Electronic Supplementary Information

Rational Design of Flu-Type Heterometallic Cluster-Based Zr-MOF

Yan-Xi Tan[a], Xue Yang[a], Bei-Bei Li[a,b], Daqiang Yuan[a,*]

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002, China, E-mail: ydq@fjirsm.ac.cn*
[b] *University of Chinese Academy of Sciences, Beijing, 100049, China.*

1. Materials and general methods

Commercially available reagents were used as received. Thermal gravimetric analysis data were obtained with a NETZSCH STA 449C analyzer. All samples and reference (Al_2O_3) were enclosed in a platinum crucible and were heated from 25 ^oC to 820 ^oC at a rate of 10 $^oC/min$ under a N_2 atmosphere. X-ray Powder diffraction (XRPD) patterns were collected on a Rigaku Mini 600 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) at a scanning rate of 5 $^o/min$ for 2θ ranging from 4 ^{o} to 40 ^{o}. Simulated XRPD patterns were calculated using Mercury from corresponding single-crystal structural models. Routine ^1H NMR spectra were recorded on a Bruker Avance 400 (400.1 MHz for ^1H NMR). The deuterated solvents used are indicated in the experimental part. GC-FID analysis were carried out on an Agilent Technologies 7820A GC system equipped with an Agilent J&W GC HP-5 capillary column (30 m × 320 μm × 0.25 μm film thickness).

Synthesis of $[Zr_6(\mu_3\text{-}OH)_8(OH)_8][Cu_4I_4(Ina)_4]_2\cdot x$guest (1). CuI (0.190 g), isonicotinic acid (0.123 g), benzoic acid (1.5 g), 0.5 mL zirconium *n*-propoxide, 6 mL DMF and 3 mL EtOH in a 20 mL Teflon-lined stainless steel vessel was stirred for 30 minutes, and then sealed and heated in an oven at 100 ^oC for 12 hours. The vessel was taken out and naturally cooled to room temperature. After washed with fresh DMF, yellow octahedral crystals were obtained in pure phase (Yield: 220 mg, 38%, based on CuI).

2. X-ray Crystallography

The diffraction data of **1** were collected on a SuperNova diffractometer equipped with a copper micro-focus X-ray sources (λ = 1.5406 Å) and an Atlas CCD detector under 240 K. Empirical absorption correction used spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm. The structure was solved by direct methods and refined with full-matrix least-squares technique using *SHELXL*-2014.[S1] All non-hydrogen atoms were refined with anisotropic displacement parameters. The diffused electron densities resulting from these residual solvent molecules were removed from the data set using the *SQUEEZE* routine of *PLATON* and refined further using the data generated.[S2] The contents of the solvent region are not represented in the unit cell contents in the crystal data.

Crystal data of 1: $C_{24}H_{24}Cu_4I_4N_4O_{16}Zr_3$, M = 1659.89, space group $I4/mmm$, a = 17.5411(5) Å, c = 34.6975(15) Å, V = 10676.1(8) Å^3, Z = 4, D_c = 1.033 g/cm^3, F_{000} = 3088, SuperNova, Dual, Cu at zero, Atlas, CuKα radiation, λ = 1.54184 Å, T = 240.0(1) K, $2\theta_{max}$ = 140.1°, 8666 reflections collected, 2805 unique (R_{int} = 0.0234). Final $GooF$ = 1.061, $R1$ = 0.0343, $wR2$ = 0.0967, R indices based on 2483 reflections with ($I > 2\sigma(I)$) (refinement on F^2).

3. GCMC simulation

The Grand canonical Monte Carlo (GCMC) simulations were performed using RASPA2 code following the reported routine. LJ parameters for **1** atoms were taken from the DREIDING force field except for the Zr atom; its parameters were taken from UFF. Partial charges for the atoms in MOF were derived from DFT calculations. Nitrogen molecules were modeled using the TraPPE force field. All GCMC simulations included a 10000-cycle equilibration period followed by a 10000-cycle production run. A cycle consists of n Monte Carlo steps; where n is equal to the number of molecules (which fluctuates during a GCMC simulation). All simulations included random insertion/deletion, translation and rotation moves of molecules with equal probabilities. Atoms in MOF were held fixed at their crystallographic positions. An LJ cutoff distance of 12.8 Å was used for all simulations. The Ewald sum technique was used to compute the electrostatic interactions. Four unit cells of **1** were used for the simulations. N_2 isotherms were simulated at 77.35 K up to 1 bar.

4. Typical experimental procedure for catalysis

The styrene oxide ring-opening reaction was carried out in a boil-proof micro-centrifuge tube (10 mL). Into the micro-centrifuge tube, styrene oxide (92 μL, 0.8 mmol), mono alcohols (3 mL) and 1-bromo-3,5-difluorobenzene (40 μL, 0.36 mmol) were added and mixed by swirling for 5 s. After adding catalyst **1** (1 mol%, calculated based on the Zr_6 cluster) into the mixture, the micro-centrifuge tube was then sealed and put onto oil bath under continuous stirring (temperature: 55 °C, agitation speed: 800 rpm). Aliquots were prepared by withdrawing 15 μL liquid from the reaction and diluted with 1.5 mL dichloromethane. For recycling test, catalyst **1** was activated by soaking in 3 mL fresh alcohol under 60 °C for one day.

5. TGA curves

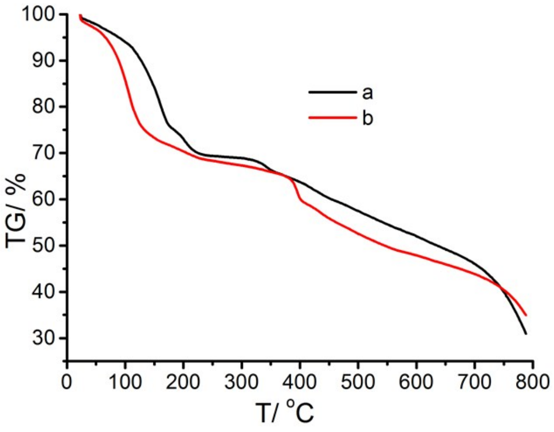

Figure S1. TGA curves of **1** (a) and $CHCl_3$-exchanged **1** (b).

6. PXRD patterns

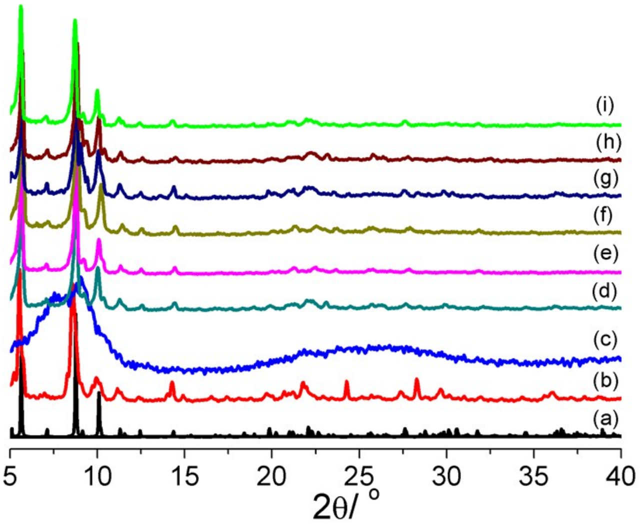

Figure S2. PXRD of simulated one (a), as-synthesized **1** (b), **1** after gas sorption (c) and the post-catalysis **1** under ethanol (d-f, three cycles), n-propyl alcohol (g), isopropyl alcohol (h) and 2-phenylethanol (i).

7. Gas sorption

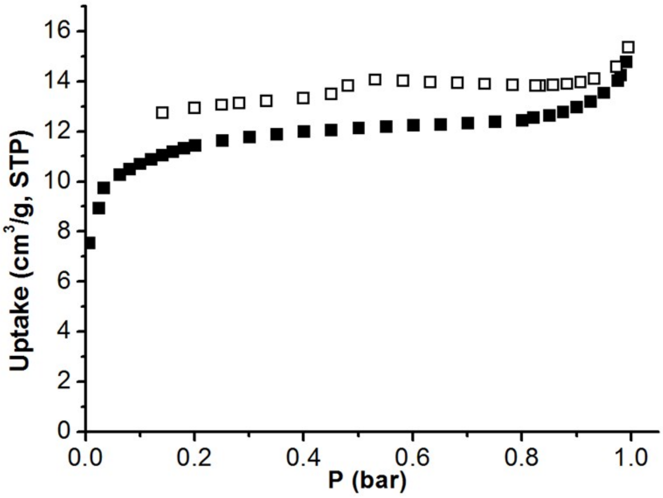

Figure S3. N_2 sorption isotherm at 77 K for **1**.

8. Gas chromatography spectrograms

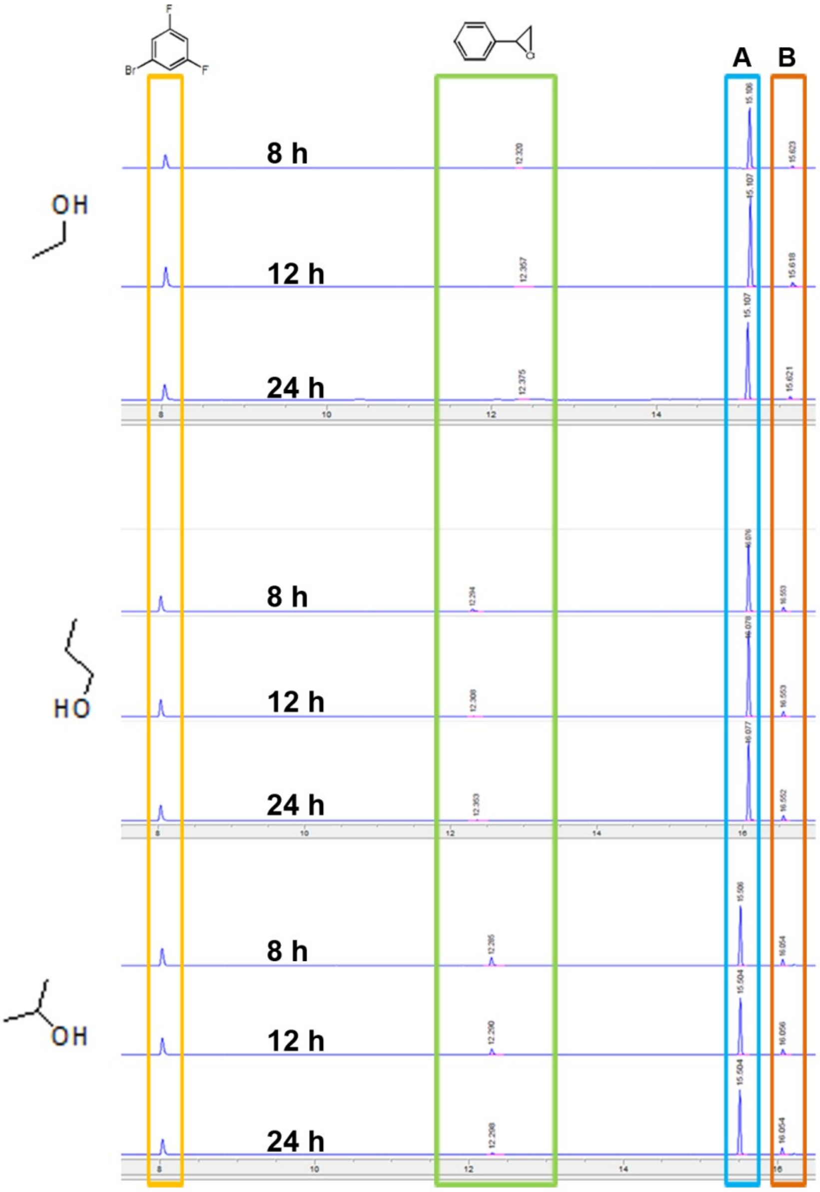

Figure S4. Gas chromatography (GC) signals of the styrene oxide ring-opening reaction with different monohydric alcohols when using **1** as the catalyst.

9. ^{1}H NMR Spectra

2-ethoxy-2-phenylethanol

^{1}H NMR (400 MHz $CDCl_3$): δ 7.40-7.31 (m, 5H), 4.47-4.42 (m, 1H), 3.69-3.60 (m, 2H), 3.55-3.52 (m, 1H), 3.51-3.41 (m, 1H), 2.38 (S, 1H), 1.26-1.22 (t, 3H).

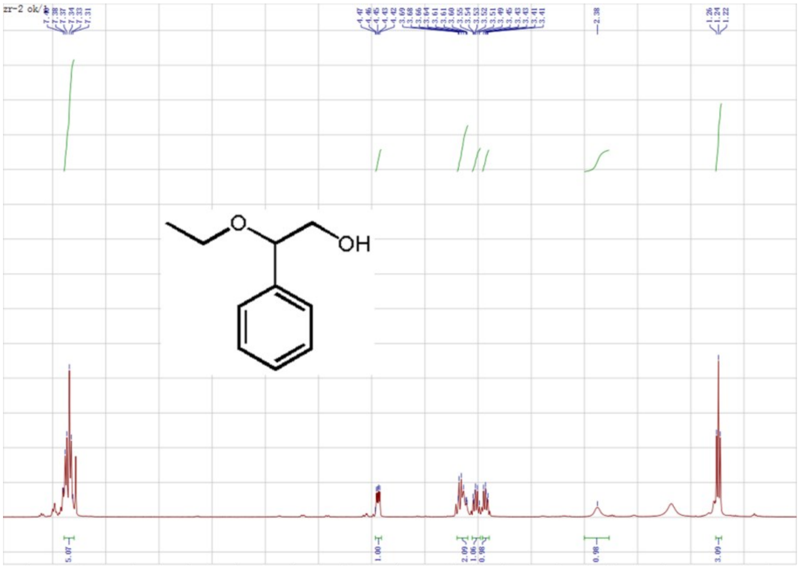

Figure S5. ^{1}H NMR spectrum of 2-ethoxy-2-phenylethanol.

2-ethoxy-2-phenylethanol

^{1}H NMR (400 MHz $CDCl_3$): δ 7.40-7.30 (m, 5H), 4.44-4.41 (m, 1H), 3.71-3.60 (m, 2H), 3.45-3.41 (m, 1H), 3.39-3.30 (m, 1H), 2.41 (S, 1H), 1.67-1.62 (m, 2H), 0.96-0.39 (t, 3H).

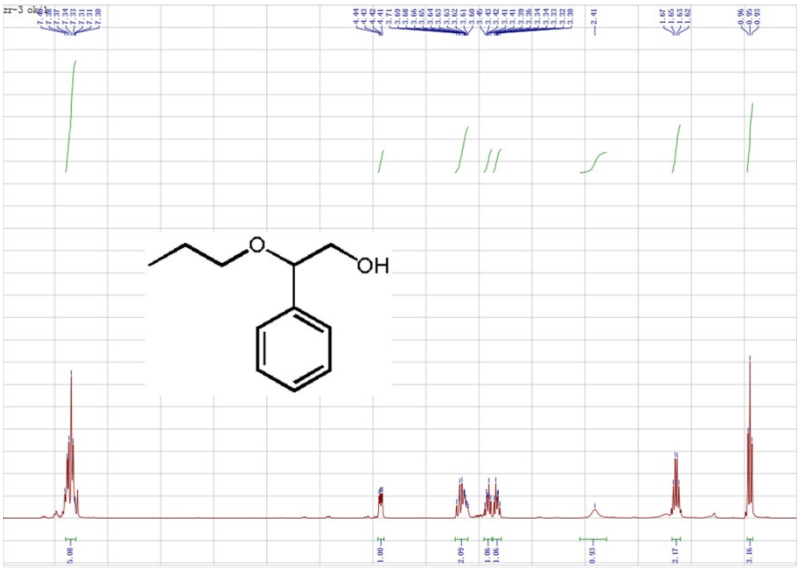

Figure S6. ^{1}H NMR spectrum of 2-ethoxy-2-phenylethanol.

2-isopropoxy-2-phenylethanol

^{1}H NMR (400 MHz $CDCl_3$): δ 7.40-7.31 (m, 5H), 4.58-4.52 (m, 1H), 3.66-3.57 (m, 3H), 2.37 (S, 1H), 1.22-1.14 (m, 6H).

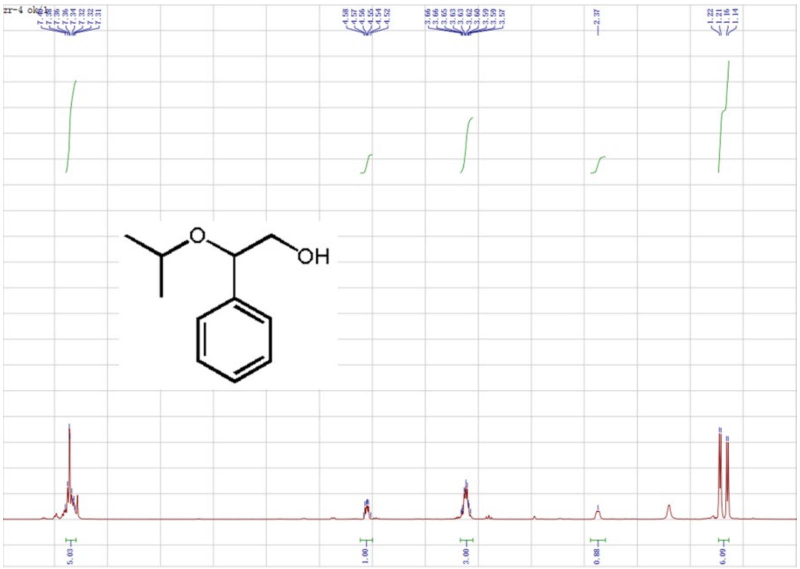

Figure S7. ^{1}H NMR spectrum of 2-isopropoxy-2-phenylethanol.

Ref

[S1] G. M. Sheldrick, *Acta crystallographica. Section C* **2015**, *71*, 3-8.

[S2] A. L. Spek, *Acta crystallographica. Section C* **2015**, *71*, 9-18.