Supporting Information

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

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1. Synthesis of HP and HTP

Experimental Section

General Methods. $^1$H 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 Pyrisl 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), Pd(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 °C under argon for 48h, cooled, evaporated to remove triethylamine, and then taken up with CH$_2$Cl$_2$, and washed with 1 M aqueous HCl. The aqueous solution was extracted with CH$_2$Cl$_2$. 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, DCM/PE = 1:4) to give
the product 2 (465 mg, 85.6 %) as a white solid.

2. Yield: 85.6 %. \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 0.20 (s, 27H), 5.30 (s, 1H), 5.32 (s, 1H), 7.11 (d, \(J = 7.6, 3\)H), 7.23-7.26 (m, 3H), 7.46(d, 3H). \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 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 C\(_{35}\)H\(_{38}\)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\textsubscript{2}Cl\textsubscript{2} (5 mL) was added a suspension of K\(_2\)CO\(_3\) (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 %. \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 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\textsubscript{3}): \(\delta\) 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 C\(_{26}\)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), Pd(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\(_2\)Cl\(_2\), and washed with 1 M
aqueous HCl. The aqueous solution was extracted with CH$_2$Cl$_2$. 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, DCM/PE = 1: 7) to give the product 3 (180 mg, 45.5 %) as white solid.

**4.** Yield: 45.5 %. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 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 C$_{44}$H$_{23}$Br$_3$: 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 CHCl$_3$/CH$_3$OH to give the product (664 mg, 62.2 %) as white solid.

**5.** Yield: 62.2 %. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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, 133.0, 133.1, 135.1, 138.5, 138.7, 139.0, 139.4. MALDI-TOF-MS: 2807 (M$^+$) Anal. Calcd for C$_{128}$H$_{71}$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) ([Ni(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 °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$_2$O, respectively, and dried in vacuo to give the product (231 mg, 84.6 %) as yellow solid.

HTP, Yield: 84.6 %. M.p. >300 °C. Anal. Calcd for C$_{128}$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) ([Ni(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 °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$_2$O, respectively, and dried in vacuo to give the product (207 mg, 92.1 %) as yellow solid.

HP, Yield: 92.1 %. M.p. >300 °C. Anal. Calcd for C$_{128}$H$_{71}$: C, 95.42; H, 4.58. Found: C, 93.28; H, 4.22.
2. $^1$H NMR and $^{13}$C NMR spectra of 2, 3, 4 and 5

**Fig. S1.** $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 2.

**Fig. S2.** $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 2.
Fig. S3. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 3.

Fig. S4. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 3.
Fig. S5. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4.

Fig. S6. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4.
Fig. S7. $^1$H 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 400-1000 cm$^{-1}$ (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 400-1000 cm$^{-1}$ (b).
5. XRD spectra of HTP and HP

![XRD spectra graph]

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

6. TGA of HTP and HP

![TGA plot graph]

**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. CO$_2$ 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.

![Graph](Fig. S13. CO$_2$ adsorption isotherms and desorption isotherms up to 1.13 bar at 298 K of HP and HTP.)