## Supporting Information

## A cage-based cationic body-centered tetragonal metal-organic framework: single-crystal to single-crystal transformation and

## selective uptake of organic dyes

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## **Experimental Section**

**Materials and Methods.** The ligands Hcpt were prepared by the literature method.<sup>1</sup> Other chemicals purchased were of reagent grade and used without further purification. Analyses for C, H, and N were carried out on a Perkin-Elmer 240 CHN elemental analyzer. IR was recorded in the range 400 - 4000 cm<sup>-1</sup> on a Bruker TENOR 27 spectrophotometer using KBr pellets. Powder X-ray diffraction measurements were recorded on a Rigaku D/Max-2500 X-ray diffractometer using Cu K $\alpha$  radiation. TGA were performed on a Labsys NETZSCH TG 209 Setaram apparatus with a heating rate of 10 °C/min in nitrogen atmosphere.

Synthesis of {[(Cu<sub>4</sub>Cl)(CPT)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]·3NO<sub>3</sub>·5NMP·3.5H<sub>2</sub>O}(1). A mixture of HCPT (20 mg, 0.1 mmol), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (24 mg, 0.1 mmol) was dissolved in a mixed solvent of NMP (2 mL), MeOH (1 mL) solution in a screw-capped vial. After addition of 10  $\mu$ L of HCl (3M, aq), the vial was heated at 80 °C for 48 h under autogenous pressure. Green polyhedral crystals were obtained after filtration, washed with NMP and MeOH in sequence, and dried in air. Yield: 45%. IR (KBr dicks, selected bands, cm<sup>-1</sup>): 3397w, 1677s, 1554s, 1384s, 1261m, 1016m, 779m. Elemental analysis found (calcd) for C<sub>61</sub>H<sub>84</sub>ClCu<sub>4</sub>N<sub>20</sub>O<sub>29.5</sub>: C, 39.19(39.41); H, 3.99(4.55); N, 14.95(15.07). IR (KBr disks, selected bands, cm<sup>-1</sup>): 3449m, 3116w, 1615s, 1558s, 1401s, 1317m, 1185s, 1077s, 835m, 775s, 632s. The crystals of 1-MeOH {[(Cu<sub>4</sub>Cl)(CPT)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]·3NO<sub>3</sub>·7MeOH}<sub>n</sub> were obtained by soaking 1 in absolute anhydrous MeOH for seven days. IR (KBr disks, selected bands, cm<sup>-1</sup>): 3386w, 1597s, 1521s, 1382s, 1106m, 1016m, 790s. Elemental analysis found (calcd) for C<sub>43</sub>H<sub>60</sub>ClCu<sub>4</sub>N<sub>15</sub>O<sub>28</sub>: C, 33.82(33.87); H, 4.22(3.97); N, 13.67(13.78).

X-ray Single Crystal Analysis. Data was collected on an Agilent Technologies SuperNova Single Crystal Diffractometer at different temperatures equipped with graphitemonochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package.<sup>2</sup> The CPT ligand is disordered over two positions (occupancy: 0.5:0.5), this is due to the fact that triazolate and carboxylate part of the ligand show similar coordination models and therefore can substitute each other at the given site. Additionally, the disorder of triazolate group leads to the carbon and nitrogen atoms share the same crystallographic positions with partial occupancies in 1. The deciphered structure is described in the main text of manuscript as shown in Fig 1. All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. For the highly disordered nature of the solvents, they could not be finely made out in the refinement, so the SQUEEZE<sup>3</sup> routine of PLATON<sup>4</sup> was applied to remove the diffraction contributed from the highly disordered guest molecules. The chemical formulas were determined by the combination of the crystal data, TGA, and elemental analysis. Crystal data for 1: C<sub>61</sub>H<sub>84</sub>ClCu<sub>4</sub>N<sub>20</sub>O<sub>29.5</sub>, *M*= 1859.09, tetragonal, space group *I*4/*mmm* (no. 139), *a* = 13.9590(3) Å, *b* = 13.9590(3) Å c = 20.0475(10) Å, V = 3906.3(2) Å<sup>3</sup>, Z = 2, T = 139(3) K, 8586 reflections measured, 1026 unique ( $R_{int} = 0.0698$ ,  $R_{sigma} = 0.0412$ ) which were used in all calculations. 88 parameters refined and 39 restraints used (The DFIX, DELU, ISOR, EXYZ and SIMU commands were used to refine the disordered CPT ligand and the highly disordered  $NO_3^-$  ions). The final  $R_1$ was 0.0564 (I >  $2\sigma(I)$ ) and  $wR_2$  was 0.1676 (all data). The goodness of fit on  $F^2$  was 1.134. Crystal

data for **1-MeOH**: C<sub>43</sub>H<sub>60</sub>ClCu<sub>4</sub>N<sub>15</sub>O<sub>28</sub>, M= 1524.67, tetragonal, space group P4/mnc (no. 128), a = 13.3088(4) Å, b = 13.3088(4) Å, c = 20.4387(8) Å, V = 3620.2(3) Å<sup>3</sup>, Z = 2, T = 129(2) K, 26058 reflections measured, 1653 unique ( $R_{int} = 0.1002$ ,  $R_{sigma} = 0.0403$ ) were used in all calculations. 149 parameters refined and 57 restraints used (The DFIX, DELU, ISOR, FLAT and SIMU commends were used to refine the disordered CPT ligand and the highly disordered NO<sub>3</sub><sup>-</sup> ions). The final  $R_1$  was 0.0632 (I > 2 $\sigma$ (I)) and  $wR_2$  was 0.1754 (all data). The goodness of fit on  $F^2$  was 1.168. CCDC-1020384 & 1020383 (1 and 1-MeOH) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.



Fig. S1. The schematic representation of the connection of the cages of 1.



Fig. S2. The schematic representation of 1D channels along *a* axis and *b* axis.



Fig. S3. The schematic representation of the  $NO_3^-$  locate in the 1D channels of 1.





Thermogravimetric analysis (TGA) for the as-synthesized **1** shows a continuous weight loss of 34.8% upon heating because of the strong interaction among the solvent molecules and the framework, as well as the high boiling point of NMP (calcd 33.9%). The post residue of 19.6% is mainly CuO (calcd 18.8%). **1-MeOH** shows a weight loss of 15.4% from 25 to 92 °C, corresponding to the loss of seven lattice MeOH molecules (calcd 14.7%). The weight loss of 4.4% from 94 °C to 190 °C is attributed to the loss of four coordinated water molecules (calcd 4.2%). Further sharp weight loss occurred from 196 °C, indicating collapse of whole framework.



**1 1-MeOH Fig. S5**. The location of the nitrate ions in 1 and 1-MeOH.



Fig. S6. Powder X-ray diffraction (PXRD) patterns.



Fig. S7. Dye uptake of 1 in excess MeOH solution of MO.



Fig. S8. The MO release of 1 a) in MeOH solution of NaCl. b) in MeOH solution.

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