Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information:

Directed formation of tri-connected Cu(I) coordination polymers

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1. Synthesis

All the reagents and solvents employed were commercially available and used without further purification. The C, H and N analyses were carried out with a Vario EL III elemental analyzer.

$[Cu_2(L_1)_3(CH_3CN)](BF_4)_2 \cdot H_2O$ (1) (L_1 = 2-diphenylphosphino-3-methyl pyridine, $C_{18}H_{16}PN$)

A mixture of $[Cu(CH_3CN)_4]BF_4$ (0.1807 g, 0.5737 mmol) and L_1 (0.2382 g, 0.8590 mmol) was refluxed in acetonitrile (10 mL) under nitrogen atmosphere for 1 h. After cooled down to room temperature, the solution was filtered. The filtrate was concentrated under reduced pressure and Et_2O (20 mL) was added to give a crude yellow solid **1** (0.3363 g, 97.85%). Slow evaporation of a mixture of CH_2Cl_2-CH_3OH (v:v = 2:1, 3 mL) containing the crude **1** (0.0214 g) afforded colorless crystals, which was washed by Et_2O and dried under vacuum (0.0153 g, 71.5%). Anal. Calcd for $Cu_2C_{56}H_{53}N_4P_3OB_2F_8$: C, 56.44; H, 4.48; N, 4.70. Found: C, 56.59; H, 4.28; N, 4.65. IR (KBr): 2927cm^{-1} (CH_3), 2271 cm^{-1} (C≡N), 1084 cm^{-1} (BF_4^-).

$[Cu_2(L_2)_3(H_2O)](BF_4)_2 \cdot 4CH_3OH$ (2) (L_2 = 2-diphenylphosphino-6-methyl pyridine, $C_{18}H_{16}PN$)

A mixture of $[Cu(CH_3CN)_4]BF_4$ (0.0767 g, 0.2435 mmol) and L_2 (0.1042 g, 0.3758 mmol) was refluxed in acetonitrile (6 mL) under nitrogen atmosphere for 1 h. After cooled down to room temperature, the solution was filtered. The filtrate was concentrated under reduced pressure and diethyl ether (20 mL) was added to give a crude yellow solid **2** (0.1240 g, 79.64%). Slow evaporation of 1.25 mL CH_2Cl_2-CH_3OH (v:v = 4:1) containing crude **2** (0.0097 g) afforded colorless crystals, which was washed by CH_3OH and dried under vacuum (0.0069 g, 71.1%). Due to the labile loss of CH_3OH and IR confirmation of the existence of CN^-, the elemental analysis was calculated based on the formula $[Cu_2(L_2)_3(H_2O)](BF_4)_2 \cdot H_2O \cdot CH_3CN$: C, 55.60; H, 4.63; N, 4.58. Found: C, 55.33; H, 4.31; N, 4.35. IR (KBr): 2929cm^{-1} (CH_3), 2271 cm^{-1} (C≡N)， 1083 cm^{-1} (BF_4^-).

$[Cu_2(L_1)_2(bipy)_3](BF_4)_2$ (3)

Reaction of **1** (0.0050 g, 0.0042 mmol) with 4,4-bipyridine (bipy, 0.0025 g, 0.016 mmol) in a solution of CH_2Cl_2-CH_3OH (2.5 mL, v:v = 4:1) afforded a yellow solution, which was evaporated slowly at room temperature, yellow-greenish needle-like crystals of **3** were obtained after 1 d (0.0019 g, 51.3%). Anal. Calcd for **3**·$2H_2O$: C, 58.29; H, 4.45; N, 8.24. Found: C, 57.94; H, 4.35; N, 8.27. IR (KBr): 2924cm^{-1} (CH_3), 1083 cm^{-1} (BF_4^-).

$[Cu_2(L_2)_2(bipy)_3](BF_4)_2$ (4).

Reaction of **2** (0.0103 g, 0.0080 mmol) with bipy (0.0047 g, 0.0301 mmol) in a solution of CH_2Cl_2-CH_3OH (2 mL, v:v = 1:1) afforded a yellow solution, which was evaporated slowly at room temperature, yellow-greenish block crystals of **4** were obtained after 1 d (0.0043 g, 58.5%). Anal. Calcd for **4**·$CH_3OH \cdot 3H_2O$: C, 57.07; H, 4.72; N, 7.95. Found: C, 57.12; H, 4.68; N, 7.99. IR (KBr): 2924 cm^{-1} (CH_3), 1060 cm^{-1} (BF_4^-).

2. X-ray experimental details

Intensity data were collected on an Oxford Gemini S Ultra system (Mo K_α). Data collections were conducted at 173 K. Data reductions were performed using CrysAlis RED program. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms (except for water molecules) using SHELXL-97. Hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 x Ueq of the attached atom (1.5 x Ueq for methyl hydrogen atoms). Due to the large number of disordered counterions and solvent molecules in **3** and **4**, SQUEEZE routine in PLATON was employed in the structural refinement of **3** and **4**.

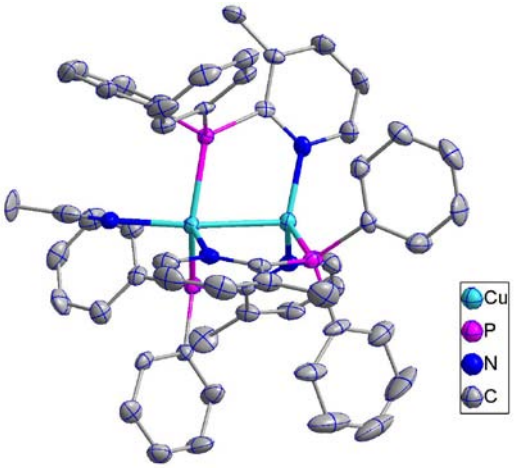

Figure S1. Molecular structure of the cationic part of $[Cu_2(L_1)_3(CH_3CN)](BF_4)_2 \cdot H_2O$ (**1**). (HT configuration).

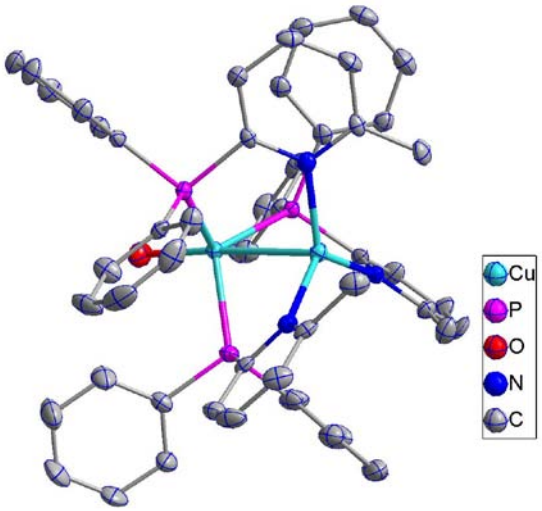

Figure S2. Molecular structure of the cationic part of $[Cu_2(L_2)_3(H_2O)](BF_4)_2 \cdot 4CH_3OH$ (**2**) (HH configuration).

3. Thermogravimetric analysis (TGA)

TGA were collected on SDTQ 600 device under N_2 atmosphere with the temperature range of 25-1000°C.

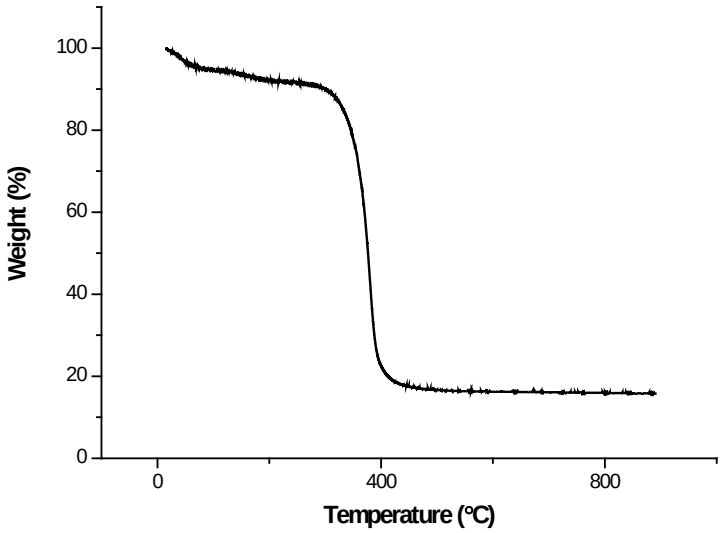

Figure S3. TGA curve of **1**.

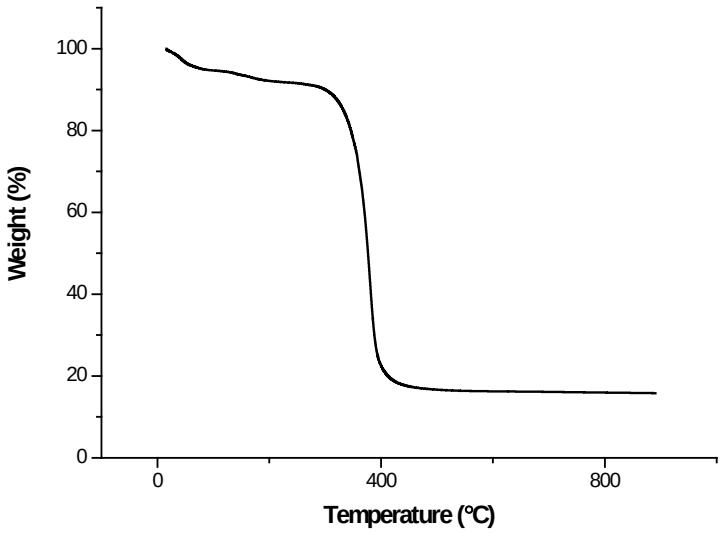

Figure S4. TGA curve of **2**.

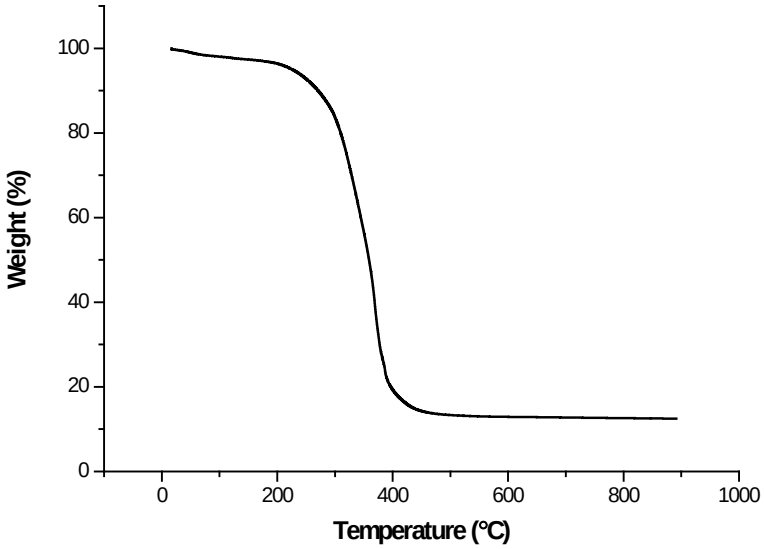

Figure S5. TGA curve of **3**.

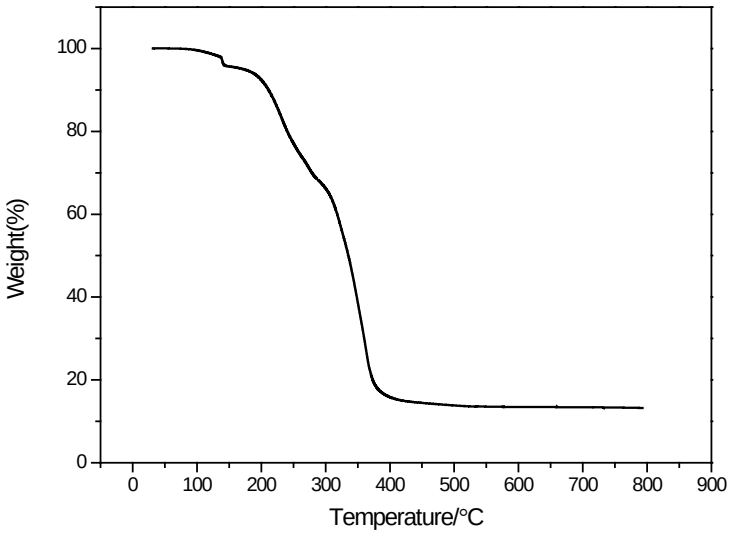

Figure S6. TGA curve of **4**.

4. UV-Vis diffuse reflectance spectroscopy

UV-Vis diffuse reflectance spectra were recorded on Cary 5000 UV-VIS-NIR spectrometer in the range of 800–200 nm.

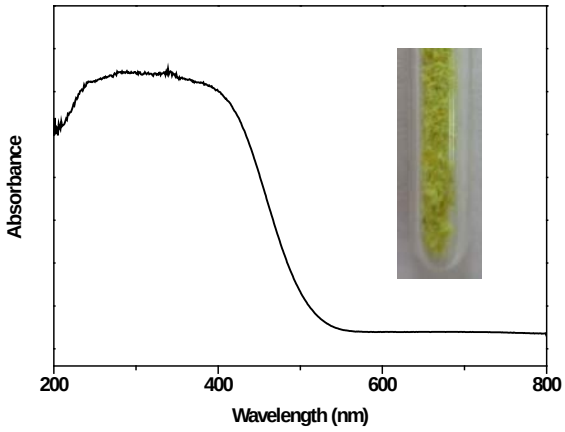

Figure S7. UV-Vis diffuse reflectance spectroscopy of **3** in the solid-state.

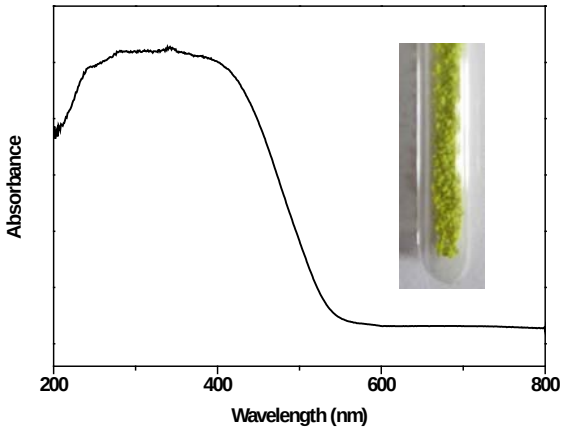

Figure S8. UV-Vis diffuse reflectance spectroscopy of **4** in the solid-state.

5. X-ray powder diffraction

X-ray powder spectra were recorded on Panalytical diffractometer with CuK_α graphite monochromatized radiation operating at 40kV/30mA and equipped with a position-sensitive detector with flat sample geometry.

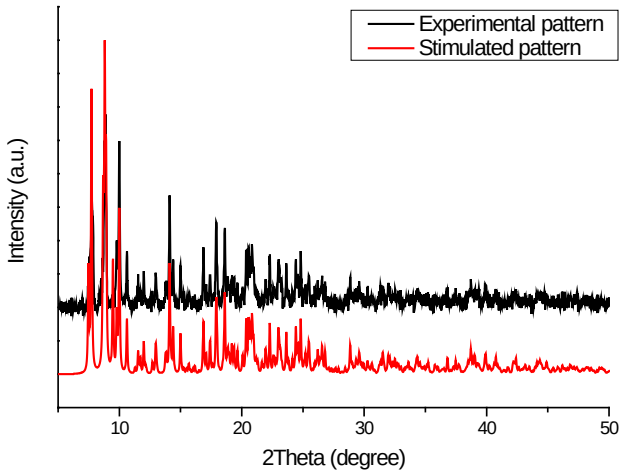

Figure S9. Measured and simulated powder X-ray diffraction patterns of **1.**

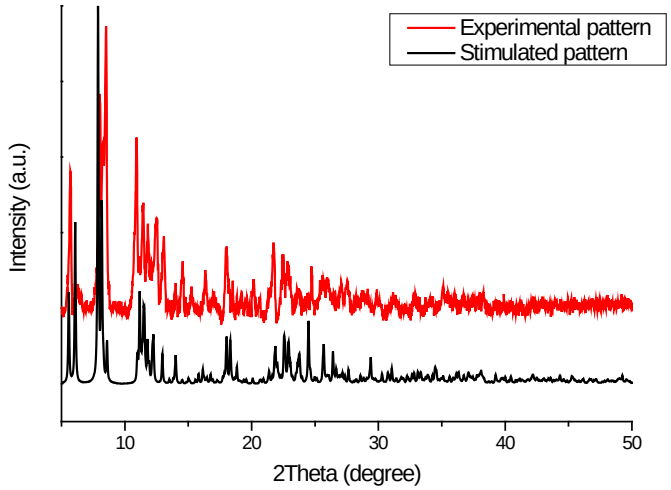

Figure S10. Measured and simulated powder X-ray diffraction patterns of **2**.

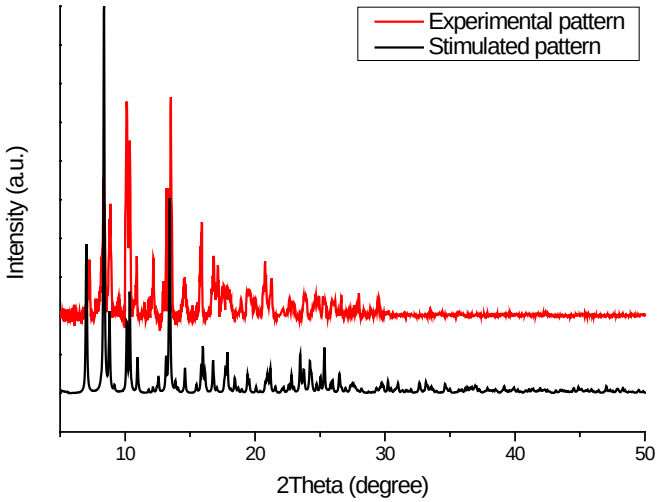

Figure S11. Measured and simulated powder X-ray diffraction patterns of **3**.

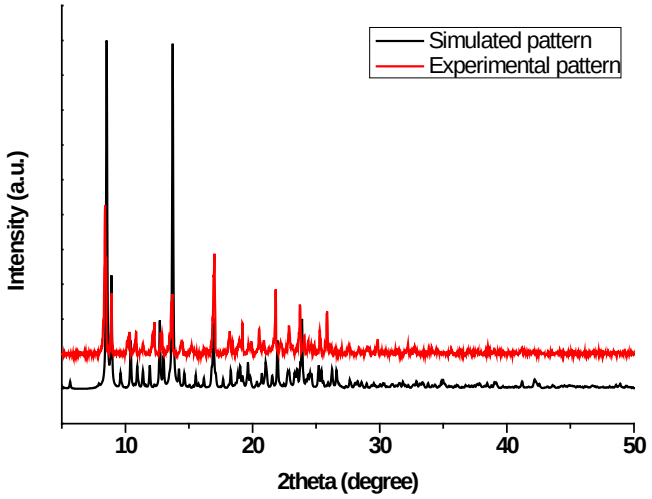

Figure S12. Measured and simulated powder X-ray diffraction patterns of **4**.