Targeted Synthesis of a Large Triazine-based [4+6] Organic Molecular Cage: Structure, Porosity and Gas Separation

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1. General Methods

Dehydrated solvents were obtained through treatment of solvents using standard procedures. (*R, R*)-cyclohexanediamine was purchased from Adamas-beta. 1,3,5-Tris-(4-formyl-phenyl)triazine was prepared according to the literature.[S1]

NMR spectra were measured on Mercury VX-300 and Bruker Fourier 500 M spectrometer. High resolution MALDI–TOF data were collected on a Bruker Solarix mass spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo iS10 infrared spectrometer. The UV-vis absorption spectrum was recorded on a Shimadzu UV-3600 and fluorescence spectra were measured on Perkin Elmer LS55 instruments. Thermogravimetric analysis from 25-800 °C was carried out on a Setsys 16TG-DTG/DSC apparatus in a nitrogen atmosphere using a 10 °C/min ramp without equilibration delay. Cyclic voltammetry (CV) was carried out in DCM under Ar atmosphere at room temperature using a CHI660C Electrochemical Workstation (Shanghai ChenHua Electrochemical Instruments). A conventional three-electrode cell consisting of a glassy carbon as the working electrode, a $Ag/AgNO_3$ reference, and a Pt wire counter electrode held in compartments separated by medium porosity glass frits. The concentration of the sample and supporting electrolyte (NBu_4PF_6 in dichloromethane) were 0.0005 mol/L and 0.1 mol/L, respectively. Fluorescence microscope images were collected on Inverted Fluerescence Microscopy IX71 Olympus.Single crystal X-ray data were collected at 298 K at the Beijing Synchrotron Radiation Facility, beam line station 3W1A equipped with a MarCCD-165 detector. See section 5 for details of data collection and refinement. CCDC 1022375 contains crystallographic data for this paper.

N_2, H_2, CH_4, and CO_2 physisorption isotherms were measured up to 1 bar using a Micrometrics ASAP 2020 surface area and pore size analyzer. Prior to the measurements, the samples were degassed for 10 h at 100 °C. UHP grade N_2, H_2, CH_4 and CO_2 were used for measurements. Oil-free vacuum pumps and oil-free pressure regulators were used for measurements to prevent contamination of the samples during the degassing process and isotherm measurement. The total pore volume was N_2 volume adsorbed at STP when P/P_0 was 0.95. The BET surface area was calculated in the 0.10-0.20 P/P_0 range, and the isotherm points chosen to calculate the BET surface area were subject to the three consistency criteria detailed by Walton and Snurr[S2].

2. Synthesis of Cage 1

Dehydrated chloroform (150 mL) was added to 1,3,5-tris-(4-formyl-phenyl)triazine (175.2 mg, 0.445 mmol) in a beaker at room temperature. Then, a dehydrated chloroform (70 mL) solution of (R, R)-cyclohexanediamine (87.1 mg, 0.762 mmol) was added. The resulting mixture was left at room temperature for 6 days without stirring and monitored by ^{1}H NMR. Cage **1** was obtained as a light yellow shining powder by removing the solvent under vacuum (219 mg, 96.4%).^{1}H NMR (CDCl$_3$, 300 MHz, 298K, ppm): δ = 8.60 (d, J = 7.5Hz, 24H), 8.31 (s, 12H), 7.78 (d, J = 7.6Hz, 24H), 3.51 (s, 12H), 1.87–1.67 (m, 48H). ^{13}C NMR (CDCl$_3$, 75 MHz, 298 K, ppm): δ = 170.8, 159.8, 139.6, 137.5, 133.0, 128.9, 128.1, 74.2, 32.7, 24.3. HR-MALDI-TOF MS: calcd for C$_{132}$H$_{120}$N$_{24}$: m/z = 2042.02061 [M+H]$^+$; found m/z = 2042.02026 [M+H]$^+$.
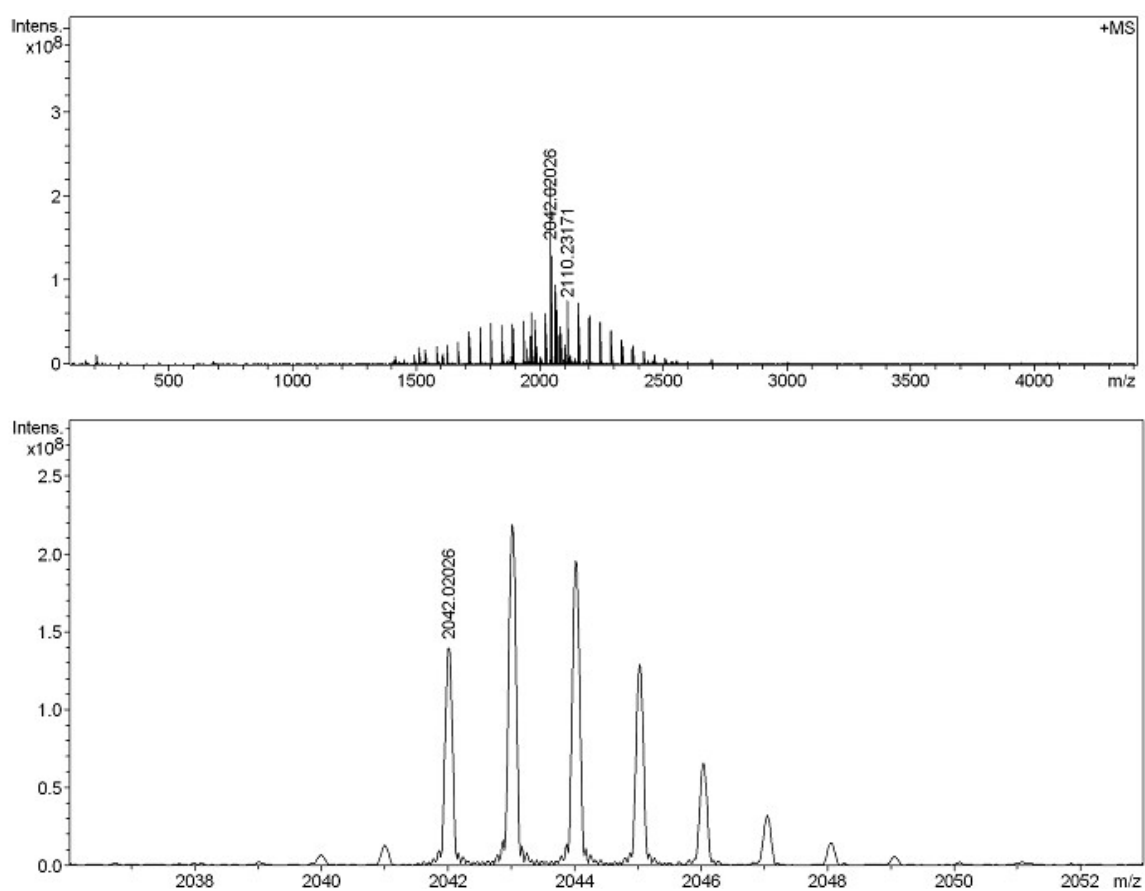
3. The tracing of cage formation
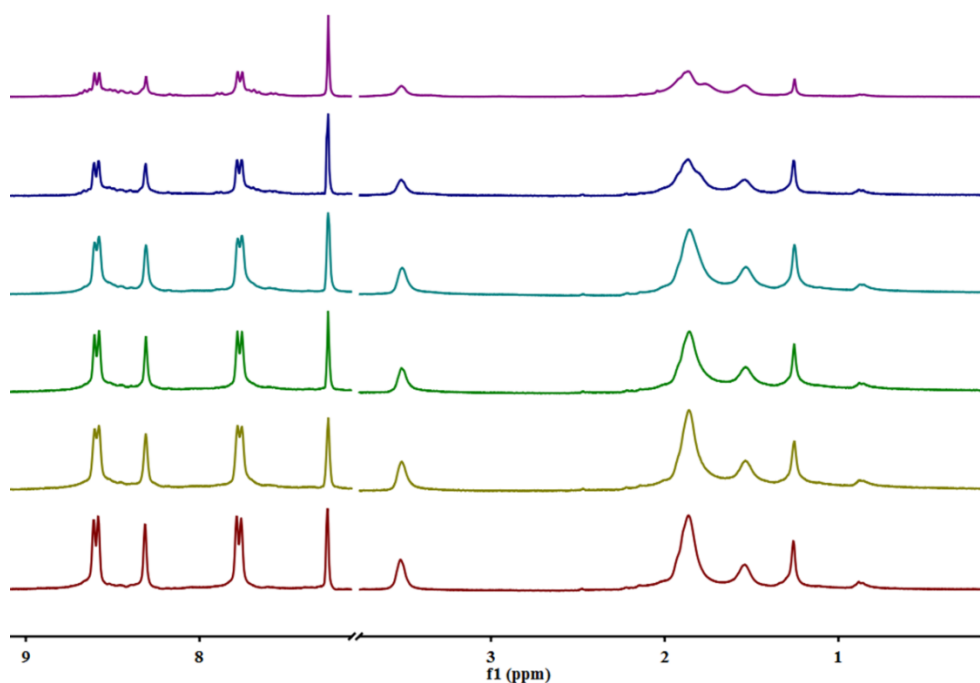
Fig. S1 Dynamic covalent formation of cage monitored by ^{1}H NMR spectroscopy (300 MHz, 298 K, CDCl$_3$) over time (purple: 1d; dark blue: 2d; blue: 3d; green: 4d; yellow: 5d; red: 6 d).
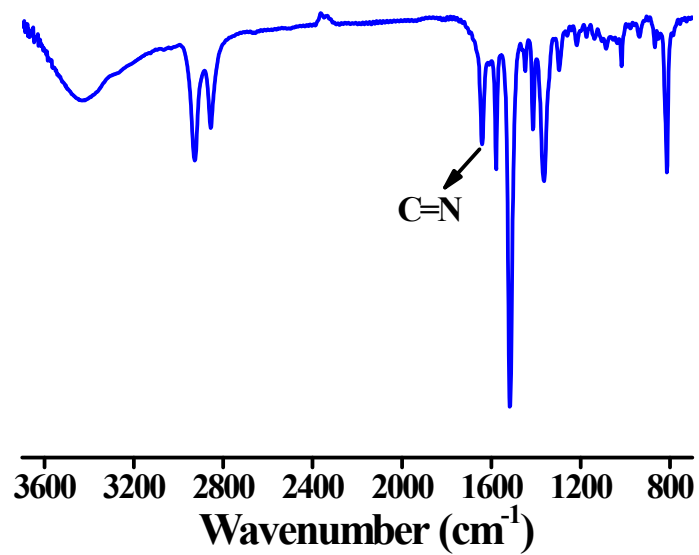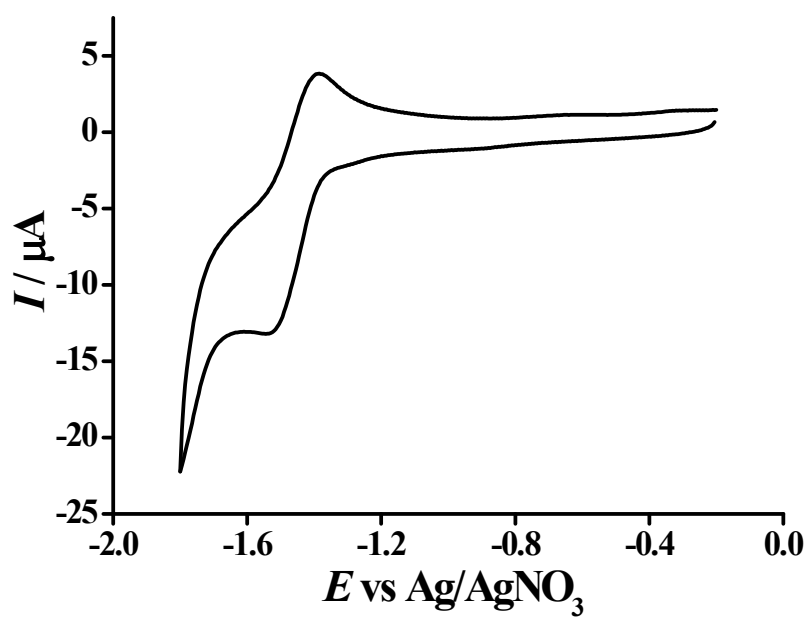
4. Characterizational data for cage 1
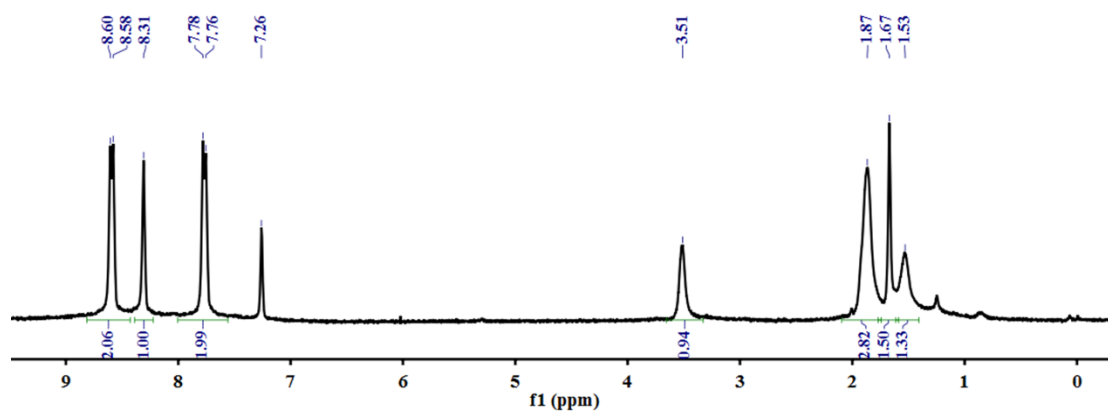
Fig. S2 ^{1}H NMR spectrum (300 MHz, 298 K, CDCl$_3$) of cage **1**
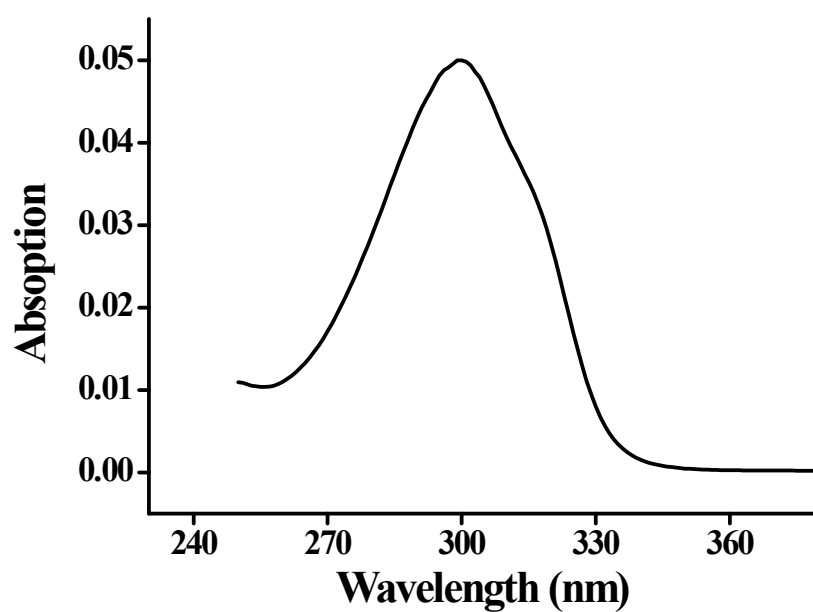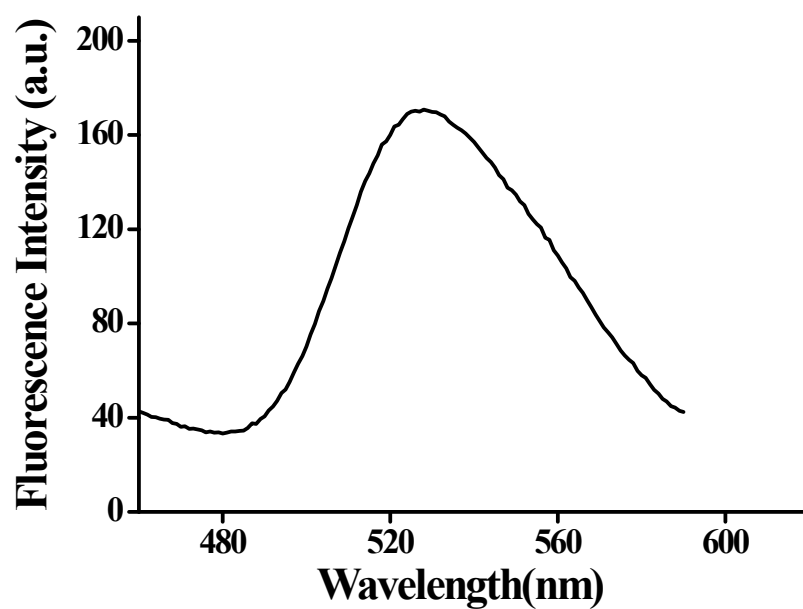

Fig. S3 HR-MALDI–TOF spectrum of cage **1**

Fig. S4. FT-IR spectrum of cage **1**

Fig. S5 CV spectrum of cage **1** (scan rate 100mV•s^{-1}; 0.1 M NBu$_4$PF$_6$ in dichloromethane)

Fig. S6 UV spectrum of cage **1** (10^{-6} mol/L in THF)

**Fig. S7** Fluorescence spectrum of cage **1** (10^{-6} mol/L in THF, $\lambda_{ex} = 305$ nm)

5. X-Ray Crystallography

Data Collection for cage 1: A colorless rod-shaped crystal, having the approximate dimensions of 0.30 × 0.20 × 0.05 mm, was mounted using oil on a glass fiber. All measurements were made at the Beijing Synchrotron Radiation Facility, beam line station 3W1A equipped with a MarCCD-165 detector (the monochrome X-ray source is produced by an accelerator and selected by a double crystal monochromator, λ = 0.8000Å). Scattering factors for the wavelength of 0.800 Å for use in Shelxl-2014 were calculated for all elements using the program WCROMER[S3] and were implemented in Shelxl-2014 using DISP commands. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using Shelxl-2014. Several low angle reflections were affected by the beam stop and were omitted from the refinement. The reflections in question are 1 0 2, 2 1 0, 0 1 2, 2 2 0, -1 2 1, -1 1 2, -1 2 2, 1 1 2, 1 3 0, 1 2 2, 3 1 0, and 2 3 0. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final refinement cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom. Large sections of the structure, 7745 $Å^3$ or 44.98% of the unit cell volume, consist of solvent filled voids. The content of the voids is partially recognizable as DMSO molecules, but mostly highly disordered. Attempts to include solvent molecules in the structural model yielded less than satisfactory results, with R_1 values around 12%. The data were thus instead corrected for the contribution of the solvate molecules to the electron density using back Fourier transform methods as implemented in the Squeeze algorithm of the Platon program package. Correction for unresolved electron density yielded 1363 electrons for the void volume. Crystal data and a structure determination summary for cage **1** are listed in Table S1.

**Table S1** Crystal Data and Structure Refinement for cage **1**

Empirical formula	$C_{132} H_{120} N_{24}$
Formula weight	2042.51
Temperature	293(2) K
Wavelength	0.800Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	$a = 23.855(5)$ Å, $\alpha = 90°$
	$b = 26.655(5)$ Å, $\beta = 90°$
	$c = 27.082(5)$ Å, $\gamma = 90°$
Volume, V	17220(6) Å^3
Z, Calculated density	4, 0.788 mg/m^3
Absorption coefficient	0.061 mm^{-1}
$F(000)$	4320
Crystal size	$0.30 \times 0.20 \times 0.05$ mm
Theta range for data collection	1.917 to 28.381°
Limiting indices	$0 \leq h \leq 26$, $-30 \leq k \leq 29$, $-32 \leq l \leq 31$
Reflections collected / unique	40104 / 22034 [$R_{int} = 0.0243$]
Completeness to theta = 28.447	74.5 %
Absorption correction	none
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	22034 / 0 /1406
Goodness-of-fit on F^2	0.958
Final R indices [$I > 2\sigma (I)$]	$R_1 = 0.0603$, wR$_2 = 0.1583$
R indices (all data)	$R_1 = 0.0798$, wR$_2 = 0.1734$
Largest diff. peak and hole	$+0.185$ and -0.187 e·Å^{-3}
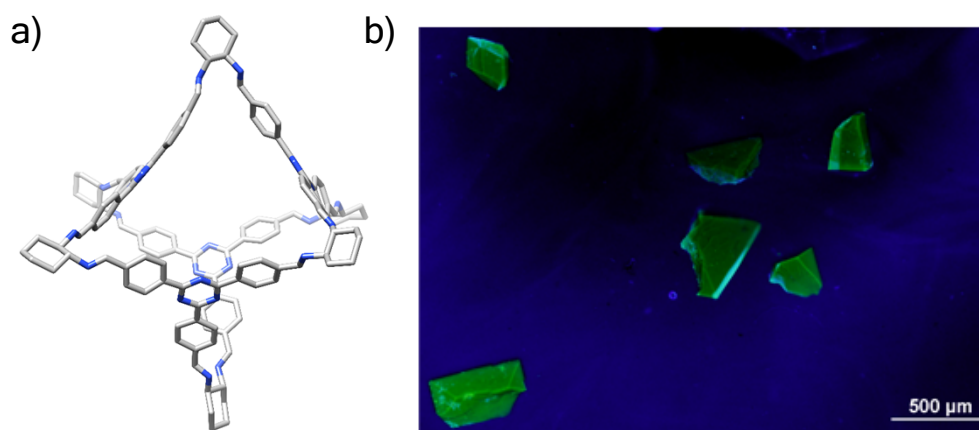
Fig. S8 a) The crystal structure of cage **1**. Hydrogen atoms are omitted for clarity. C: light gray; N: blue; b) Fluorescence microscope image of the crystal.

6. Thermogravimetric Analyses of desolvated cage 1
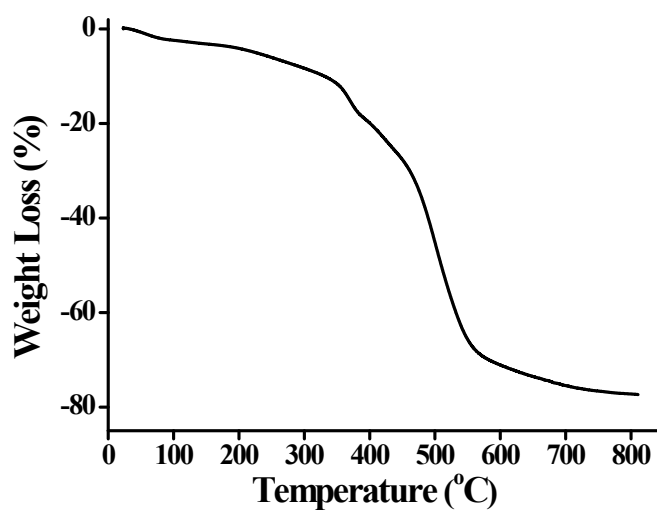
Fig. S9 TGA spectrum of the desolvated cage **1**

7. Gas absorption and separation

In order to compare the efficacy of cage **1** for CO_2/N_2 and CO_2/CH_4 separation, we used the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz along with

pure component isotherm fits to determine the molar loadings in the mixture for specified partial pressures in the bulk gas phase. The measured experimental data on pure component isotherms for CO_2, N_2 and CH_4, in terms of excess loadings, were first converted to absolute loading using the Peng-Robinson equation of state for estimation of the fluid densities. The pore volume of cage **1** used for this purpose was 0.54 cm³/g. The absolute component loadings at 273 K were fitted with either a single-site Langmuir-Freundlich model (Equation 1), where a is saturation capacity and b and c are constants.
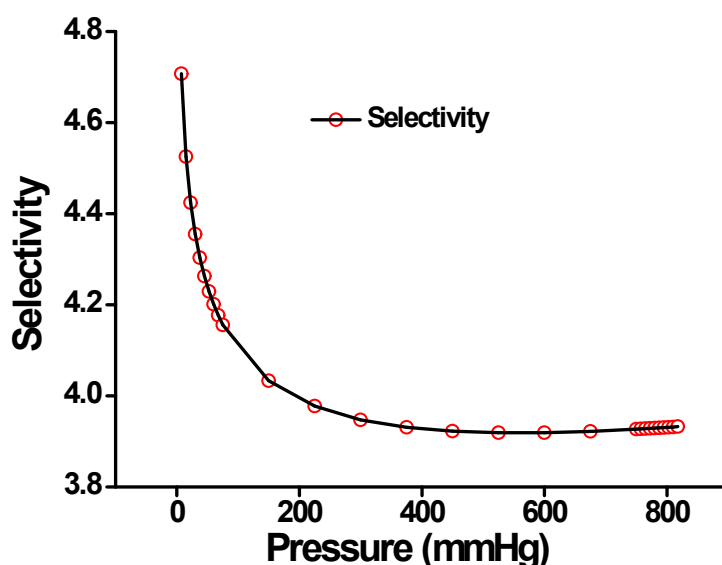
$$N = a \times \frac{bp^c}{1+bp^c}$$

(Equation 1)

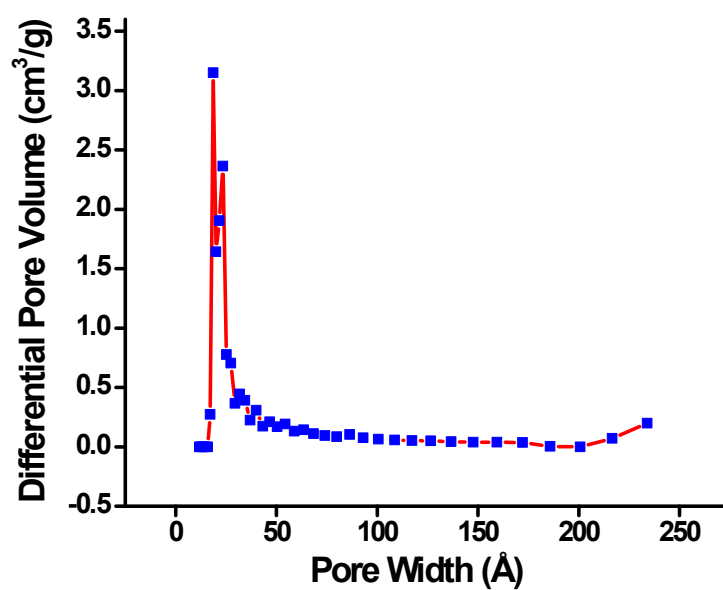The adsorption selectivities, S_{ads}, is for binary mixtures defined by $S_{ads} = \frac{x_1/x_2}{y_1/y_2}$

S_{ads}: adsorption selectivity

x_i: the mole fractions of component i in the adsorbed phases

y_i: the mole fractions of component i in the bulk phases

Fig. S10 IAST predicted selectivity for CO_2/CH_4 with 50:50 mole ratios for cage **1**

Fig. S11 The pore-size distribution of Cage **1** in amorphous state.

8. References:

S1   S.-H. Li, H.-P. Huang, S.-Y. Yu and X.-P. Li, *Chin. J. Chem.* 2006, **24**, 1225–1229.

S2   K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.* 2007, **129**, 8552-8556.

S3   L. Kissel and R. H. Pratt, *Acta Cryst.* 1990, **A46**, 170–175.