Electronic supplementary information (ESI) for

Microporous organic polymers with acetal linkages: synthesis, characterization, and gas sorption properties

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Synthesis of 4,4'-Biphenyldicarboxaldehyde (M2)

4,4'-Biphenyldicarboxaldehyde (M2) was prepared following a modified procedure given in the literature. 4-Bromobenzaldehyde (100 mg, 0.54 mmol) and 4-formylphenylboronic acid (81 mg, 0.54 mmol) were dissolved in 10 mL of tetrahydrofuran. Aqueous solution of potassium carbonate (5.0 mL, 2.0 mol L⁻¹) was added into the solution under nitrogen atmosphere. After the addition of bis(triphenylphosphine)palladium(II) dichloride (30 mg), the mixture was refluxed for 12 h. The solution was extracted thrice with dichloromethane (3 × 100 mL). The obtained organic layer was washed with plenty of water and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column to give a yellow solid with 93% yield. M.p.: 146–147 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.09 (s, 2H, −CHO), 8.02 (d, J = 8.0 Hz, 4H, Ar–H), 7.82 (d, J = 8.0 Hz, 4H, Ar–H); IR (KBr, cm⁻¹): 3075, 2986, 2896, 1664, 1575, 1466, 1390, 1335, 1274, 1205, 1143, 1061, 890, 808, 685, 589, 507.

Synthesis of 1,3,5-tris(4-formylphenyl)benzene (M3)

1,3,5-Tris(4-formylphenyl)benzene (M3) was prepared following a modified procedure given in the literature. 1,3,5-Tribromobenzene (100 mg, 0.32 mmol), 4-formylphenylboronic acid (145 mg, 0.94 mmol), and bis(triphenylphosphine)palladium(II) dichloride (30 mg) were reacted in tetrahydrofuran and aqueous solution of potassium carbonate to afford
1,3,5-tris(4-formylphenyl)benzene (M3) in 92% yield. M.p.: 245–247 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 10.10 (s, 3H, −CHO), 8.02 (d, \(J = 8.0\) Hz, 6H, Ar−H), 7.91 (s, 3H, Ar−H), 7.86 (d, \(J = 8.0\) Hz, 6H, Ar−H); IR (KBr, cm\(^{-1}\)): 3051, 2927, 2811, 2720, 1603, 1389, 1317, 1220, 1174, 1109, 863, 817, 687, 519.

**Synthesis of 1,3,5-tris(4-formylbiphenyl)benzene (M4)**

1,3,5-Tris(4-formylbiphenyl)benzene (M4) was prepared following a modified procedure given in the literature.\(^{S1}\) 1,3,5-Tri(4-bromophenyl)benzene (100 mg, 0.19 mmol), 4-formylphenylboronic acid (83 mg, 0.57 mmol), and bis(triphenylphosphine)palladium(II) dichloride (30 mg) were reacted in tetrahydrofuran and aqueous solution of potassium carbonate to afford 1,3,5-tris(4-formylbiphenyl)benzene (M4) in 88% yield. M.p.: 158–160 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 10.09 (s, 3H, −CHO), 7.99 (d, \(J = 8.0\) Hz, 6H, Ar−H), 7.92 (s, 3H, Ar−H), 7.85 (t, \(J = 8.0\) Hz, 12H, Ar−H), 7.79 (d, \(J = 8.0\) Hz, 6H, Ar−H); IR (KBr, cm\(^{-1}\)): 3032, 2928, 2817, 2726, 1707, 1602, 1388, 1311, 1214, 1168, 1116, 1006, 857, 817, 720, 642, 500.

**Synthesis of tris(4-formylbiphenyl)amine (M5)**

Tris(4-formylbiphenyl)amine (M5) was prepared following a modified procedure given in the literature.\(^{S1}\) Tris(4-iodophenyl)amine (100 mg, 0.16 mmol), 4-formylphenylboronic acid (72 mg, 0.48 mmol), and
bis(triphenylphosphine)palladium(II) dichloride (30 mg) were reacted in tetrahydrofuran and aqueous solution of potassium carbonate to afford tris(4-formylbiphenyl)amine (M5) in 81% yield. M.p.: 277–279 °C; \^1H NMR (400 MHz, CDCl3): δ (ppm) 10.05 (s, 3H, −CHO), 7.96 (d, J = 8.0 Hz, 6H, Ar–H), 7.77 (d, J = 8.0 Hz, 6H, Ar–H), 7.62 (d, J = 8.0 Hz, 6H, Ar–H), 7.29 (d, J = 8.0 Hz, 6H, Ar–H); IR (KBr, cm\(^{-1}\)): 3032, 2830, 2732, 1701, 1590, 1525, 1499, 1285, 1180, 824, 714, 649, 571.

References:

Fig. S1 Linear acetal-linked structures (a) and branched hemiacetal-linked structures (b) in APOPs.
**Fig. S2** EDX spectrum of APOP-1.

**Fig. S3** EDX spectrum of APOP-2.
Fig. S4 EDX spectrum of APOP-3.

Fig. S5 EDX spectrum of APOP-4.
Fig. S6 EDX spectrum of APOP-5.
Fig. S7 FT-IR spectra of terephthalic aldehyde (M1), APOP-1, and model compound (MC).

Fig. S8 FT-IR spectra of 4,4'-Biphenyldicarboxaldehyde (M2), APOP-2, and model compound (MC).
**Fig. S9** FT-IR spectra of 1,3,5-tri(4-formylbiphenyl)benzene (M4), APOP-4, and model compound (MC).

**Fig. S10** FT-IR spectra of tri(4-formylbiphenyl)amine (M5), APOP-5, and model compound (MC).
**Fig. S11** Solid-state $^{13}$C CP/MAS NMR spectrum of APOP-2 recorded at the MAS rate of 5 kHz.

**Fig. S12** Solid-state $^{13}$C CP/MAS NMR spectrum of APOP-3 recorded at the MAS rate of 5 kHz.
**Fig. S13** Liquid $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of model compound dibenzalpenlpentaerythritol.

**Fig. S14** Solid-state $^{13}$C CP/MAS NMR spectrum of model compound dibenzalpenlpentaerythritol recorded at the MAS rate of 5 kHz.
Fig. S15 SEM images of APOP-1 (a), APOP-2 (b), APOP-3 (c), APOP-4 (d), and APOP-5 (e).

Fig. S16 HR-TEM images of APOP-1 (a), APOP-2 (b), APOP-3 (c), APOP-4 (d), and APOP-5 (e).
Fig. S17 BET specific surface area plots for APOP-1 (a and b), APOP-2 (c and d), APOP-3 (e and f), APOP-4 (g and h) and APOP-5 (i and j) calculated over different relative pressure ranges: $P/P_0 = 0.01–0.10$ (a, c, e, g, and i) and $P/P_0 = 0.05–0.20$ (b, d, f, h, and j), respectively.

Table S1. BET specific surface area data calculated over different pressure ranges

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P/P_0$ range</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Correlation coefficient</th>
<th>Points</th>
<th>$C$ constant $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>APOP-1</td>
<td>0.01–0.10</td>
<td>580</td>
<td>0.9999</td>
<td>5</td>
<td>1158</td>
</tr>
<tr>
<td>APOP-1</td>
<td>0.05–0.20</td>
<td>530</td>
<td>0.9993</td>
<td>8</td>
<td>−121</td>
</tr>
<tr>
<td>APOP-2</td>
<td>0.01–0.10</td>
<td>740</td>
<td>0.9999</td>
<td>5</td>
<td>658</td>
</tr>
<tr>
<td>APOP-2</td>
<td>0.05–0.20</td>
<td>690</td>
<td>0.9995</td>
<td>8</td>
<td>−185</td>
</tr>
<tr>
<td>APOP-3</td>
<td>0.01–0.10</td>
<td>960</td>
<td>0.9999</td>
<td>5</td>
<td>343</td>
</tr>
<tr>
<td>APOP-3</td>
<td>0.05–0.20</td>
<td>930</td>
<td>0.9998</td>
<td>8</td>
<td>−4576</td>
</tr>
<tr>
<td>APOP-4</td>
<td>0.01–0.10</td>
<td>980</td>
<td>0.9999</td>
<td>5</td>
<td>305</td>
</tr>
<tr>
<td>APOP-4</td>
<td>0.05–0.20</td>
<td>950</td>
<td>0.9998</td>
<td>8</td>
<td>7274</td>
</tr>
<tr>
<td>APOP-5</td>
<td>0.01–0.10</td>
<td>940</td>
<td>0.9999</td>
<td>5</td>
<td>281</td>
</tr>
<tr>
<td>APOP-5</td>
<td>0.05–0.20</td>
<td>920</td>
<td>0.9998</td>
<td>8</td>
<td>431</td>
</tr>
</tbody>
</table>

$^a$ The low relative pressure range of 0.01–0.10 using five points gives the higher $C$ constant values and therefore the best fit to the BET equation.