Supporting Information

Construction and adsorption properties of Porous Aromatic Frameworks via 
AlCl₃-triggered Coupling Polymerization

Lina Li, Hao Ren*, Ye Yuan, Guangli Yu and Guangshan Zhu

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**Synthetic procedures**

*Synthesis of PAF-41:* Anhydrous aluminium chloride (500 mg, 3.75 mmol) was added to a 100 mL round-bottomed flask. Then, after pumped to vacuum, the system was inflated with inert gas N₂ for 3 times. Next, dried chloroform (40 mL) was injected through a syringe and the mixture was heated to 60 °C for 3 h. Then triphenylamine (1.5 mmol, 367 mg) in 20 mL CHCl₃ was added into the system and the mixture kept stirring at 60 °C for 24 h. After cooling down to room temperature, the crude product was obtained by filtration and washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification of product was carried out by Soxhlet extraction with ethanol, THF, and CHCl₃ for 48 h. The product was dried in vacuum for 8 h at 80 °C to give PAF-42 (364 mg, 98.6% yield).

*Synthesis of PAF-42:* Anhydrous aluminium chloride (500 mg, 3.75 mmol) was added to a 100 mL round-bottomed flask. Then, after pumped to vacuum, the system was inflated with inert gas N₂ for 3 times. Next, dried chloroform (40 mL) was injected through a syringe and the mixture was heated to 60 °C for 3 h. Then tetraphenylmethane (1.5 mmol, 480 mg) in 20 mL CHCl₃ was added into the system and the mixture kept stirring at 60 °C for 24 h. After cooling down to room temperature, the crude product was obtained by filtration and washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification of product was carried out by Soxhlet extraction with ethanol, THF, and CHCl₃ for 48 h. The product was dried in vacuum for 8 h at 80 °C to give PAF-42 (469 mg, 96.1% yield).

*Synthesis of PAF-43:* Anhydrous aluminium chloride (500 mg, 3.75 mmol) was added to a 100 mL round-bottomed flask. Then, after pumped to vacuum, the system was inflated with inert gas N₂ for 3 times. Next, dried chloroform (40 mL) was injected through a syringe and the mixture was heated to 60 °C for 3 h. Then tetraphenylsilane (1.5 mmol, 504 mg) in 20 mL CHCl₃ was added into
the system and the mixture kept stirring at 60 °C for 24 h. After cooling down to room temperature, the crude product was obtained by filtration and washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification of product was carried out by Soxhlet extraction with ethanol, THF, and CHCl₃ for 48 h. The product was dried in vacuum for 8 h at 80 °C to give PAF-42 (469 mg, 96.0% yield).

Synthesis of PAF-44: Anhydrous aluminium chloride (500 mg, 3.75 mmol) was added to a 100 mL round-bottomed flask. Then, after pumped to vacuum, the system was inflated with inert gas N₂ for 3 times. Next, dried chloroform (40 mL) was injected through a syringe and the mixture was heated to 60 °C for 3 h. Then tetraphenylgermane (1.5 mmol, 570 mg) in 20 mL CHCl₃ was added into the system and the mixture kept stirring at 60 °C for 24 h. After cooling down to room temperature, the crude product was obtained by filtration and washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification of product was carried out by Soxhlet extraction with ethanol, THF, and CHCl₃ for 48 h. The product was dried in vacuum for 8 h at 80 °C to give PAF-42 (535.8 mg, 93.8% yield).

Table S1. Raw material input and yield of PAF-41, PAF-42, PAF-43, and PAF-44.

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<th>Monomers</th>
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<td>500 mg, 3.75 mmol</td>
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<tr>
<td>PAF-44</td>
<td>570 mg, 1.5 mmol</td>
<td>500 mg, 3.75 mmol</td>
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Fig. S1. FTIR spectra of monomers (black) and corresponding polymerization products (red), PAF-41 (a), PAF-42 (b), PAF-43 (c) and PAF-44 (d), respectively.
Table S2. Characteristic peaks in FIIR spectra of benzene ring

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<th>Category</th>
<th>PAFs</th>
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<th>Product (Disubstituted Benzene, cm$^{-1}$)</th>
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<td>1507 &amp; 1481</td>
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<td>PAF-44</td>
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<td>C-H deformation vibration of ring hydrogens:</td>
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Fig. S2. PXRD patterns of the PAFs, PAF-41 (black), PAF-42 (blue), PAF-43 (olive), and PAF-44 (red).
Fig. S3. TEM images of PAF-41 (a), PAF-42 (b), PAF-43 (c) and PAF-44 (d).
Fig. S4. CO$_2$ and CH$_4$ adsorption (solid circles) and desorption (open circles) isotherms of PAF-41.

Fig. S5. CO$_2$ and CH$_4$ adsorption (solid circles) and desorption (open circles) isotherms of PAF-42.
Fig. S6. CO₂ and CH₄ adsorption (solid circles) and desorption (open circles) isotherms of PAF-43.

Fig. S7. CO₂ and CH₄ adsorption (solid circles) and desorption (open circles) isotherms of PAF-44.
Table S3. Porosity data of PAFs synthesized at different temperature.

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Table S4. Comparison of CO₂ uptakes and isosteric heat of adsorption in POFs

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<th>S$_{BET}$/m$^2$ g$^{-1}$</th>
<th>CO₂ uptake mmol g$^{-1}$</th>
<th>T (K)</th>
<th>Q$_{stCO2}$/KJ mol$^{-1}$</th>
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Table S5. Comparison of CH\textsubscript{4} uptakes and isosteric heat of adsorption in POFs

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<th>material</th>
<th>(S\textsubscript{BET}/m^2\textsubscript{g}^{-1})</th>
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<th>(Q\textsubscript{stCH4}/K_Jmol^{-1})</th>
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