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SUPPLEMENTARY MATERIAL

Guest exchange in porous cucurbit[6]uril-based metal–organic rotaxane framework probed by NMR and X-ray crystallography

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Experiment Section

Materials and Physical Measurements.

$[PR44]^{2+}\cdot 2[NO_3]^-$ and CB[6] were synthesized according to references.[1,2] Other purchased chemicals were used without further purification. ^1H and ^{19}F NMR spectra were recorded on Bruker 600MHz instrument. Single-crystal X-ray diffraction data were recorded by using a Bruker Apex CCD diffractometer with graphite-monochromated Mo *Kα* radiation (λ = 0.71069 Å) at 173K. The IR spectra were recorded using KBr pellets in the range of 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TG-7 analyzer over the temperature 20–800 °C in a nitrogen-gas atmosphere with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (XRD) measurements were recorded on a Rigaku/Dmax 2200 pc diffractometer with Cu-Kα (λ = 1.5418 Å) radiation in the range 5–50°.

Preparationof $[PR44]^{2+}\cdot 2[PF6]^-$.

$[PR44]^{2+}\cdot 2[PF6]^-$ was obtained by ion exchange in KPF_6 saturated aqueous solution water. 0.5g of $[PR44]^{2+}\cdot 2[NO_3]^-$ was dissolved in 10 mL of deionized water and stirred at ambient condition for 10 min. Then the clear solution was dropwise added to a saturated aqueous solution (10 mL) containing KPF_6 (0.93 g, 5 mmol) under continuous stirring. After stirring for 1h at ambient condition, the white precipitate was collected by filtration and washed twice with deionized water. The product was dried at 70 ºC overnight (85.7% yield based on $[PR44]^{2+}\cdot 2[NO_3]^-$).

Preparation of $[Cu_2(PR44)_{0.5}(BDC)_2Cl]\cdot 3DMF$ (MORF-1)

A mixture of H_2BDC (0.0335g, 0.18mmol), $[PR44]^{2+}\cdot 2[PF_6]^-$ (0.0364g,0.02mmol) and $CuCl_2\cdot 2H_2O$ (0.0382 g, 0.22mmol) was dissolved in 4 mL of DMF. The mixture was sealed into a 18mL Teflon-lined stainless steel container and heated at 100 ºC for 3 days and then cooled down to room temperature. Blue crystals of MORF-**1** were collected and washed with DMF and dried in air to give the product (yield: 37.5 % based on Cu). Elemental analysis calc. for $C_{51}H_{59}ClCu_2N_{17}O_{17}$ (%): Calc: C 45.55, H

4.42, N 17.71; Found: C 45.79, H 4.63, N 17.84.

X-ray Crystallographic Analysis

X-ray single-crystal data collection of MORF-**1** and benzene-MORF-**1** were obtained on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromator using Mo Kα radiation (λ = 0.71073 Å) at 173 K. A multiscan technique was used to perform adsorption corrections. Both the crystal structures were solved using direct methods and refined using the full matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXL-2014 program.[3] All hydrogen atoms were located in calculated positions and refined isotropically. In MORF-**1**, the solvent molecules were highly disordered, so the SQUEEZE routine of PLATON to remove the diffused electron densities. The formula was determined by the combination of elemental analysis, TGA data and the SQUEEZE results. In benzene-MORF-**1**, the guest benzene molecules were disordered and split over two sites with occupancy of 0.5. The crystallographic data of MORF-**1** and benzene-MORF-**1** have been deposited in the Cambridge Crystallographic Data Center as supplementary publication with CCDC 1835828 and 1835829.

Table S1. Crystallographic data and structure refinement summary for MORF-**1** and benzene-MORF-**1**.

	MORF-**1**	benzene-MORF-**1**
Empirical formula	$[Cu_2(PR44)_{0.5}(BDC)_2Cl]\cdot 3DMF$	$[Cu_2(PR44)_{0.5}(BDC)_2Cl]\cdot 2.5Ph$
Mr	1344.68	1316.63
T/K	173K	173K
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnnm*	*Pnnm*
a/*Å*	16.418(7)	16.261(11)
b/*Å*	29.213(13)	29.33(2)
c/*Å*	14.052(5)	14.304(9)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
V/Å^3	6739(5)	6821(8)
Z	4	4
Dc/mg m^{-3}	1.325	1.282
μ/mm^{-1}	0.745	0.730
measured reflections	17592	27618
independent reflections	6189	6141
data/restraints/parameters	6189 / 0 / 346	6141/699/470
goodness-of-fit on F^2	1.013	1.081
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0402	0.0573
$wR_2{}^b$ (all data)	0.1188	0.1756

$^aR_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^bwR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o{}^2)]^{1/2}$.

Table S2. Selected bond length (Å) for MORF-**1**.

Cu(1)-O(2)	1.9764(19)	Cu(2)-O(4)	1.965(5)
Cu(1)-O(3)	1.977(2)	Cu(2)-O(1)	1.9615(19)
Cu(1)-Cl(1)	2.3863(14)	Cu(2)-N(1)	2.173(3)

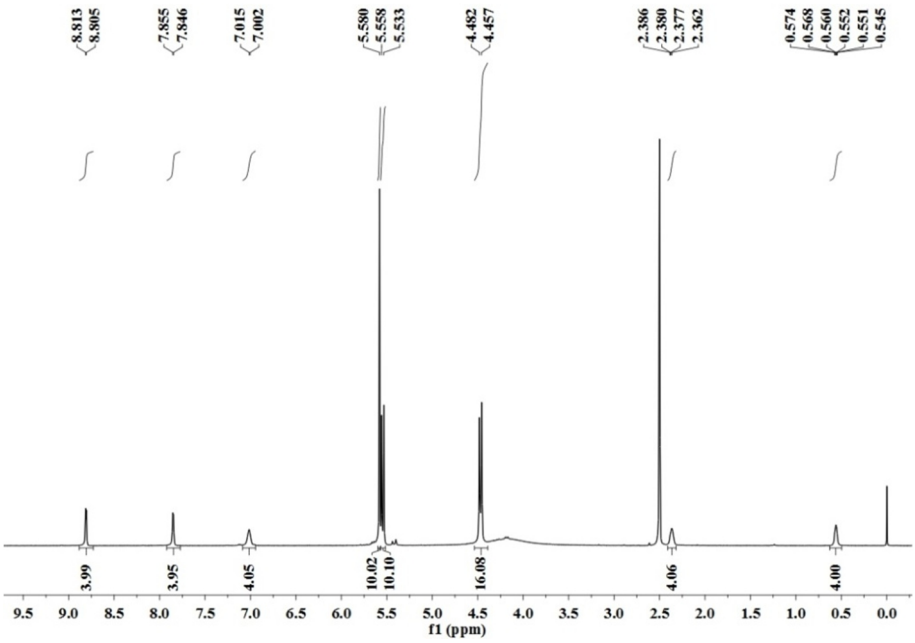

Fig. S1 ^{1}H NMR spectrum (600 MHz, DMSO-d^6, 25 °C) of $[PR44]^{2+}\cdot 2[PF6]^{-}$.

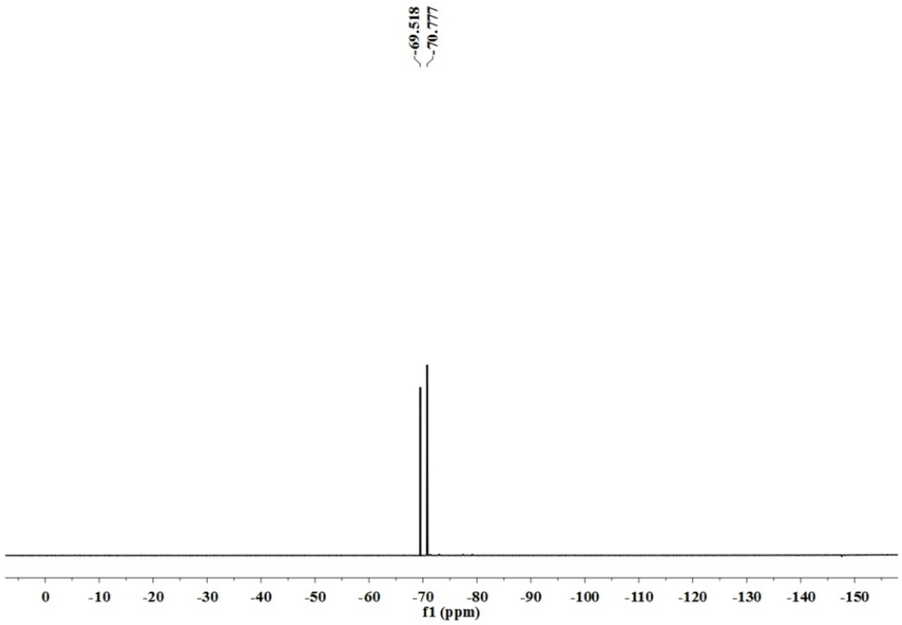

Fig.S2 ^{19}F NMR spectrum (600 MHz, DMSO-d^6, 25 °C) of $[PR44]^{2+}\cdot 2[PF6]^{-}$.

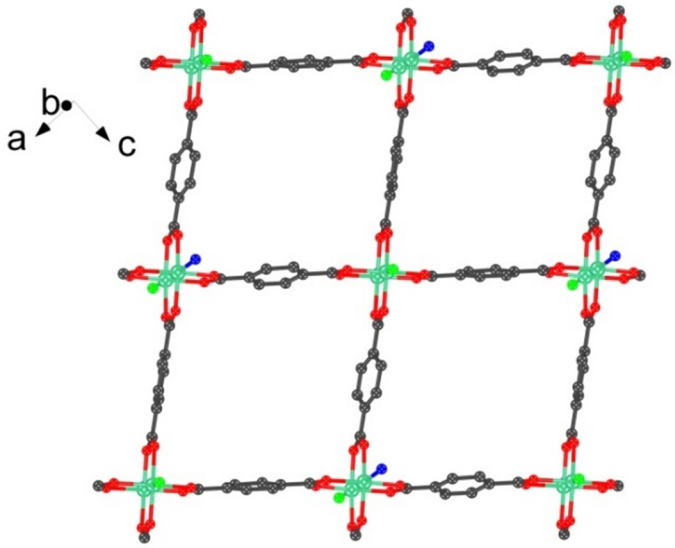

Fig. S3 Ball-and-stick representation of 2D layers formed by the binuclear copper clusters and BDC ligands in MORF-**1**.

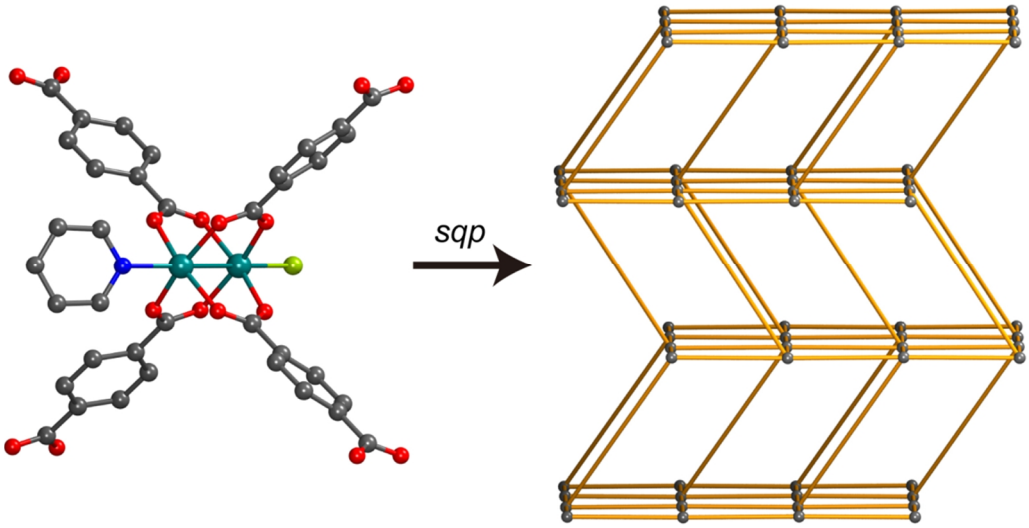

Fig. S4 The 5-connected node based on binuclear Cu cluster and the ***sqp*** topology of MORF-**1.**

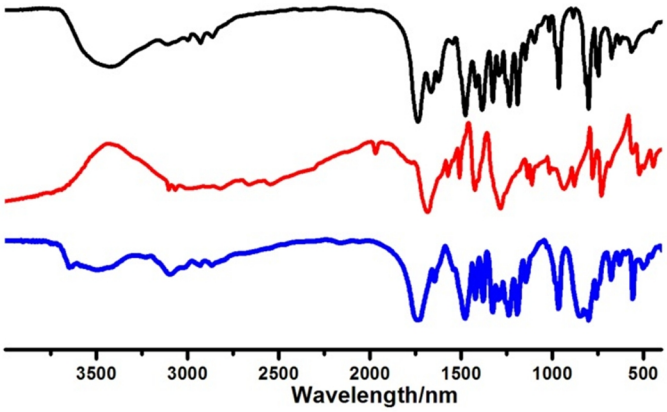

Fig. S5 The FT-IR curves for MORF-**1** (black), [PR44]·2[PF_6] (red) and H_2BDC (blue).

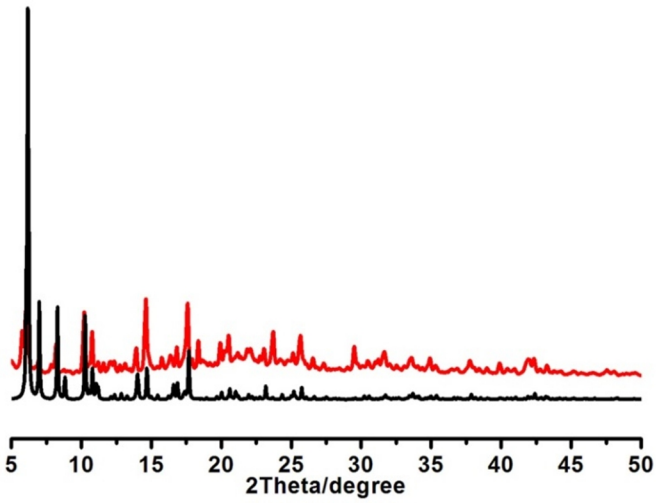

Fig. S6 X-Ray powder diffraction patterns of simulated (black) and as-synthesized MORF-**1**(red)**.**

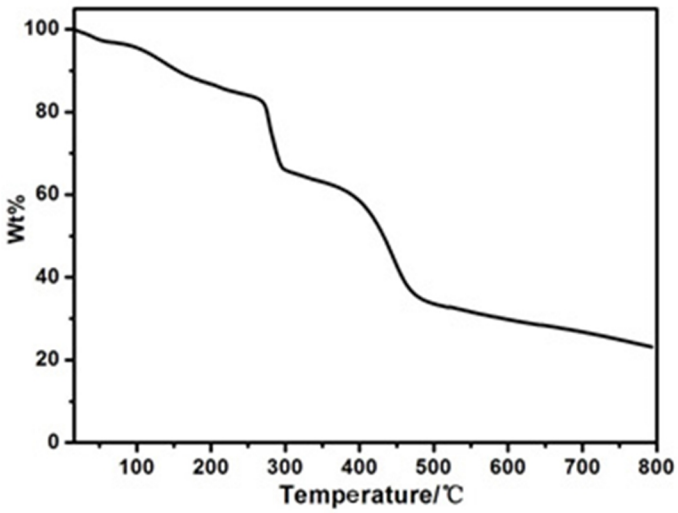

Fig. S7 TG curve of MORF-**1**.

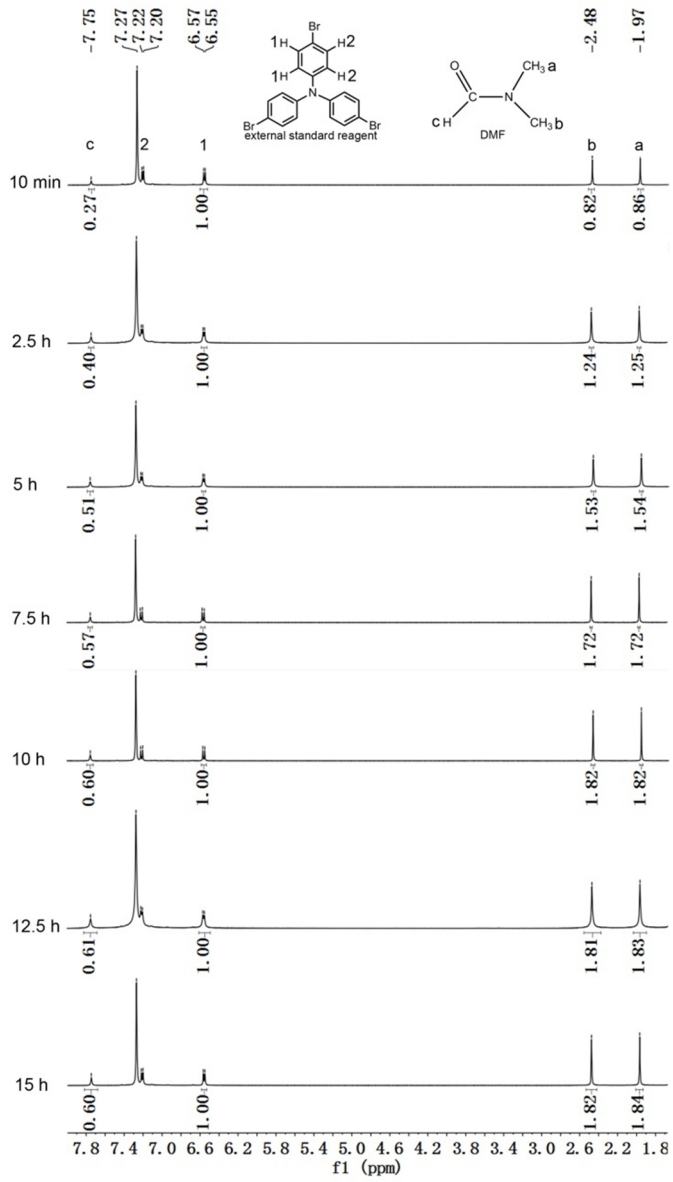

Fig. S8 ^{1}H NMR spectroscopy monitor the amount of DMF exited from MORF-**1**.

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2 D. Bardelang, K. A. Udachin, D. M. Leek, J. C. Margeson, G. Chan, C. I. Ratcliffe and J. A. Ripmeester, *Cryst. Growth Des.*, 2011, **11**, 5598-5614.

3. Sheldrick, G. M. (2015). *Acta Cryst.* C 71 , 3–8.