

Supporting Information

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

Zhen Wang,^{a,*} Yan-Qun Liu,^b Yu-Hang Zhao,^a Qing-Pu Zhang,^a Yu-Ling Sun,^a Bin-Bing Yang,^a Jian-Hua Bu^{c,*} and Chun Zhang^{a,*}

^a College of Life Science and Technology, National Engineering Research Center for Nanomedicine, Huazhong University of Science and Technology, Wuhan, 430074, China.

^b Henan Industry and Trade Vocational College, Zhengzhou, Henan. 451191, China.

^c Xi'an Modern Chemistry Research Institute, Xi'an, Shanxi, 710065, China.

Corresponding Author:

Chun Zhang, Email: chunzhang@hust.edu.cn

Zhen Wang, Email: zhenwang89@hust.edu.cn

Jian-Hua Bu, Email: bujianhua@gmail.com

CONTENTS

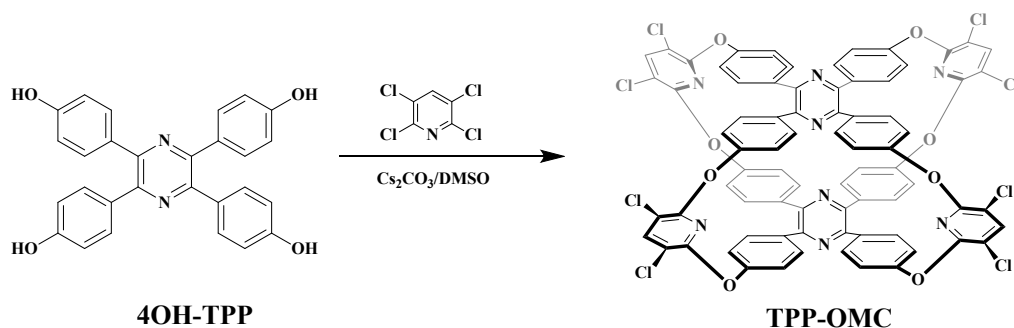
1. General information.....	S1
2. Experimental details	S1
3. ¹ H NMR of TPP-OMC.	S3
4. MALDI-TOF mass spectrometry of TPP-OMC.....	S3
5. Simulated chemical structures of TPP-OMC.....	S4
6. FT-IR spectra of TPP-OMC and TPP-pOMC.	S4
7. Powder X-ray diffraction spectra of TPP-pOMC.....	S5
8. Thermo gravimetric analysis spectra of TPP-pOMC.	S5
9. Brunauer-Emmett-Teller (BET) surface areas of TPP-pOMC.....	S6
10. Isosteric enthalpies of adsorption for CO ₂ of TPP-pOMC.....	S7

1. General information.

Materials obtained commercially were used without further purification. ^1H 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.

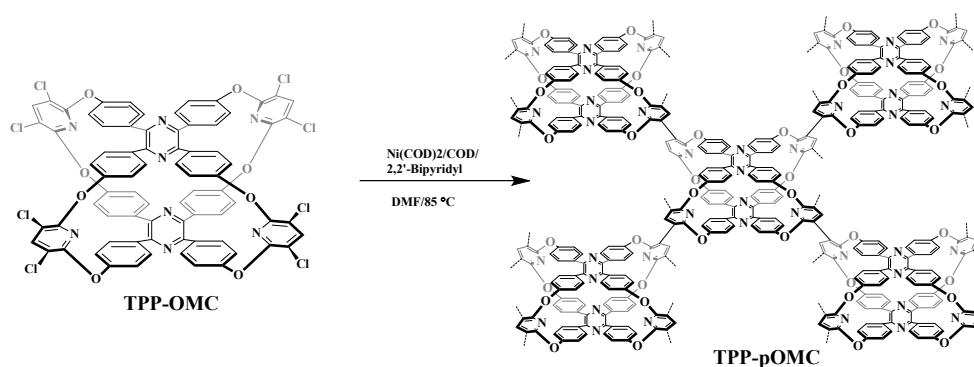


Scheme S1. Synthesis of TPP-based tricyclooxacalixarene cage TPP-OMC.

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_2CO_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_2Cl_2 (40 mL) and H_2O (40 mL), separated, the aqueous layer was extracted twice with CH_2Cl_2 (20 mL). The combined

organics were dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuum. The residue was purified by column chromatography to afford TPP-OMC as white solid (24 mg, 24 %). ^1H 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_2Cl_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. ^1H NMR of TPP-OMC.

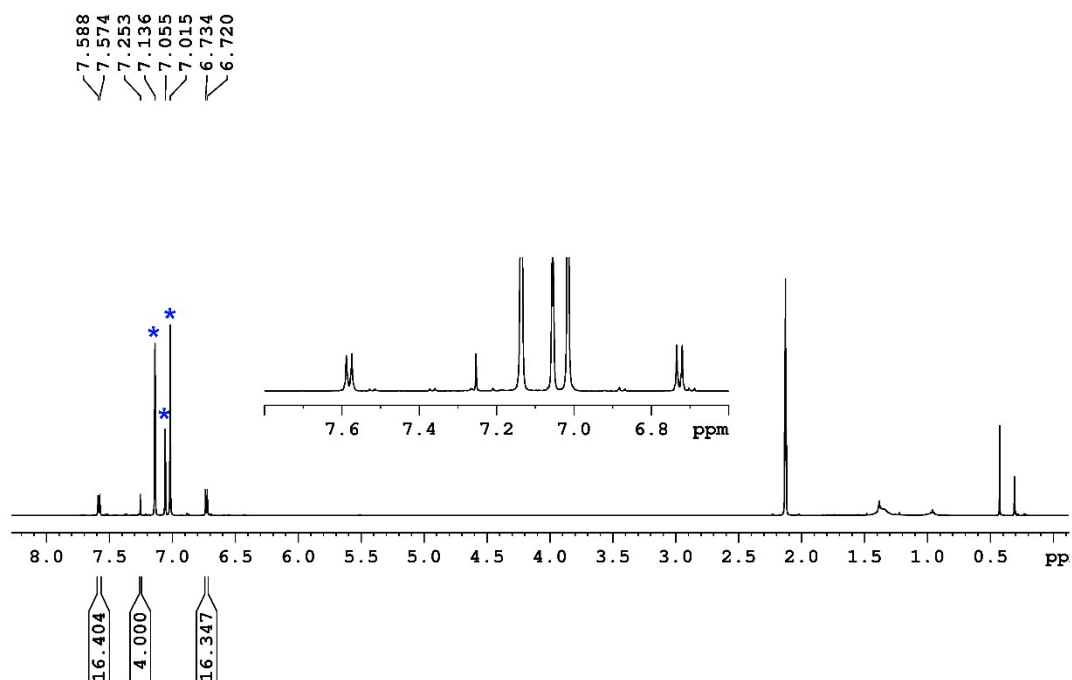


Figure S1. ^1H NMR spectra of TPP-OMC in d_8 -Toluene (Bruker, 600 MHz) (*asterisk denote the proton peaks of the solvent d_8 -Toluene.).

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

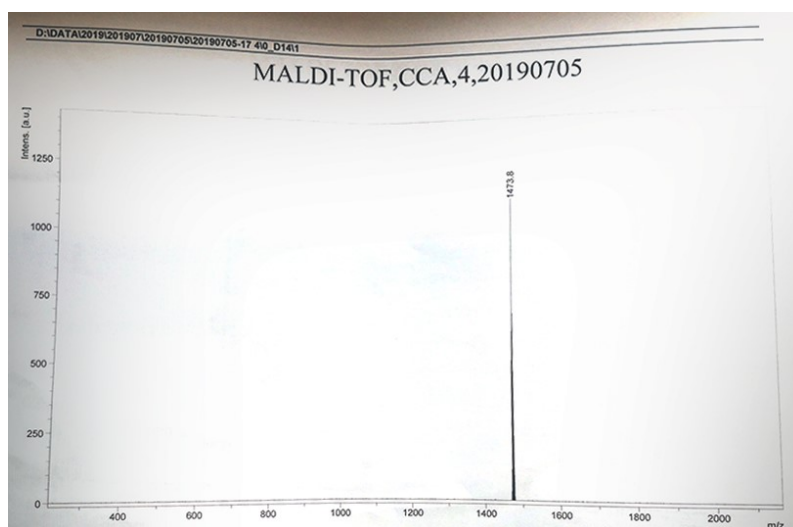


Figure S2. MALDI-TOF MS spectrum of TPP-OMC.

5. Simulated chemical structures of TPP-OMC.

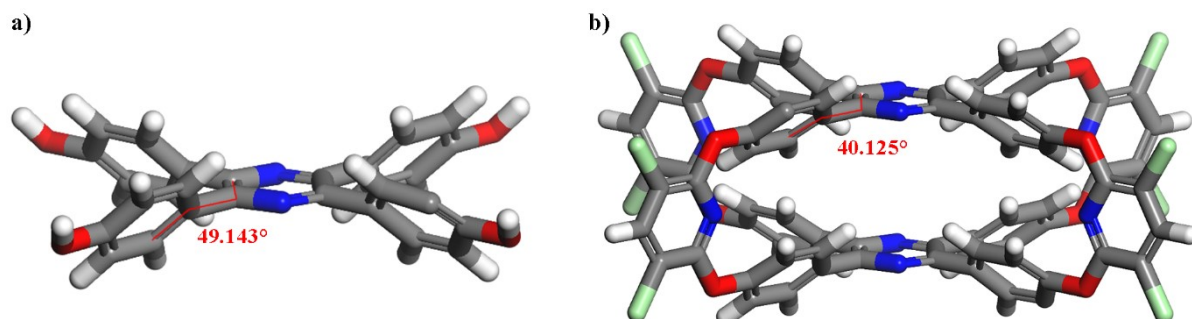


Figure S3. Simulated chemical structures of 4OH-TPP (a) and TPP-OMC (b) with torsion angle measured by Materials Studio 7.0 (Accelrys).

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

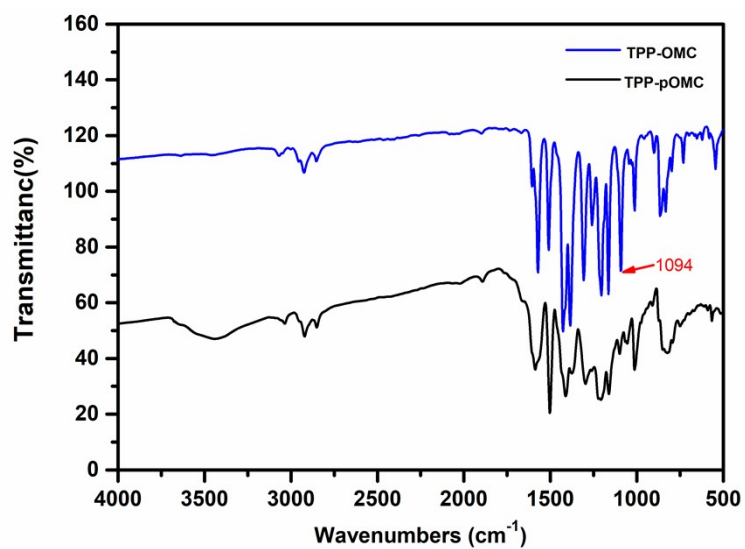


Figure S4. FT-IR spectra of TPP-OMC and TPP-pOMC.

7. Powder X-ray diffraction spectra of TPP-pOMC.

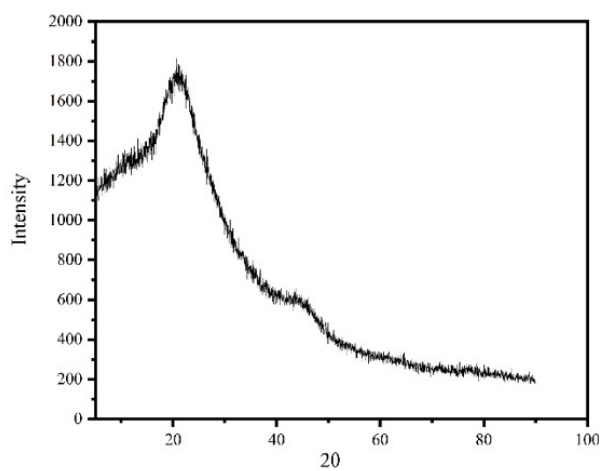


Figure S5. PXRD spectra TPP-pOMC.

8. Thermo gravimetric analysis spectra of TPP-pOMC.

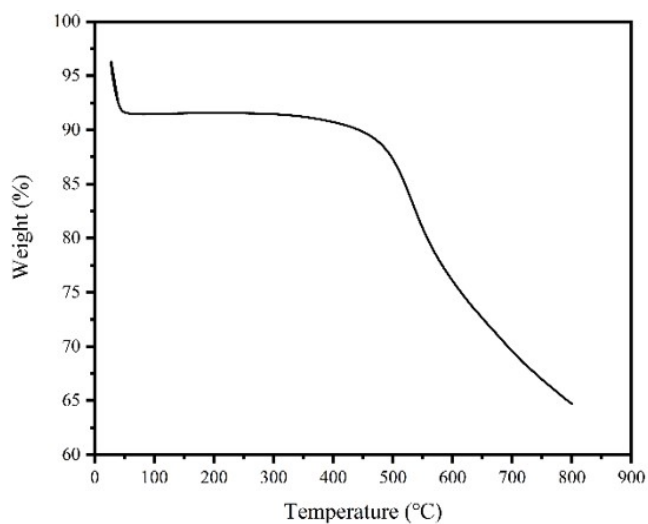


Figure S6. TGA spectra of TPP-pOMC.

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,

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

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

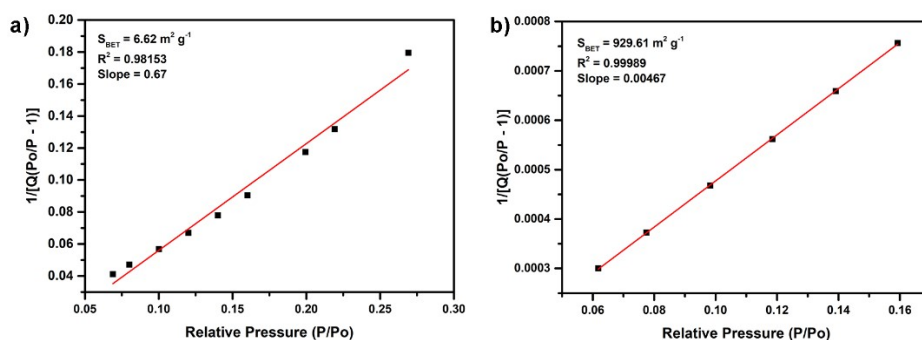


Figure S7. The Brunauer-Emmett-Teller (BET) surface areas of TPP-OMC (a), TPP-pOMC (b) calculated from nitrogen sorption analysis at 77K.

10. Isothermic enthalpies of adsorption for CO₂ 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.

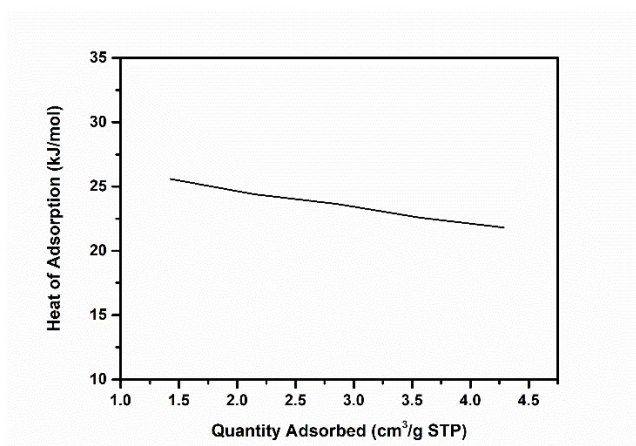


Figure S8. Isothermic enthalpies of adsorption for CO₂ of TPP-pOMC.

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.