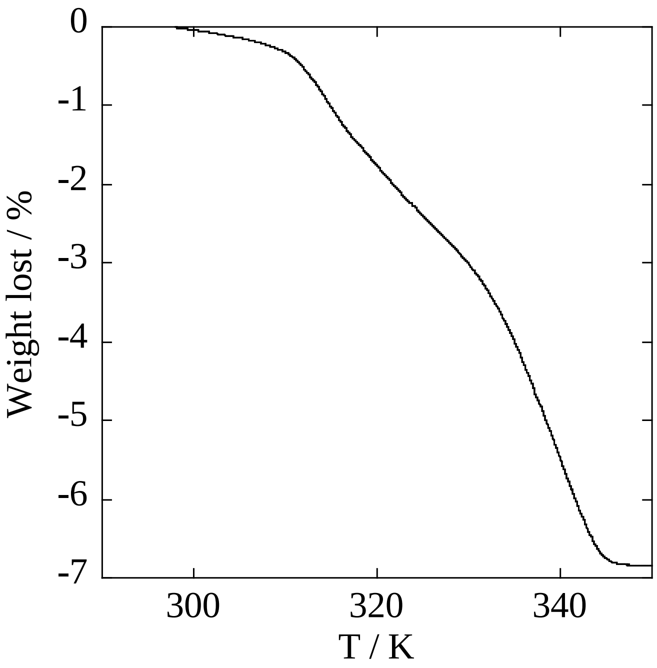


Figure S6. TG curves of **1** at heating rate of 10 °C/min.

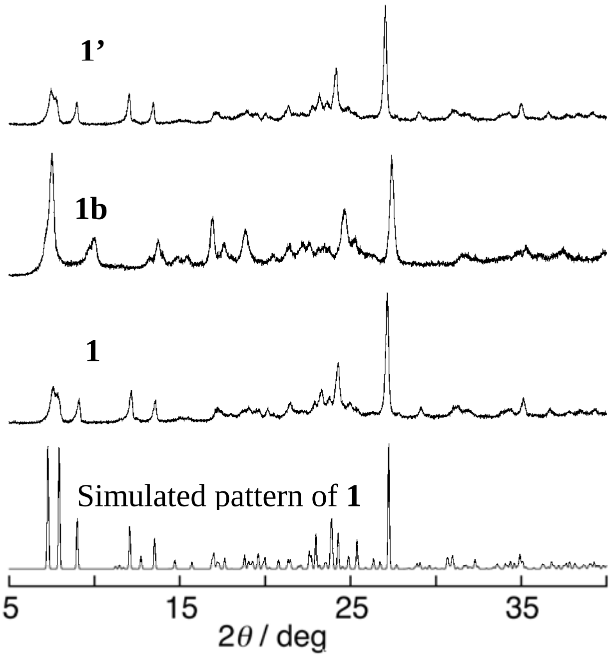


Figure S7. XRPD patterns of the original form **1**, the anhydrous form **1b**, the rehydrated form **1'** and the simulated pattern of **1.**

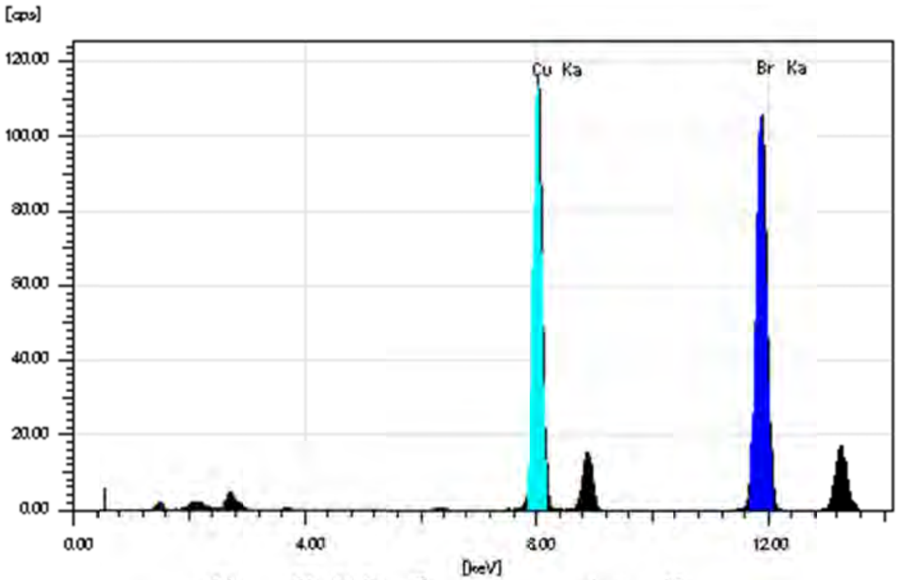


Figure S8. X-Ray fluorescence analysis of **1.**

Element	Concentration (wt%)	Intensity (cps / keV)
Cu	44.33 (±2σ 0.23)(wt%)	1063.446 (± 5.511)(cps / keV)
Br	55.67 (±2σ 0.27)(wt%)	1131.751 (± 5.684)(cps / keV)

$$(44.33/63.55)/(55.67/79.90)=1.001$$

$$\therefore \mathrm{Cu} : \mathrm{Br} = 1 : 1$$

Experimental

Synthesis

All solvents and chemicals were purchased and used without further purification.

$[Cu_2(\mu\text{-bpypz})_2Br_{1.25}(H_2O)_{0.75}]Br_{0.75}\cdot 2.25H_2O$ (**1**): An aqueous solution of copper(II) bromide (2 mL, 4 mmol L^{-1}) was transferred to a glass tube. A methanolic solution (2 mL) of Hbpypz (4 mmol L^{-1}) was poured into the tube without mixing the two solutions. Dark green block crystals began to form within two weeks. One of these crystals was used for X-ray crystallography. Physical measurements were conducted on a polycrystalline powder that was synthesized as follows: A solution of Hbpypz (2.0 mmol) in MeOH (50 mL) was added dropwise to copper(II) bromide (2.0 mmol) dissolved in water (30 mL). Upon stirring of the mixture, green powder appeared immediately. Yield: 90%. Calcd (%) for $C_{26}H_{24}Br_2Cu_2N_8O_3$: C, 39.86; H, 3.09; N, 14.30. Found (%): C, 39.90; H, 3.06; N, 14.24.

$[Cu_2(\mu\text{-bpypz})_2Br_2]\cdot 2H_2O$ (**1a**) and *syn*-$[Cu_2(\mu\text{-bpypz})_2Br_2]$ (**1b**): The single crystal of the dehydrated form, syn-$[Cu_2(\mu\text{-bpypz})_2Br_2](H_2O)_2$ (**1a**), and anhydrous form, syn-$[Cu_2(\mu\text{-bpypz})_2Br_2]$ (**2b**) were prepared in vacuum at room temperature for 12 hours and 3 days, respectively. TG analysis of **1** shows a two-step weight loss up to 80 °C, of which each step corresponds to the release of water molecules (see text). The compositions of **1a** and **1b** correspond to those at 60 °C and at 80 °C for TG analysis curve of **1**, respectively.

anti-$[Cu_2(\mu\text{-bpypz})_2Br_2]$ (**2**): A methanolic solution of copper(II) bromide (2 mL, 4mmol L^{-1}) was transferred to a glass tube. A methanolic solution (2 mL) of Hbpypz (4 mmol L^{-1}) was poured into the tube without mixing the two solutions. Green pillar crystals began to form within two weeks. Calcd (%) for C26H18Br2Cu2N8: C, 42.81; H, 2.49; N, 15.36. Found (%): C, 42.85; H, 2.54; N, 15.37.

Measurements

UV/Vis absorption spectra were measured on a Jasco V-570 spectrophotometer. X-ray powder diffraction data were collected on a Rigaku RINT 2000 diffractometer using CuKa radiation. Thermal gravimetric (TG) analyses were carried out with a Seiko Instruments SSC5200 Thermo analyzer in a nitrogen atmosphere (heating rate: 10 Kmin^{-1}). The adsorption isotherms for water were measured using a BELSORP-aqua3 volumetric-adsorption instrument from BEL Japan, Inc. Magnetic susceptibility data were recorded over the temperature range from 2 to 300 K with a SQUID susceptometer (Quantum Design, San Diego, CA). All data were corrected for diamagnetism, which was calculated from Pascal s tables. ESR spectra were recorded at X-band frequency with a Bruker EMX 8/2.7 spectrometer operating at 9.5 GHz. X-Ray fluorescence spectrum was measured using a SEA2200A from SII.

X-ray Crystallography

The data collections for **1**, **1a**, and **2** were carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated MoKa radiation. The data collection for **1b** was carried out on a Rigaku RAXIS-RAPID II with graphite-monochromated MoKa radiation. The structures were solved by direct methods (Rigaku CrystalStructure crystallographic software package of Molecular Structure Corporation) and refined with full-matrix least-squares technique (SHELXL-97).[10]

Crystal data for **1** $C_{26}H_{24}Br_2Cu_2N_8O_3$: T = 200(1) K: green, triclinic, space group P-1 (No. 2), Z = 2, a = 9.900(4), b = 11.605(4), c = 12.558(5) Å, a = 104.791(10) °, b = 89.286(9)°, g = 97.093(10)°, V = 1384.0(10) $Å^3$, d_{calcd} = 1.880 g cm^{-3}, m = 4.478 mm^{-1}. 13606 reflections were collected in the range 2q < 55.0° and 6225 independent reflections R_{int} = 0.039 were used in the structural analysis. R_1 = 0.0352 for F^2 > 2s (F^2), wR_2 = 0.0941 and GOF = 0.999 for F^2.

Crystal data for **1a** $C_{26}H_{22}Br_2$ $Cu_2N_8O_2$: T = 200(1) K: green, triclinic, space group P-1 (No. 2), Z = 2, a = 10.17(5), b = 11.52(6), c = 11.77(5) Å, a = 77.82(6)°, b = 86.94(6)°, g = 85.43(8)°, V = 1342(11) $Å^3$, d_{calcd} = 1.880 g cm^{-3}, m = 4.612 mm^{-1}. 12759 reflections were collected in the range 2q < 55.0 ° and 6073 independent reflections R_{int} = 0.179 were used in the structural analysis. R_1 = 0.1718 for F^2 > 2s (F^2), wR_2 = 0.4726 and GOF = 1.127 for F^2.

Crystal data for **1b** $C_{26}H_{18}Br_2Cu_2N_8$: T = 200(1) K: green, triclinic, space group P-1 (No. 2), Z = 1, a = 9.105(14), b = 12.40(2), c = 12.57(2) Å, a = 100.78(4), b = 96.00(3), g = 94.43(4), V = 1379(4) $Å^3$, d_{calcd} = 1.756 g cm^{-3}, m = 4.478 mm^{-1}. 13228 1eflections were collected in the range 2q < 55.0 ° and 6263 independent reflections R_{int} = 0.183 were used in the structural analysis. R_1 = 0.3495 for F^2 > 2s (F^2), wR_2 = 0.6973 and GOF = 1.476 for F^2.

Crystal data for **2** C26H18Br2Cu2N8: T = 200(1) K: green, monoclinic, space group $P2_1/c$ (No. 14), Z = 2, a = 6.382(2), b = 10.275(4), c = 18.954(7) Å, b = 93.034 (4)°, V = 1241.2(8) $Å^3$, d_{calcd} = 1.880 g cm^{-3}, m = 4.980 mm^{-1}. 11428 reflections were collected in the range 2q < 55.0° and 2813 independent reflections R_{int} = 0.031 were used in the structural analysis. R_1 = 0.0220 for F^2 > 2s (F^2), wR_2 = 0.0610 and GOF = 1.021 for F^2.

All non-hydrogen atoms were refined anisotropically for **1**, and **2**, except for some atoms of **1a** and **1b** that were refined isotropically. CCDC-704683 (**1**), CCDC-704684 (**1a**), CCDC-704681 (**1b**), and CCDC-704685 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/services/stucture_deposit/