Supporting Information

Highly covalent molecular cage based porous organic polymer: pore size controlling and pore properties enhancement

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1. General information.

Materials obtained commercially were used without further purification. $^1$H NMR spectra were recorded on a DMX600 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Sample was degassed at 120 °C for 10 h under vacuum before analysis. H$_2$ isotherms were measured at 77 K up to 1.0 bar using a Micromeritics ASAP 2020 volumetric adsorption analyzer with the same degassing procedure. CO$_2$ isotherms were measured at 273 and 298 K up to 1.0 bar using a Micromeritics ASAP 2020 volumetric adsorption analyzer with the same degassing procedure.

2. Experimental details

Synthesis of TPP based oxacalixarene cage TPP-OMC.

The 4OH-TPP was synthesized according to literature.$^1$ 4OH-TPP (100 mg, 0.22 mmol), 2,3,5,6-tetrachloropyridine (95 mg, 0.44 mmol) and Cs$_2$CO$_3$ (287 mg, 0.88 mmol) were added to a 50 mL round bottom flask. DMSO (10 mL) was added, and then the combined mixture was stirred vigorously at 120 °C overnight. After the raw materials was consumed, the reaction was allowed to cool down to RT, and the mixture was partitioned between CH$_2$Cl$_2$ (40 mL) and H$_2$O (40 mL), separated, the aqueous layer was extracted twice with CH$_2$Cl$_2$ (20 mL). The combined

Scheme S1. Synthesis of TPP-based tricyclooxacalixarene cage TPP-OMC.
organics were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuum. The residue was purified by column chromatography to afford TPP-OMC as white solid (24 mg, 24 %). $^1$H NMR (600 MHz, Toluene-$d_8$): $\delta = 7.59$ (d, $J = 8.4$ MHz, 16H), 7.25 (s, 4H), 6.72 (d, $J = 8.4$ MHz, 16H). MALDI-TOF-MS: m/z 1473.8 (M$^+$).

**Scheme S2.** Synthesis of TPP-pOMC.

Under a dry argon atmosphere, TPP-OMC (305 mg, 0.2 mmol), 2-2'-bipyridyl (374 mg, 2.4 mmol) and Bis(1,5-cyclooctadiene) nickel (660 mg, 2.4 mmol) were added to a 100 mL two-neck round bottom flask, followed by a solution of 1,5- cyclooctadiene (259 mg, 2.4 mmol) in 30 mL DMF added by syringe. The combined mixture was stirred at 85 °C for 5 d before the reaction was allowed to cool down to RT, 40 mL 2M HCl was added into the reaction solution, stirred for 0.5 h, the precipitated polymer was collected by filtration and washed with a large amount of water, the products were successively washed with excess THF and CH$_2$Cl$_2$, and then sequentially purified by Soxhlet extraction with methanol, the purified products were dried in a vacuum oven at 60 °C for 12 h to obtain the final TPP-pOMC 280 mg.
3. $^1$H NMR of TPP-OMC.

*Figure S1.* $^1$H NMR spectra of TPP-OMC in $d_8$-Toluene (Bruker, 600 MHz) (*asterisk denote the proton peaks of the solvent $d_8$-Toluene*).

4. MALDI-TOF mass spectrometry of TPP-OMC.

*Figure S2.* MALDI-TOF MS spectrum of TPP-OMC.
5. Simulated chemical structures of TPP-OMC.

*Figure S3.* Simulated chemical structures of 4OH-TPP (a) and TPP-OMC (b) with torsion angle measured by Materials Studio 7.0 (Accelrys).

6. FT-IR spectra of TPP-OMC and TPP-pOMC.

*Figure S4.* FT-IR spectra of TPP-OMC and TPP-pOMC.
7. Powder X-ray diffraction spectra of TPP-pOMC.

![Figure S5. PXRD spectra TPP-pOMC.](image1)

8. Thermo gravimetric analysis spectra of TPP-pOMC.

![Figure S6. TGA spectra of TPP-pOMC.](image2)
9. Brunauer-Emmett-Teller (BET) surface areas of TPP-pOMC.

The calculation of specific surface areas ($S_{BET}$) were based on the BET equation in its linearized form,

$$\frac{P}{P_0} V_{ads} \left(1 - \frac{P}{P_0}\right) \left[\frac{1}{V_m C_{BET}} + \frac{C_{BET} - 1}{V_m C_{BET}} \times \frac{P}{P_0}\right]$$

with $P/P_0$ the relative pressure; $V_{ads}$ the adsorbed volume; $V_m$ the monolayer volume and the constant $C_{BET}$.

**Figure S7.** The Brunauer-Emmett-Teller (BET) surface areas of TPP-OMC (a), TPP-pOMC (b) calculated from nitrogen sorption analysis at 77K.
10. Isosteric enthalpies of adsorption for CO$_2$ of TPP-pOMC.

The calculation of adsorption enthalpies ($Q_{st}$) were based on Clausius-Clapeyron formula, 

$$Q_{st} = \frac{RT_1T_2 \ln(P_2/P_1)}{T_2 - T_1}$$

With $Q_{st}$ the adsorption enthalpies; $R$ the gas constant; $T$ the adsorbed temperature; $P$ the adsorbed pressure.

**Figure S8.** Isosteric enthalpies of adsorption for CO$_2$ of TPP-pOMC.
Reference

1 M. Chen, L. Li, H. Nie, J. Tong, L. Yan, B. Xu, J. Z. Sun, W. Tian, Z. Zhao, A. Qin and B. Z. Tang, Chem. Sci. 2015, 6, 1932-1937.