## Electronic Supplementary Information

# A Highly Porous Metal-Organic Framework for Large Organic Molecule Capture and Chromatographic Separation

Pei-Zhou Li,<sup>†a</sup> Jie Su,<sup>†b</sup> Jie Liang,<sup>†a</sup> Jia Liu,<sup>a</sup> Yuanyuan Zhang,<sup>a</sup> Hongzhong Chen<sup>a</sup> and Yanli Zhao<sup>\*a,c</sup>

<sup>a</sup>Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, 637371, Singapore E-mail: zhaoyanli@ntu.edu.sg <sup>b</sup>Berzelii Centre EXSELENT on Porous Materials and Inorganic and Structural Chemistry, Department of Materials and Environmental Chemistry, Stockholm University, 106 91 Stockholm, Sweden <sup>c</sup>School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

<sup>†</sup>These authors contributed equally to this work.

\*Corresponding author.

#### **General information**

All starting materials are commercially available and were used as received unless specifically mentioned: *tert*-butyl 4-aminobenzoate ( $\geq$ 98%, Sigma-Aldrich), copper (II) sulphate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O, 99%, Alfa Aesar), N,N'-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), hydrochloric acid (HCl, 37w%, MSR), sodium *L*-ascorbate ( $\geq$ 98%, Sigma-Aldrich), sodium azide (NaN<sub>3</sub>,  $\geq$ 99.5%, Sigma-Aldrich), sodium nitrite (NaNO<sub>2</sub>,  $\geq$ 97%, Sigma-Aldrich), 1,3,5-triethynylbenzene (97%, Sigma-Aldrich), and zinc(II) nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%, Sigma-Aldrich).

<sup>1</sup>H NMR measurements were conducted on a JEOL ECA400SL NMR spectrometer at ambient temperature. All <sup>1</sup>H NMR spectra were reported as chemical shift  $\delta$  in units of parts per million (ppm) downfield with reference to deuteratred solvent (2.50 ppm for DMSO-*d*<sub>6</sub> and 7.26 ppm for CDCl<sub>3</sub>) or TMS (0.00 ppm). Multiplicities were presented as: s (singlet); d (doublet); t (triplet); and m (multiplet). Coupling constant *J* values were expressed in Hz and the number of protons was expressed as *n*H. <sup>13</sup>C NMR spectra were obtained from a JEOL ECA400SL NMR spectrometer at ambient temperature. Spectra were reported as chemical shift  $\delta$  in units of parts per million (ppm) downfield with reference to deuteratred solvent (39.81 ppm for DMSO-*d*<sub>6</sub> or 77.16 ppm for CDCl<sub>3</sub>-*d*<sub>1</sub>). High resolution mass spectra (HRMS) were carried out on a Waters Q-tof Premier mass spectrometry.

Single crystal X-ray diffraction measurements were performed on a SuperNova X-ray Diffraction System from Agilent Technologies. Powder X-ray diffraction (PXRD) data were collected at 40 keV, 15 mA on a Rigaku Miniflex 600 benchtop analyzer using Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å) over 2 $\theta$  range of 2.0° - 40° at room temperature. Thermogravimetric analyses (TGA) were carried out on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> flow (60 mL/min) from room temperature to 700 °C. Gas sorption analyses were conducted using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with extra-high pure gases.

#### **Experimental section**



Scheme S1. Synthetic routes for the preparation of ligand H<sub>3</sub>L1.

*tert*-Butyl 4-azidobenzoate (2). It was synthesized in accordance to literature reported method with slight modifications.<sup>S1,S2</sup> *tert*-Butyl 4-aminobenzoate (1.93 g, 10 mmol) was added into a mixture of MeOH (60 mL) and HCl (0.5 M, 60 mL) at 0 °C. Subsequently, a water solution of NaNO<sub>2</sub> (2.1 g, 30 mmol in 10mL H<sub>2</sub>O) was slowly added into the above mixture, and the resulted mixture solution was stirred at 0 °C for 1.5 h. Then, a solution of NaN<sub>3</sub> (1.95 g, 30 mmol in 10 mL H<sub>2</sub>O) was slowly poured into the mixture solution at 0 °C with stirring for 2 h, followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> (50 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under vacuum. The crude product was purified by silica gel flash column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub>, 100/20) to give compound **2** as a yellow liquid (2.11 g, 9.63 mmol, yield 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 1.57 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.1, 144.3, 131.3, 128.7, 118.7, 81.3, 28.3. FTIR (KBr) u/cm<sup>-1</sup>: 2978.1(m), 2931.8(m), 2125.6(s), 2090.8(s), 1712.8(s), 1604.8(s), 1504.5(m), 1396.5(m), 1288.5(s), 1257.6(m), 1165.0(s), 1130.3(s), 1111.0(s), 1014.6(w), 852.5(m), 767.7(m), 690.5(w). ESI-TOF-HRMS: *m/z* calcd for C<sub>11</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub>: 220.1086, found: 220.1081 [M+H]<sup>+</sup>.

**Tri-***tert*-**butyl** 4,4',4''-**benzene-1,3,5-triyl-tri**(1*H*-1,2,3-triazol-1-yl)benzoate ('Bu<sub>3</sub>L1). 'Bu<sub>3</sub>L1 was synthesized in accordance to literature reported method with slight modifications.<sup>S1-S3</sup> Above synthesized compound 2 (1.58 g, 7.2 mmol), and 1,3,5-triethynylbenzene (3, 0.30 g, 2.00 mmol) were added into a mixture of THF/H<sub>2</sub>O (150 mL/40 mL). Then, CuSO<sub>4</sub> (0.06 g, 0.22 mmol in 10 mL H<sub>2</sub>O) and excess sodium *L*-ascorbate (0.5 g, 2.5 mmol in 10 mL H<sub>2</sub>O) were added into the above solution, and the mixture solution was stirred at 50 °C under N<sub>2</sub> for 3 days. The mixture solution was poured into water (50 mL) and then extracted by CH<sub>2</sub>Cl<sub>2</sub> (50 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under vacuum. The crude product was purified by silica gel flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/EtOAc, 100/5) to give compound **'Bu<sub>3</sub>L1** as a light yellow solid (1.49 g, 1.84 mmol, yield 92 %, melting point: 192-197 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.45 (s, 3H), 8.41 (s, 3H), 8.17 (d, *J* = 8.8 Hz, 6H), 7.87 (s, *J* = 8.8 Hz, 6H), 1.64 (s, 27H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.5, 147.8, 139.6, 132.3, 131.4, 131.3, 122.9, 119.7, 118.2, 81.9, 28.3. FTIR (KBr) v/cm<sup>-1</sup>: 2974.0(m), 2931.8(m), 1712.8(s), 1608.6(m), 1516.1(m), 1458.2(w), 1400.3(w), 1369.5(w), 1296.2(s), 1234.4(m), 1165.0(s), 1118.7(s), 1041.6(m), 987.6(w), 852.5(m), 771.5(m), 690.5(w). ESI-TOF-HRMS: *m/z* calcd for C<sub>45</sub>H<sub>46</sub>N<sub>9</sub>O<sub>6</sub>: 808.3571, found: 808.3578 [M+H]<sup>+</sup>.

**4,4',4''-benzene-1,3,5-tryl-tri(1***H***-1,2,3-triazol-1-yl)benzoic acid (H<sub>3</sub>L1).** To a CH<sub>2</sub>Cl<sub>2</sub> solution (20 mL) of the ester <sup>t</sup>**Bu<sub>3</sub>L1** (1.35 g, 1.67 mmol) was added trifluoroacetic acid (TFA, 6 mL). The mixture solution was stirred at room temperature over 5 h, obtaining light-yellow precipitates. The suspension was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>, and the obtained solid was dried under vacuum to afford the compound **H<sub>3</sub>L1** (0.98 g, 1.53 mmol, yield 92%, became black before melting at above 290 °C) as light-yellow solid. <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  13.24 (s, 3H), 9.55 (s, 3H), 8.52 (s, 3H), 8.18 (m, *J* = 8.8 Hz, 12H). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  166.9, 147.5, 140.0, 132.0, 131.7, 131.2, 122.6, 120.7, 120.1. FTIR (KBr) v/cm<sup>-1</sup>: 3433.3(s), 1705.1(s), 1608.6(s), 1519.9(m), 1435.0(w), 1404.2(m), 1315.5(w), 1234.4(s), 1176.6(m), 1114.9(w), 1053.1(m), 991.4(m), 856.4(w), 798.5(m), 771.5(m), 686.7(w). ESI-TOF-HRMS: *m/z* calcd for C<sub>33</sub>H<sub>22</sub>N<sub>9</sub>O<sub>6</sub>: 640.1693, found: 640.1694 [M+H]<sup>+</sup>.

**MOF 1**. Compound **H<sub>3</sub>L1** (15 mg, 0.023 mmol) and  $Zn(NO_3)_2 \cdot 6H_2O$  (30 mg, 0.10 mmol) were dissolved in *N*,*N*'-dimethylformamide (DMF, 10 mL). Then, the mixture solution was placed in a tightly capped 20 mL vial after dropping 1 drop HNO<sub>3</sub> into the solution. The vial was heated in an oven at 90 °C for 4 days. The colorless block crystals were collected after cooling the sample down to room temperature. The crystals were washed by fresh DMF for

three times and dried naturally at room temperature to yield MOF **1** (32.9 mg). The assynthesized crystals of MOF **1** are insoluble and stable in common organic solvents including dichloromethane, chloroform, acetonitrile, toluene, DMF, and dimethyl sulfoxide (DMSO).

X-ray crystallography. The single crystal of 1 suitable for X-ray analysis was picked up under a microscope from the freshly synthesized solution, and then sealed in a glass tube immediately with DMF solvent and mounted. The diffraction data were collected at room temperature using graphite-monochromated Cu-Ka radiation ( $\lambda = 1.54178$  A) on a SuperNova X-ray Diffraction System from Agilent Technologies. Data reduction and empirical absorption correction were applied with CrysAlisPro.<sup>S4</sup> The structure was solved by direct methods using program SHELXS-97.55 All Zn and O atoms and part of ligands could be located directly from the difference Fourier maps, and the rest of non-hydrogen atoms were located in successive difference Fourier syntheses. Framework hydrogen atoms were placed geometrically and constrained using the riding model to the parent atoms. Finally, the structure refinement was carried out with program SHELXL-97<sup>S5</sup> by minimizing the sum of squared deviations of  $F^2$  using a full-matrix technique. The isolated solvent molecules in the MOF are highly disordered and cannot be modeled, and thus the SQUEEZE routine of PLATON was applied to remove the contributions of the solvent molecules to the scattering.<sup>S6</sup> Further details of crystallographic data and structural analyses are summarized in Table S1.

CCDC 1502165 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Gas sorption.** Low-pressure gas sorption measurements were performed by using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with the extra-high pure gases. The as-synthesized crystals of MOF 1 were immersed in dried CH<sub>3</sub>Cl (20 mL) for 3 days, during which time CH<sub>3</sub>Cl was replaced several times. Then, the samples were moved into a sample cell and dried under vacuum at 60 °C by using the "outgasser" function for 6 h before the measurements. The Brunauer–Emmett–Teller (BET) surface area and total pore

volume were calculated from the  $N_2$  sorption isotherms at 77 K, and the pore size distribution was calculated based on the  $N_2$  sorption isotherm by using Non-Local Density Functional Theory (NL-DFT, a zeolite/silica model containing spherical/cylindrical pores) model in the Quantachrome ASiQwin 2.01 software package.

**Molecule soaking**. DMF solutions of related molecules or mixtures were firstly prepared. Then, activated MOF crystals in  $CH_3Cl$  were moved by glass pipette into the prepared DMF solution of related molecules or mixtures and kept for about 2 h. The crystals were picked out and washed by fresh DMF for taking photos under a microscope.

**Dye molecule uptake or mixture separation**. Fishebrand<sup>®</sup> 5.75mm Disposable Pasteur Pipets (Borosilicate Glass/Non-sterile) were packed by MOF crystals to form ~1 cm chromatographic columns. DMF solutions of related dyes or dye mixtures were dropped into the homemade column and naturally passed through the columns under gravity, and then the residues were collected. The UV-Vis spectra of the final effluents were examined.

	1	
Formula	$C_{132}H_{72}N_{36}O_{27}Zn_6$	
Mr	2986.48	
Temperature /K	293(3)	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	<i>C222</i> <sub>1</sub>	
<i>a,b,c</i> / Å	a = 29.72(6) Å,	
α, β, γ / °	<i>b</i> = 37.891(16) Å,	
	c = 37.65(3) Å	
$V/\text{\AA}^3$	42402(90)	
Ζ	4	
$D_{\text{calc}} (g \cdot \text{cm}^{-3})$	0.468	
Crystal size (mm)	$0.36 \times 0.18 \times 0.12$	
Theta range (deg)	3.78 to 39.96	
Reflections unique/collected	5669/7595	
R <sub>1</sub> , wR2	0.0692, 0.2004	
Goodness-of-fit on $F^2$	1.038	

**Table S1.** Crystallographic data and structure refinement summary for MOF 1.

Figures



Fig. S1. Photograph of as-synthesized crystals of 1.



**Fig. S2**. (a) Chemical structure of the "clicked" ligand  $H_3L1$ , (b)  $H_3L1$  connected three Zn<sub>3</sub> units, (c) 1D porous channels along *c*-axis in 3D framework of 1, (d) 1D porous channels perpendicular to (110) plane in 1; (e) (10,3)-network of 1 in a chiral SrSi<sub>2</sub> topology.



**Fig. S3.** Powder XRD patterns of activated, as-synthesized, and calculated **1**, indicating that the framework was retained after the activation process.



**Fig. S4.** TGA plot of as-synthesized **1**, indicating that the framework was stable up to  $\sim$ 300 °C. The initial sharp weight loss can be attributed to the weight loss of solvents (water and DMF) in the pores of the framework.



Fig. S5.  $CO_2$  and  $N_2$  adsorption isotherms of activated 1 showing  $CO_2$  and  $N_2$  adsorption values of 121.8 and 5.6 cm<sup>3</sup> g<sup>-1</sup> at 1 atm and 273 K respectively, and 62.7 and 2.1 cm<sup>3</sup> g<sup>-1</sup> at 1 atm and 298 K, respectively.



Fig. S6.  $H_2$  adsorption isotherm of activated MOF 1 at 77 K, showing  $H_2$  adsorption capability of 164.6 cm<sup>3</sup> g<sup>-1</sup> at 1 atm and 77K.

Dye molecule	Chemical structure	Photo of Dye@1
Blank		44
Methyl Yellow		0
Toluylene Red	$H_{3}C^{N} \xrightarrow{N} V_{CH_{3}} H_{2}$	
Methylene Blue	$\begin{array}{c} CH_3 & C\Gamma & CH_3 \\ H_3C \cdot N & & & & \\ \end{array} \\ \begin{array}{c} & & \\ $	-
Rhodamine B	H <sub>3</sub> C, CH <sub>3</sub> H <sub>3</sub> C, N, CH <sub>3</sub> Cr COOH	•
Rhodamine 6G	H <sub>3</sub> CH <sub>2</sub> C(H)N H <sub>3</sub> C H <sub>3</sub> C CH <sub></sub>	
Brilliant Blue R	SO,Na CH <sub>3</sub> H <sub>1</sub> C SO, CH <sub>3</sub> H <sub>1</sub> C C CH <sub>3</sub> H <sub>1</sub> C C CH <sub>2</sub> CH <sub>3</sub>	S

Fig. S7. Dye molecules and the crystal colors of 1 after dye/DMF solution soaking.



Fig. S8. Image and illustration of MOF 1-packed column.

**Characterization spectra** 



<sup>13</sup>C NMR spectrum of *tert*-butyl 4-azidobenzoate in CDCl<sub>3</sub>.

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HRMS spectrum of tert-butyl 4-azidobenzoate



FT-IR spectrum of tert-butyl 4-azidobenzoate

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<sup>13</sup>C NMR spectrum of tri-tert-butyl 4,4',4"-benzene-1,3,5-triyl-tri(1H-1,2,3-triazol-1-yl)benzoate ('Bu<sub>3</sub>L1) in

CDCl<sub>3</sub>.



HRMS spectrum of tri-tert-butyl 4,4',4"-benzene-1,3,5-triyl-tri(1H-1,2,3-triazol-1-yl)benzoate ('Bu<sub>3</sub>L1)



FT-IR spectrum of tri-tert-butyl 4,4',4"-benzene-1,3,5-triyl-tri(1H-1,2,3-triazol-1-yl)benzoate ('Bu<sub>3</sub>L1)

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<sup>1</sup>H NMR spectrum of 4,4',4"-benzene-1,3,5-tryl-tri(1H-1,2,3-triazol-1-yl)benzoic acid (H<sub>3</sub>L1) in DMSO-d<sub>6</sub>



<sup>13</sup>C NMR spectrum of 4,4',4"-benzene-1,3,5-tryl-tri(1H-1,2,3-triazol-1-yl)benzoic acid (H<sub>3</sub>L1) in DMSO-d<sub>6</sub>



HRMS spectrum of 4,4',4"-benzene-1,3,5-tryl-tri(1H-1,2,3-triazol-1-yl)benzoic acid (H<sub>3</sub>L1)



FT-IR spectrum of 4,4',4"-benzene-1,3,5-tryl-tri(1H-1,2,3-triazol-1-yl)benzoic acid (H<sub>3</sub>L1)

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