Electronic Supplementary Information

Tetraphenyladamantane-based microporous polyimide for adsorptions of carbon dioxide, hydrogen, organic and water vapors

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Fig. S5 $^1$H NMR spectrum of 1,3,5,7-tetrakis(4-aminophenyl)adamantane.

Experimental Section
<table>
<thead>
<tr>
<th>Gas</th>
<th>T/K</th>
<th>$K_H$/mol g$^{-1}$ Pa$^{-1}$</th>
<th>$A_0$/ln(mol g$^{-1}$ Pa$^{-1}$)</th>
<th>$Q_0$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>77</td>
<td>1.27 × 10$^{-6}$</td>
<td>-13.58</td>
<td>6.76</td>
</tr>
<tr>
<td></td>
<td>87</td>
<td>3.74 × 10$^{-7}$</td>
<td>-14.79</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>273</td>
<td>1.47 × 10$^{-7}$</td>
<td>-15.73</td>
<td>34.4</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>4.14 × 10$^{-8}$</td>
<td>-17.00</td>
<td></td>
</tr>
</tbody>
</table>

Fig. S1 FTIR spectrum of the polyimide network.
**Fig. S2** $^{13}$C CP/MAS NMR spectrum for the polyimide network.

**Fig. S3** $^1$H NMR spectrum of 1,3,5,7-tetrakis(4-nitrophenyl)adamantane.
**Fig. S4** FTIR spectrum of 1,3,5,7-tetrakis(4-aminophenyl)adamantane.

**Fig. S5** $^1$H NMR spectrum of 1,3,5,7-tetrakis(4-aminophenyl)adamantane.
Experimental Section

Instrumentation. Fourier transform infrared spectra (FTIR) were recorded using a Nicolet 20DXB FT-IR spectrophotometer in the 400-4000 cm$^{-1}$ region. Samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks. $^1$H NMR spectra were measured on a 400 MHz Varian INOVA NMR spectrometer, using tetramethylsilane as an internal reference. Molecular mass was determined on an electron impact ionization time-of-flight mass spectrometer (EI-TOF MS). Melting points were performed using an X-4 melting-point apparatus with microscope. Solid-state $^{13}$C CP/MAS (cross-polarization with magic angle spinning) spectra was recorded on a Varian Infinity-Plus 400 spectrometer at 100.61 MHz at an MAS rate of 10.0 KHz using zirconia rotors 4 mm in diameter using a contact time of 4.0 ms and a relaxation delay of 2.0 s. The $^1$H $\pi/2$ pulse was 3.75 $\mu$s, and two-pulse phase modulation (TPPM) decoupling was during the data acquisition. Elemental analyses were determined with an Elementar Vario EL III elemental analyzer. All the sorption measurements for gases, organic and water vapors were performed on an Autosorb iQ (Quantachrome) analyzer. Before sorption measurement, the sample was degassed at 150 °C under high vacuum for 24 h. $\text{N}_2$ sorption was measured at 77 K. The apparent surface area ($S_{\text{BET}}$) was calculated using Brunauer-Emmett-Teller (BET) model. Hydrogen sorption was measured at 77 K and 87 K up to 1 bar. Carbon dioxide sorption was measured at 273 K and 298 K up to 1 bar. Sorptions for water, benzene, n-hexane and cyclohexane vapors were measured at 298 K up to their saturated vapor pressures.
**Materials.** Adamantane and pyromellitic dianhydride (PMDA) were purchased from Shanghai Chemical Reagent Corp. PMDA was purified by sublimation prior to use. *m*-Cresol was purified by refluxing over P$_2$O$_5$ and distillation under reduced pressure. Other commercial reagents were of analytical grade and used without further purification unless otherwise stated.

**Synthesis of 1,3,5,7-tetrakis(4-nitrophenyl)adamantane (TNPA).**

1,3,5,7-Tetraphenyladamantane was synthesized in the reference of the procedure in the literature with some modifications. TPA (4 g) was added slowly into fuming nitric acid (35 mL) and the mixture was stirred for 30 min. Then acetic acid (15 mL) and acetic anhydride (12 mL) were charged into the flask. The mixture was stirred for 15 min and diluted with additional acetic acid (50 mL). The precipitate was filtered and washed with ethanol. Crystallization from *N*,*N*-dimethylformamide (DMF) gave 2.3 g solid with yield of 38.7%. m. p. >300 °C; *^1^H* NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) 8.20-8.22 (d, 8H), 7.91-7.93 (d, 8H), 2.25 (s, 12H); IR (KBr, cm$^{-1}$): 3113, 3028 (=C-H stretching vibration), 2932, 2903, 2854 (C-H stretching vibration), 1599, 1516 (aromatic ring C=C vibration), 1343 (N=O stretching vibration), 856 (C-H banding in phenyl rings).

**Synthesis of 1,3,5,7-tetrakis(4-aminophenyl)adamantane (TAPA).** TNPA (0.4g, 0.645mmol), tetrahydrofuran (THF, 80 mL), Pd/C (10 wt%, 0.2g) and *N*,*N*-dimethylformamide (DMF, 10 mL) was added into a hydrogenator. After purging with nitrogen several times, the mixture was stirred under 2.0 Mpa hydrogen pressure at room temperature for 2 days. After filtration, the solution was precipitated with
deionized water (100 mL). Collecting precipitate and drying under vacuum to afford colorless powder with 90.6% yield. m. p. >300 °C; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 7.11-7.13 (d, 8H), 6.50-6.52 (d, 8H), 4.86 (s, 8H), 1.82 (s, 12H); IR (KBr, cm⁻¹): 3426, 3324 (N-H stretching vibration), 3018 (=C-H stretching vibration), 2921, 2848 (C-H stretching vibration), 1623, 1514 (N-H deformation vibration), 1273 (C-N stretching vibration), 842 (C-H banding in phenyl rings).

**Synthesis of the polyimide network.** TAPA (0.5 g) and PMDA (0.4360 g) were added into m-cresol (10 mL) and stirred at ice-bath temperature under a nitrogen flow 2 h. Then the reaction system was slowly heated to room temperature and stirred overnight. When the reaction temperature was raised to 60 °C, several drops isoquinoline were added as catalyst. And then the resulting mixture was heated under atmosphere at 80 °C for 2 h, 120 °C for 4 h, 180 °C for 8 h, 200 °C for 12 h and 220 °C for 10 h. The gel obtained was rushed and extracted with THF in a Soxhlet apparatus for 48 h. The solid was then dried under vacuum at 150 °C for 2 days, Quantitative yield. Elemental analysis calculated for C₅₄H₃₂N₄O₈: C, 74.99; H, 3.73; N, 6.48; O, 14.80%. Found: C, 72.93; H, 4.77; N, 4.97%.

**References**