

Supporting Information

Organic Microporous Polymer from Hexaphenylbenzene Based Triptycene Monomer: Synthesis and Its Gas Storage Properties

Chun Zhang,^{*a} Lian-Hui Peng,^a Buyi Li,^b Ying Liu,^a Peng-Cheng Zhu,^a Zhen Wang,^a
Deng-Huang Zhan,^a Bien Tan,^{*b} Xiang-Liang Yang^a and Hui-Bi Xu^a

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

^b School of Chemistry and Chemical Engineering, Huazhong University of Science
and Technology, Hubei, 430074, China

Email: chunzhang@hust.edu.cn

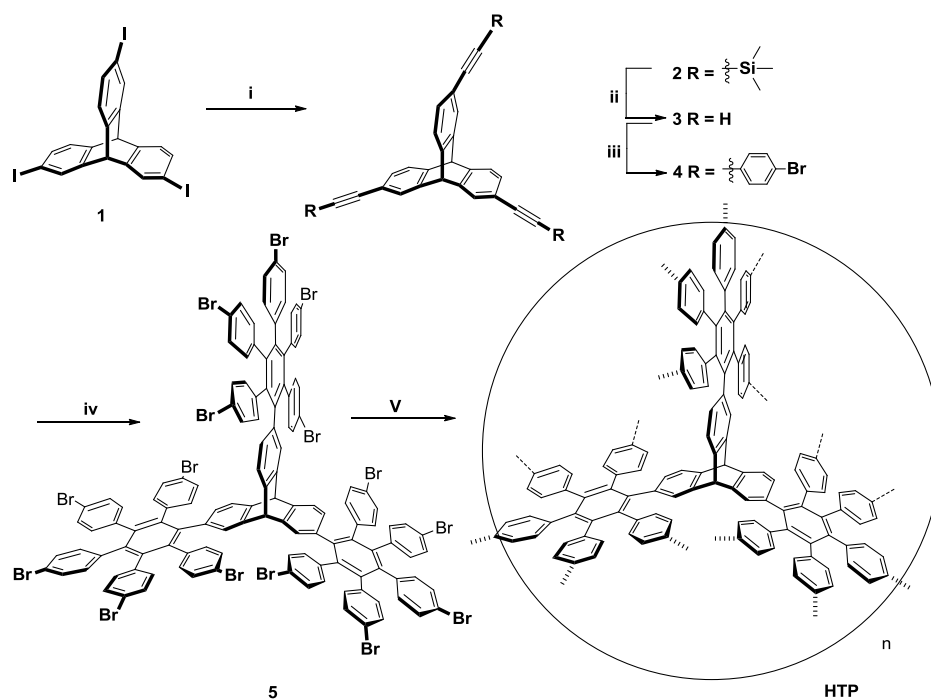
Table of contents

1. Synthesis of HP and HTP -----	S2
2. ¹ H NMR and ¹³ C NMR spectra of 2 , 3 , 4 and 5 -----	S6
3. IR spectra of HP and 6 -----	S10
4. IR spectra of HTP and 5 -----	S10
5. XRD spectra of HP and HTP -----	S11
6. TGA of HP and HTP -----	S11
7. Gas Sorption Analysis of HP and HTP -----	S12

1. Synthesis of HP and HTP

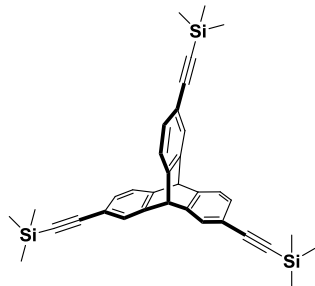
Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a DMX400 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 2 ms (ramp 100) and pulse delay of 3 s. SEM measurements were performed on a Sirion 200 field emission scanning electron microscope. TEM studies were conducted on a Tecnai G220 electron microscope. TGA measurements were performed on Pyris1 TGA. Materials obtained commercially were used without further purification.



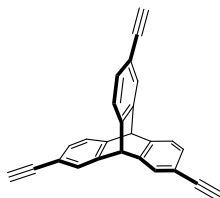
Synthesis of **2**. 2,6,14-triiodotriptycene (632 mg, 1.0 mmol), trimethylsilyl acetylene (635 μL , 4.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (80 mg, 0.07 mmol), and CuI (20 mg, 0.11 mmol) were mixed in triethylamine (40 mL). The mixture was stirred at 70 $^\circ\text{C}$ under argon for 48h, cooled, evaporated to remove triethylamine, and then taken up with CH_2Cl_2 , and washed with 1 M aqueous HCl. The aqueous solution was extracted with CH_2Cl_2 . The organic extracts were combined, washed successively with aqueous NaHCO_3 and brine, dried over anhydrous MgSO_4 . The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, $\text{DCM/PE} = 1:4$) to give

the product **2** (465 mg, 85.6 %) as a white solid.



2, Yield: 85.6 %. ^1H NMR (400 MHz, CDCl_3): δ 0.20 (s, 27H), 5.30 (s, 1H), 5.32 (s, 1H), 7.11 (d, $J = 7.6$, 3H), 7.23-7.26 (m, 3H), 7.46(d, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 0.0, 53.3, 53.5, 93.5, 105.1, 120.1, 120.2, 123.6, 127.2, 129.4, 144.3, 144.7, 144.8. EI-MS: m/z 542 (M^+). Anal. Calcd for $\text{C}_{35}\text{H}_{38}\text{Si}_3$: C, 77.43; H, 7.05; Found: C, 77.59; H, 7.41.

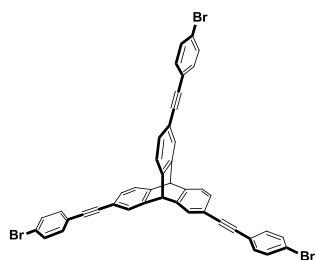
Synthesis of **3**. To a solution of **2** (648 mg, 1.19 mmol) in CH_2Cl_2 (5 mL) was added a suspension of K_2CO_3 (494 mg, 3.58 mmol) in methanol (25 mL). The mixture was stirred overnight and quenched by adding the water. The organic phase was extracted with dichloromethane and washed with brine, dried over anhydrous MgSO_4 . The organic solvent was removed under vacuum to afford 316 mg white solid (87.0%).



3, Yield: 87.0 %. ^1H NMR (400 MHz, CDCl_3): δ 2.97(s, 3H), 5.37 (s, 1H), 5.39 (s, 1H), 7.17 (dd, $J = 7.6$, 1.2 Hz, 3H), 7.33 (d, $J = 7.6$ Hz, 3H), 7.50 (d, $J = 1.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 53.2, 53.4, 76.6, 83.5, 119.2, 119.3, 123.7, 123.8, 127.3, 127.4, 129.7, 144.2, 144.3, 144.8, 144.9. EI-MS: m/z 326 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{14}$: C, 95.68; H, 4.32; Found: C, 95.50; H, 4.40.

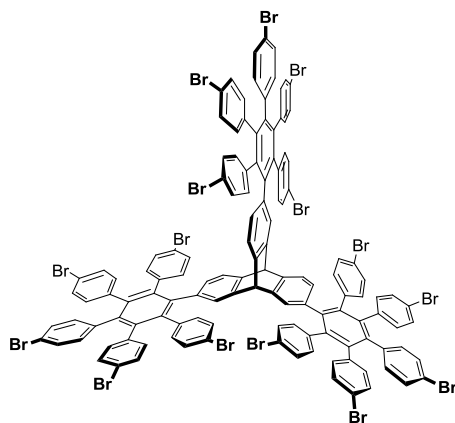
Synthesis of **4**. **3** (163mg, 0.5mmol), 1-bromo-4-iodobenzene (495 mg, 1.75 mmol), $\text{Pd}(\text{PPh}_3)_4$ (40 mg, 0.035 mmol), and CuI (10 mg, 0.05 mmol) were mixed in triethylamine (30 mL). The mixture was stirred at 70 °C under argon for 48h, cooled, evaporated to remove triethylamine, taken up in CH_2Cl_2 , and washed with 1 M

aqueous HCl. The aqueous solution was extracted with CH₂Cl₂. The organic extracts were combined, washed successively with aqueous NaHCO₃ and brine, dried over anhydrous MgSO₄. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, DCM/PE = 1: 7) to give the product **3** (180 mg, 45.5 %) as white solid.



4, Yield: 45.5 %. ¹H NMR (400 MHz, CDCl₃): δ 5.42 (s, 1H), 5.43 (s, 1H), 7.21 (dd, *J* = 7.6, 1.4 Hz, 3H), 7.33-7.38 (m, 9H), 7.46 (d, *J* = 8.4 Hz, 6H), 7.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 53.3, 53.5, 87.8, 90.5, 120.0, 120.1, 122.2, 122.4, 123.8, 126.8, 129.2, 131.6, 132.9, 144.3, 144.4, 144.6, 144.7. EI-MS: *m/z* 790 (M⁺). Anal. Calcd for C₄₄H₂₃Br₃: C, 66.78; H, 2.93; Found: C, 66.82; H, 3.10.

Synthesis of **5**. A mixture of **4** (300 mg, 0.38 mmol) and tetra(4- bromophenyl) cyclopentadienone (849 mg, 1.21 mmol) in diphenyl ether (2 mL) were heated to 250 °C under argon for 3 days. After being allowed to cool to room temperature, the reaction mixture was subjected to column chromatography (silica gel, DCM/PE = 1: 2), followed by crystallization from CHCl₃/CH₃OH to give the product (664 mg, 62.2 %) as white solid.



5, Yield: 62.2 %. ¹H NMR (400 MHz, CDCl₃): δ 4.21 (s, 1H), 4.54 (s, 1H), 6.28 (dd, *J*

= 7.6, 1.5 Hz, 2H), 6.32-12.36 (m, 4H), 6.42-12.72 (m, 38H), 6.84 (dd, $J = 8.2, 1.9$ Hz, 2H), 6.94 (dd, $J = 8.2, 1.9$ Hz, 4H), 7.01-7.05 (m, 19H). ^{13}C NMR (100 MHz, CDCl_3): δ 52.7, 53.1, 119.8, 120.1, 122.4, 122.7, 126.1, 126.4, 128.2, 128.8, 129.8, 130.0, 130.1, 130.3, 132.6, 132.7, 132.9, 132.9, 133.0, 133.1, 135.1, 138.5, 138.7, 139.0, 139.4. MALDI-TOF-MS: 2807 (M^+) Anal. Calcd for $\text{C}_{128}\text{H}_{71}\text{Br}_{15}$: C, 54.76; H, 2.55; Found: C, 54.90; H, 2.32.

Synthesis of **HTP**. 1,5-cyclooctadiene (COD, 430 μL , 3.5 mmol) was added to a solution of **5** (478 mg, 0.17 mmol), bis(1,5-cyclooctadiene)nickel(0) ($[\text{Ni}(\text{cod})_2]$, 1.00 g, 3.5 mmol) and 2,2'-bipyridyl (547 mg, 3.5 mmol) in dehydrated DMF (40 ml), and the mixture was reflux at 85 $^\circ\text{C}$ under argon for 96 h. After cooling to room temperature, concentrated HCl was added to the mixture. After filtration, the residue was washed with CHCl_3 , THF and H_2O , respectively, and dried in vacuo to give the product (231 mg, 84.6 %) as yellow solid.

HTP, Yield: 84.6 %. M.p. >300 $^\circ\text{C}$. Anal. Calcd for $\text{C}_{128}\text{H}_{71}$: C, 95.55; H, 4.45. Found: C, 92.88; H, 4.08.

Synthesis of **HP**. 1,5-cyclooctadiene (COD, 430 μL , 3.5 mmol) was added to a solution of **6** (429 mg, 0.425 mmol), bis(1,5-cyclooctadiene)nickel(0) ($[\text{Ni}(\text{cod})_2]$, 1.00 g, 3.5 mmol) and 2,2'-bipyridyl (547 mg, 3.5 mmol) in dehydrated DMF (40 ml), and the mixture was reflux at 85 $^\circ\text{C}$ under argon for 96 h. After cooling to room temperature, concentrated HCl was added to the mixture. After filtration, the residue was washed with CHCl_3 , THF and H_2O , respectively, and dried in vacuo to give the product (207 mg, 92.1 %) as yellow solid.

HP, Yield: 92.1 %. M.p. >300 $^\circ\text{C}$. Anal. Calcd for $\text{C}_{128}\text{H}_{71}$: C, 95.42; H, 4.58. Found: C, 93.28; H, 4.22.

2. ^1H NMR and ^{13}C NMR spectra of 2, 3, 4 and 5

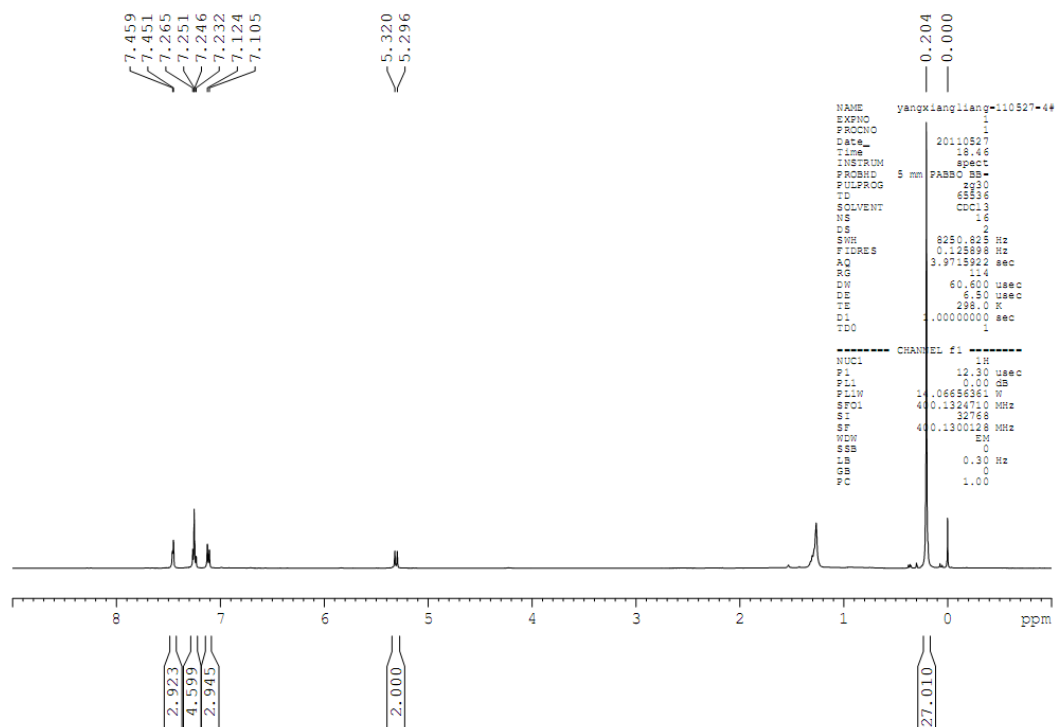


Fig. S1. ^1H NMR spectrum (400 MHz, CDCl_3) of 2.

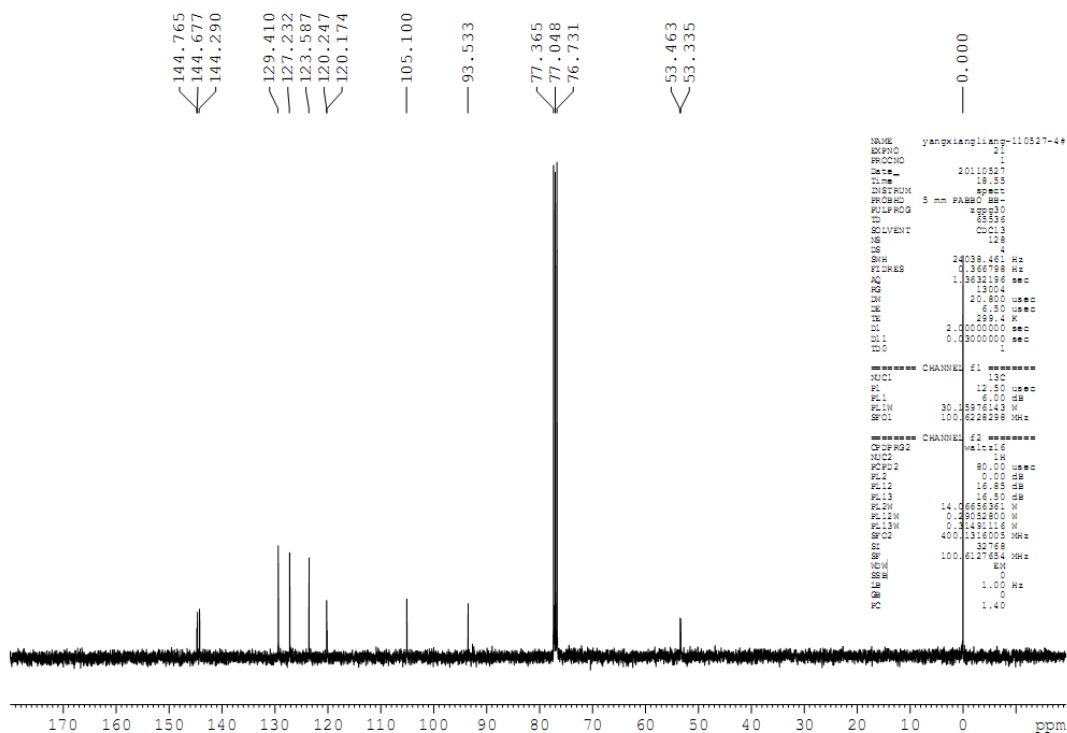


Fig. S2. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 2.

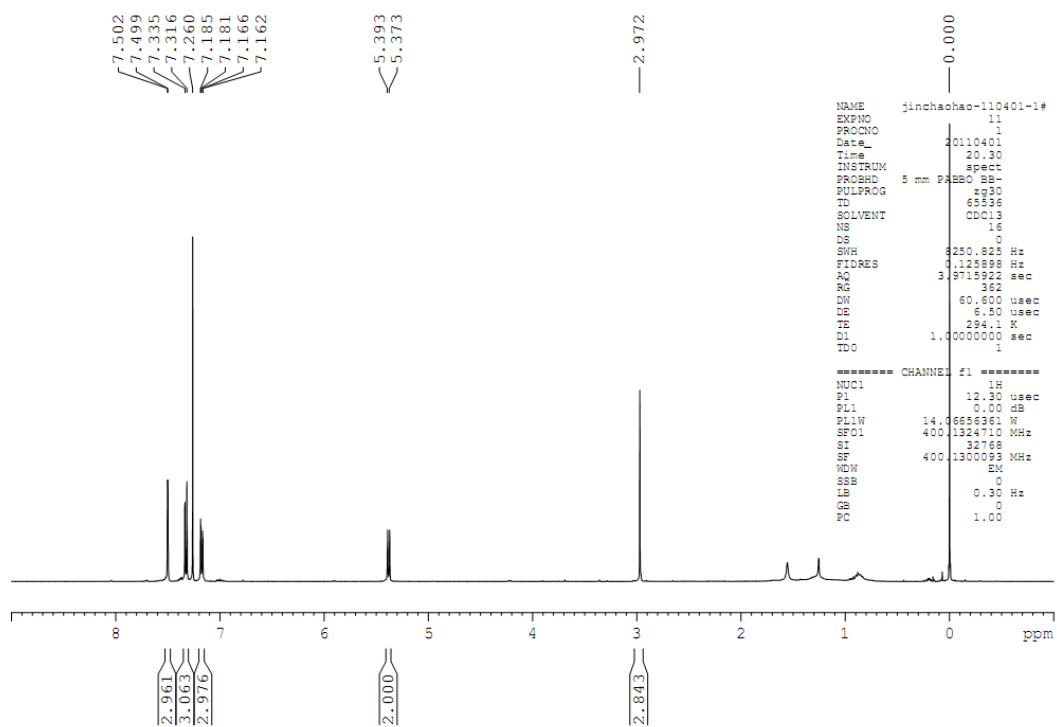


Fig. S3. ¹H NMR spectrum (400 MHz, CDCl₃) of **3**.

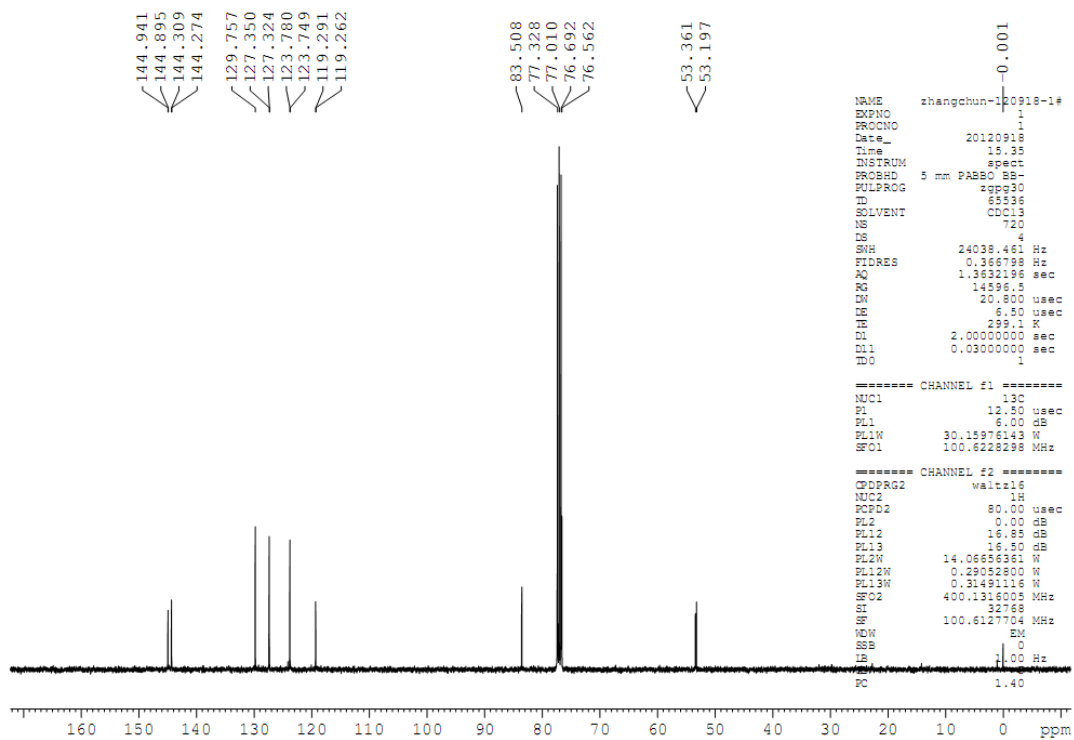


Fig. S4. ¹³C NMR spectrum (100 MHz, CDCl₃) of **3**.

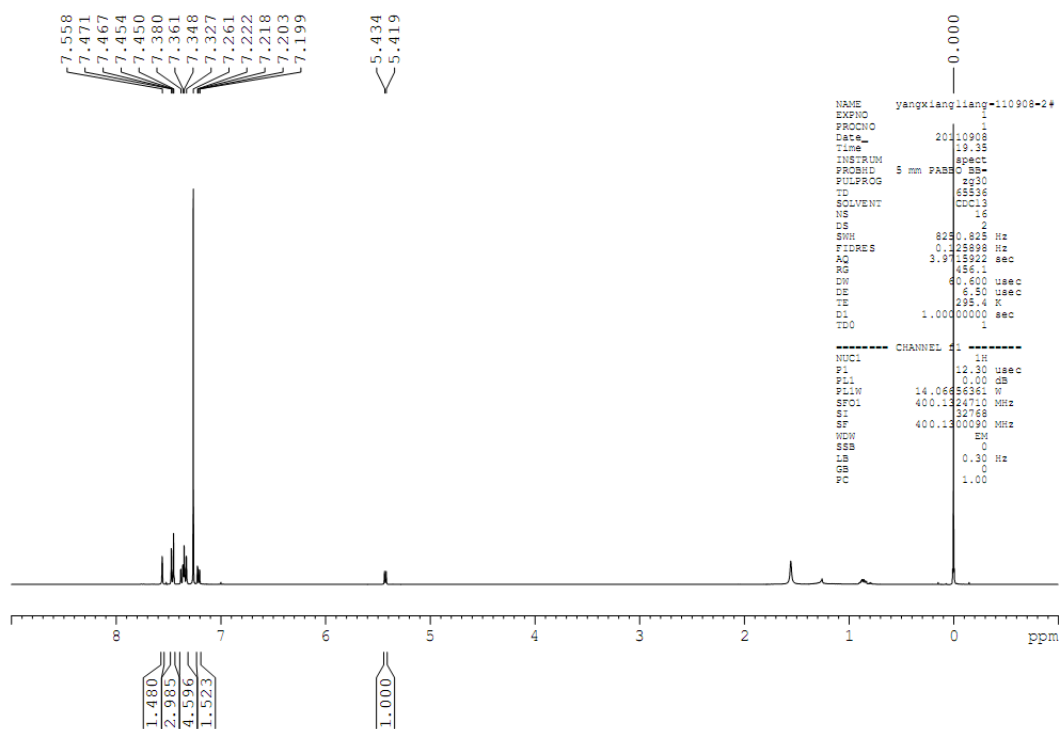


Fig. S5. ^1H NMR spectrum (400 MHz, CDCl_3) of 4.

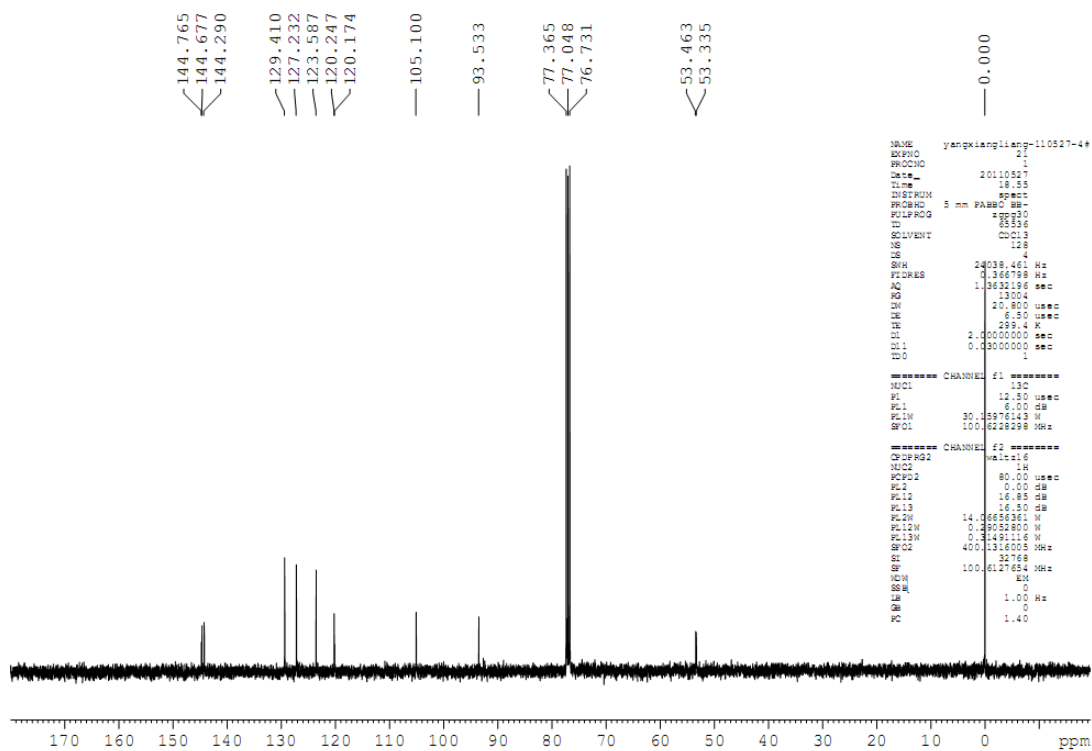


Fig. S6. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 4.

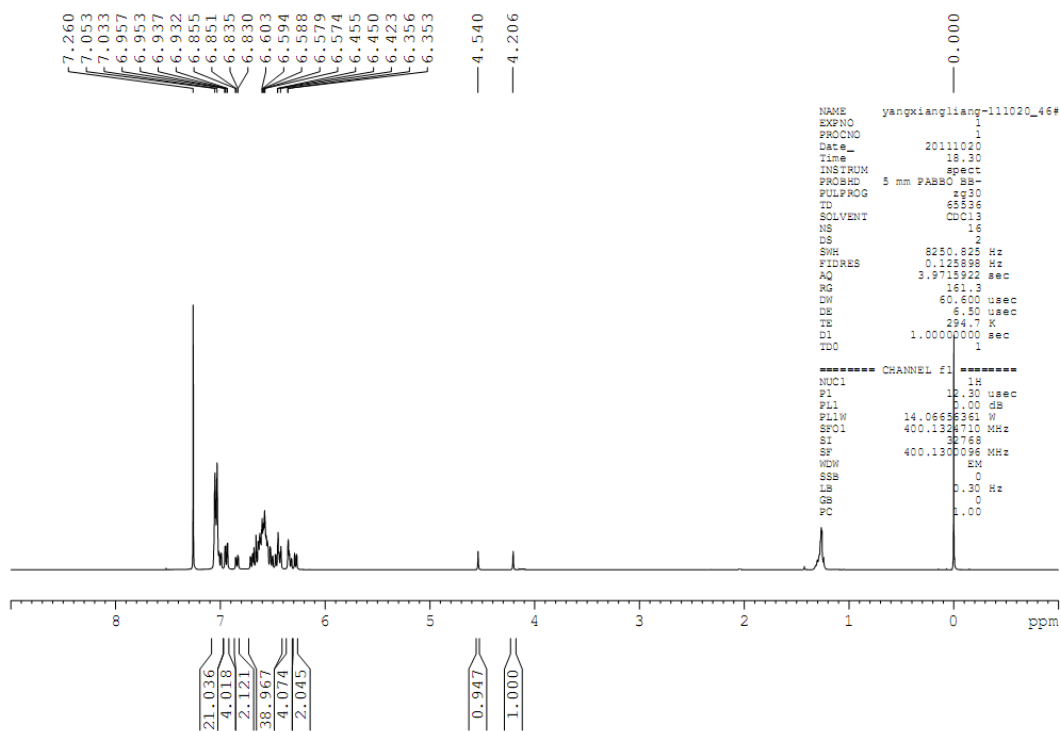


Fig. S7. ^1H NMR spectrum (400 MHz, CDCl_3) of **5**.

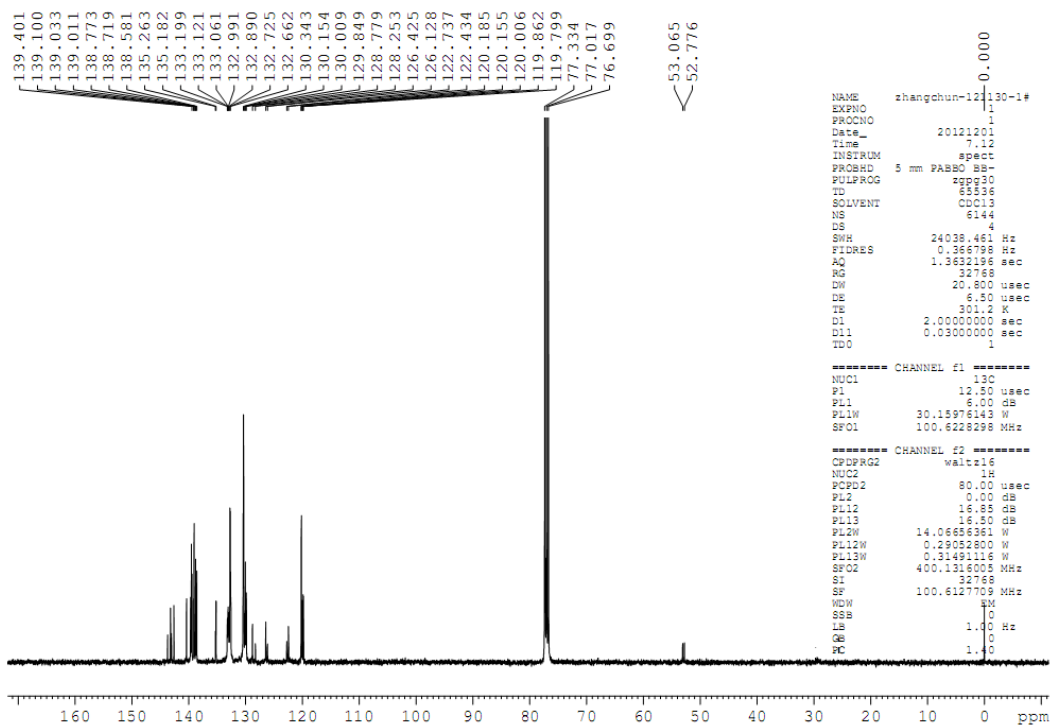


Fig. S8. ^{13}C NMR spectrum (100 MHz, CDCl_3) of **5**.

3. IR spectra of HP and 6

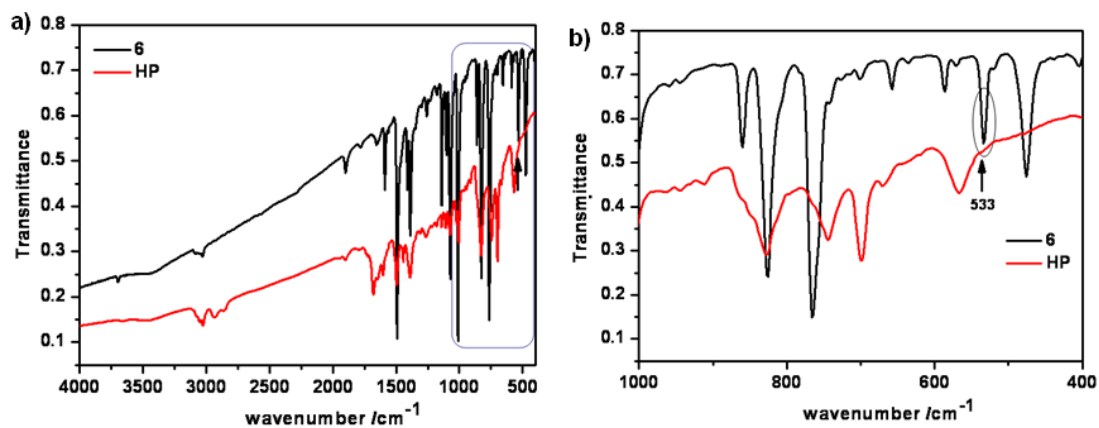


Fig. S9. FTIR spectra of **HP** (red line) and its precursor **6** (black line) from 400-4000 cm⁻¹ (a) and 400-1000cm⁻¹ (b).

4. IR spectra of HTP and 5

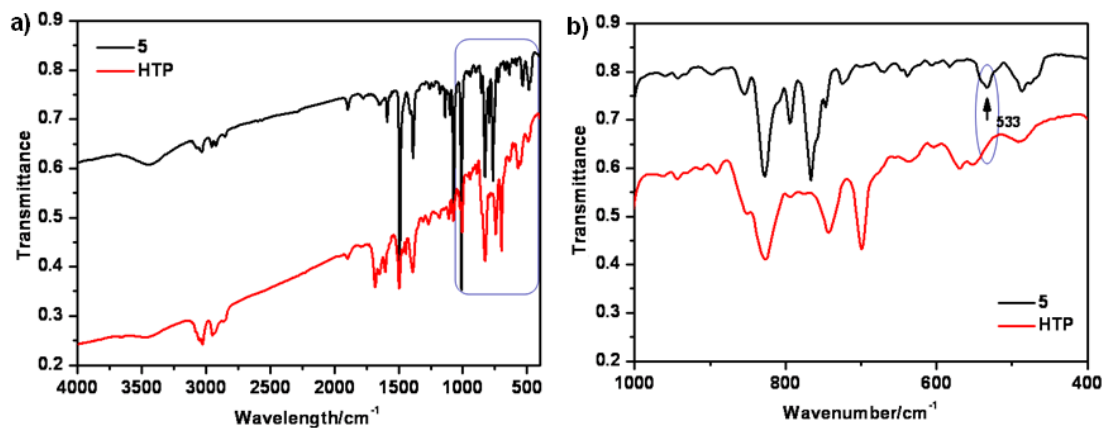


Fig. S10. IR spectra of **HTP** (red line) and its precursor **5** (black line) from 400-4000 cm⁻¹ (a) and 400-1000cm⁻¹ (b).

5. XRD spectra of HTP and HP

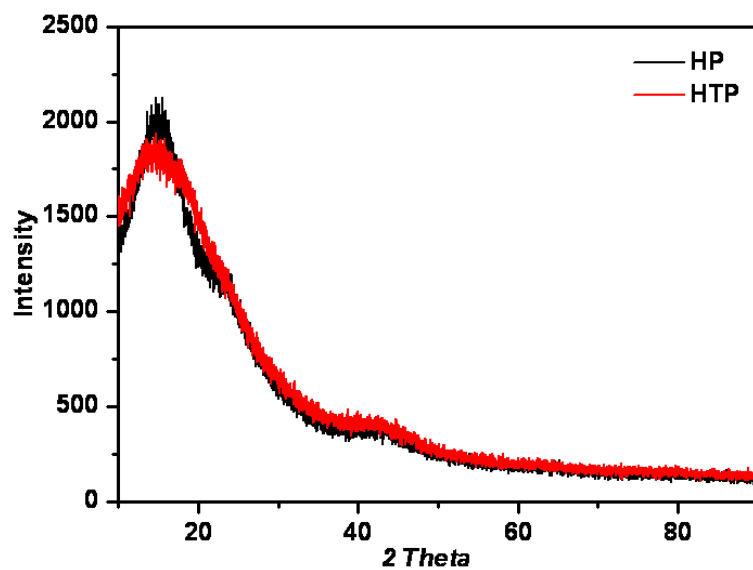


Fig. S11. XRD spectra of **HP** and **HTP** at 298K

6. TGA of HTP and HP

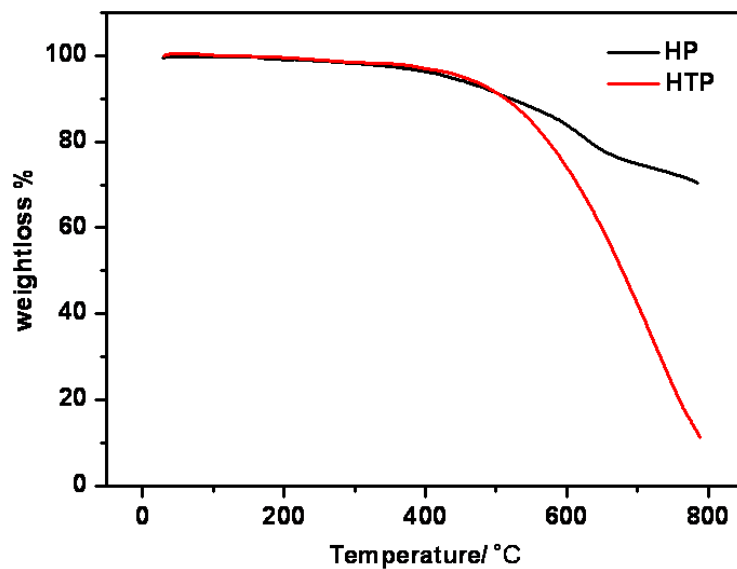


Fig. S12. TGA plots of **HP** and **HTP** at air condition.

7. Gas Sorption Analysis of HP and HTP

Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Sample was degassed at 110 °C for 15 h under vacuum before analysis. CO₂ isotherms were measured at 273 K and 298 K up to 1.13 bar using a Micromeritics ASAP 2020 volumetric adsorption analyzer with the same degassing procedure.

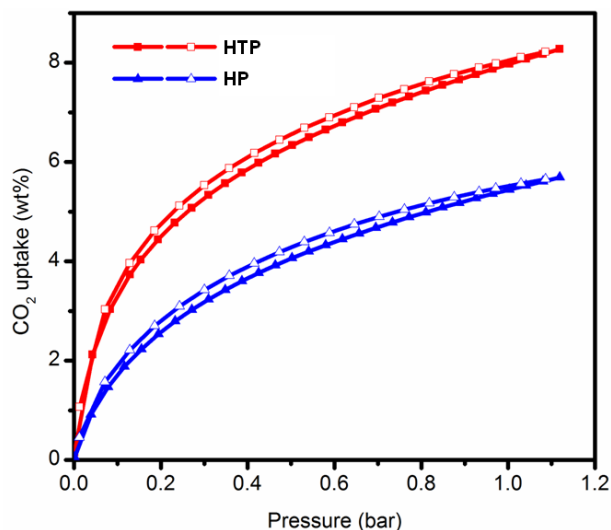


Fig. S13. CO₂ adsorption isotherms and desorption isotherms up to 1.13 bar at 298 K of **HP** and **HTP**.