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.[S1] 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; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.09 (s, 2H, –C*H*O), 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.[S1] 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, $CDCl_3$): δ (ppm) 10.10 (s, 3H, –C*H*O), 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, $CDCl_3$): δ (ppm) 10.09 (s, 3H, –C*H*O), 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; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.05 (s, 3H, –C*H*O), 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:

(S1) Y.-C. Zhao, T. Wang, L.-M. Zhang, Y. Cui and B.-H. Han, Facile approach to preparing microporous organic polymers through benzoin condensation. *ACS Appl. Mater. Interfaces*, 2012, **4**(12), 6975–6981.

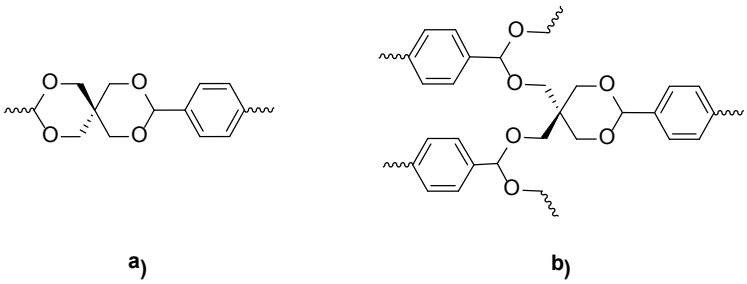


Fig. S1 Linear acetal-linked structures (a) and branched hemiacetal-linked structures (b) in **APOPs**.

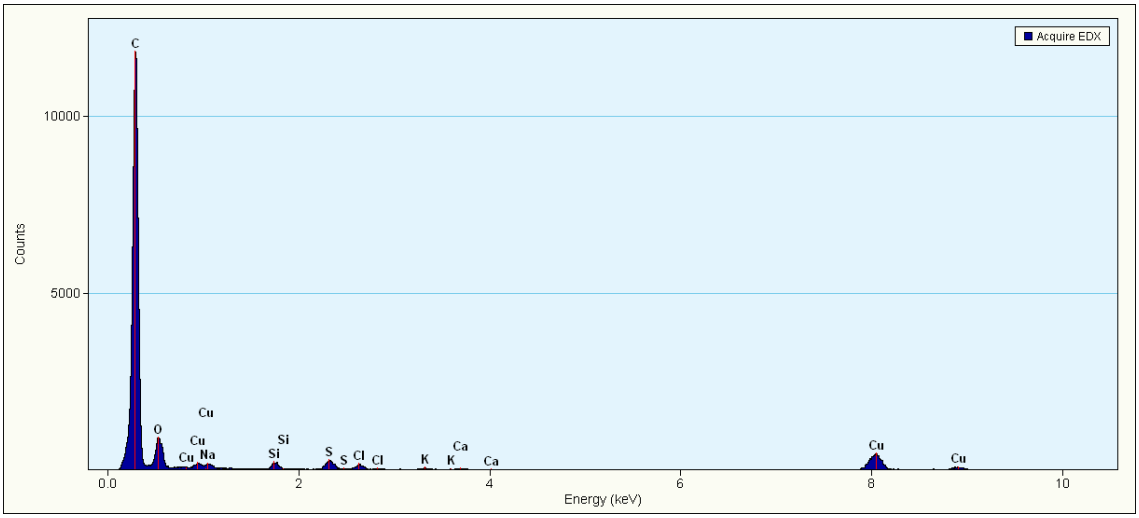


Fig. S2 EDX spectrum of **APOP-1**.

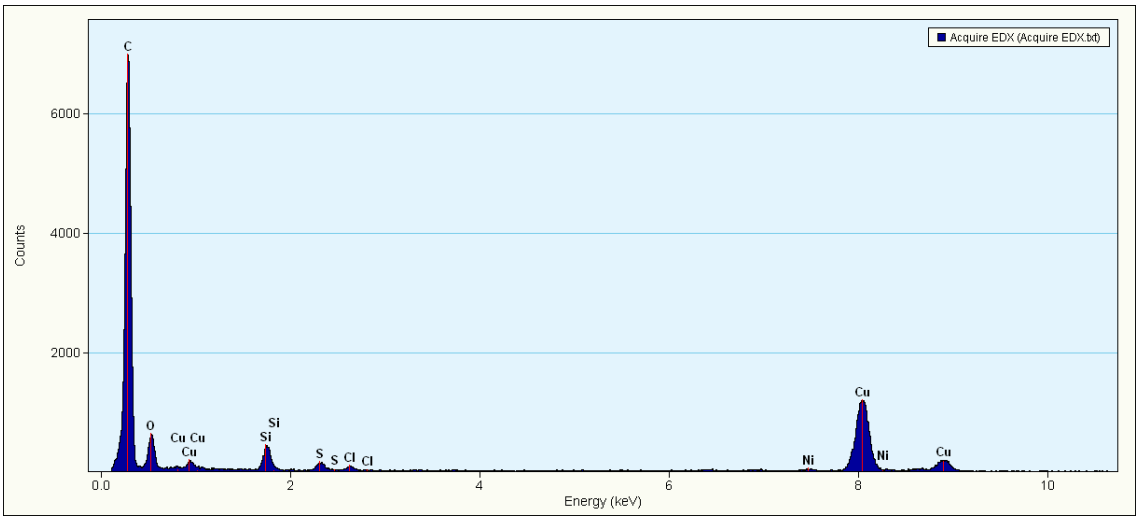


Fig. S3 EDX spectrum of **APOP-2**.

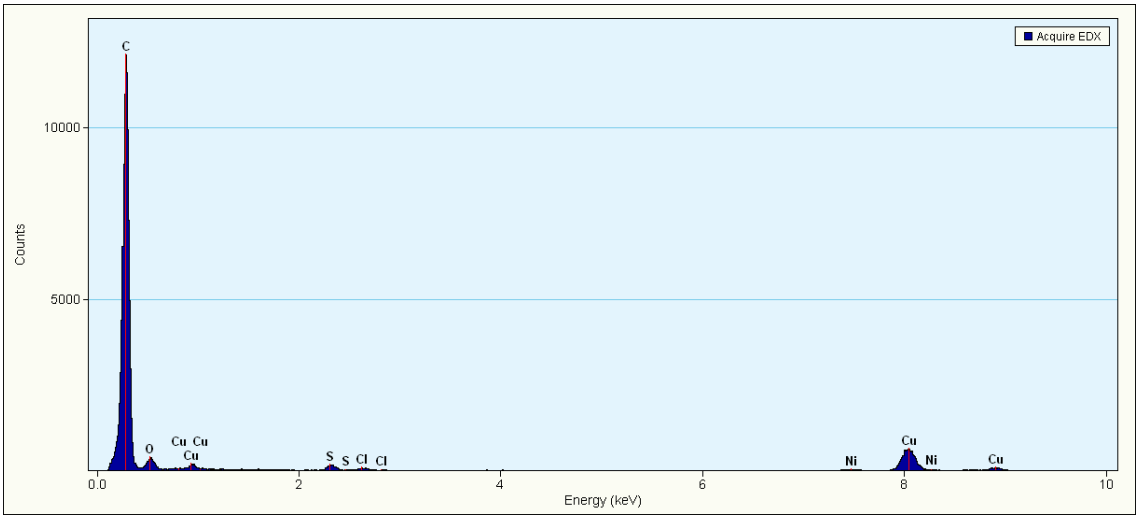


Fig. S4 EDX spectrum of **APOP-3**.

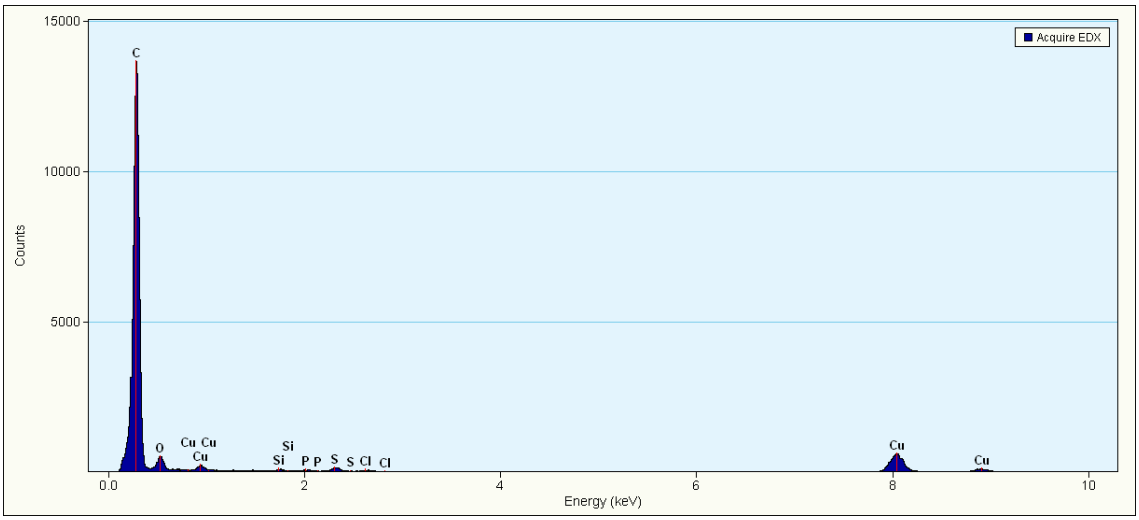


Fig. S5 EDX spectrum of **APOP-4**.

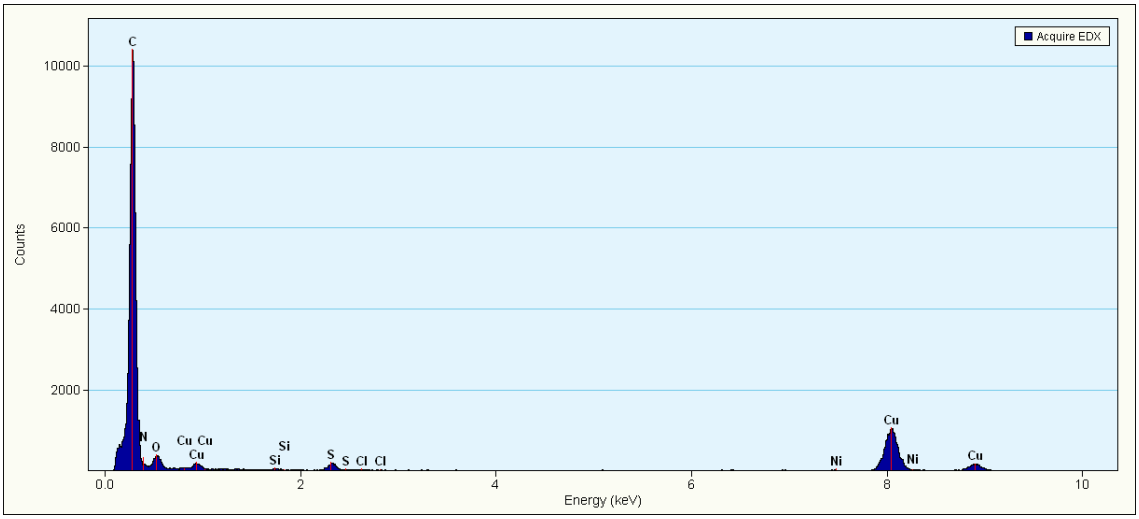


Fig. S6 EDX spectrum of **APOP-5**.

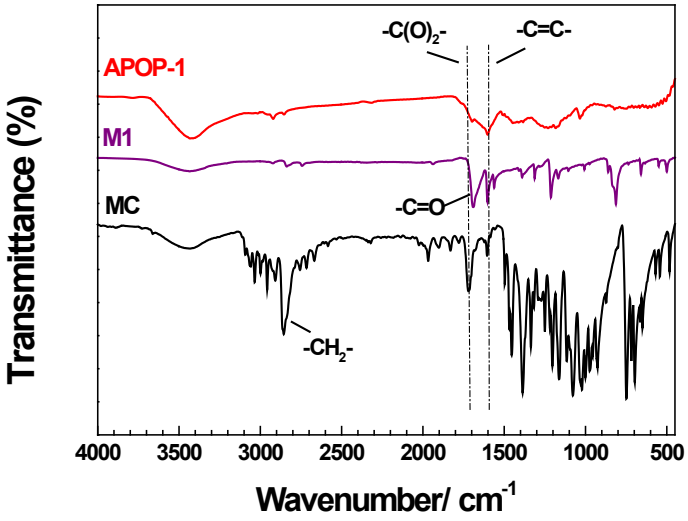


Fig. S7 FT-IR spectra of terephthalic aldehyde (**M1**), **APOP-1**, and model compound (**MC**).

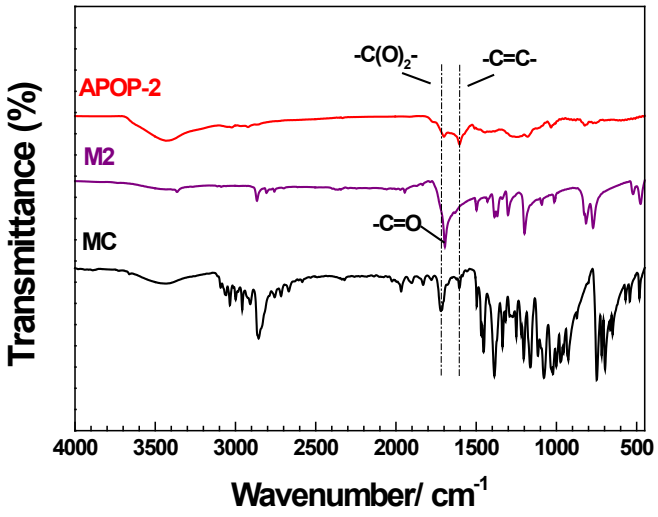


Fig. S8 FT-IR spectra of 4,4'-Biphenyldicarboxaldehyde (**M2**), **APOP-2**, and model compound (**MC**).

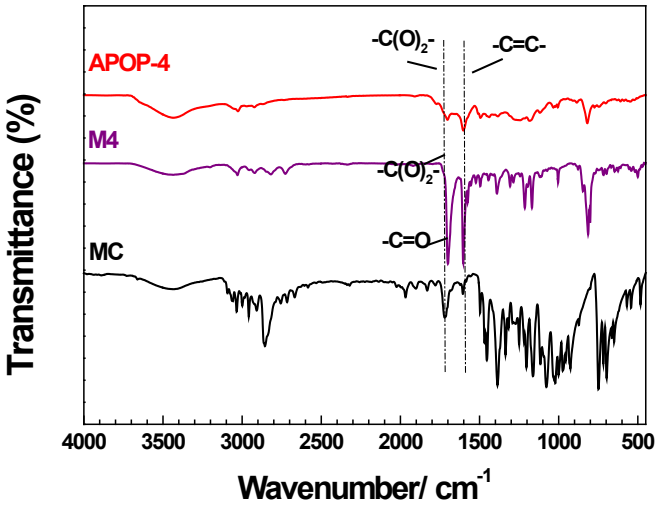


Fig. S9 FT-IR spectra of 1,3,5-tri(4-formylbiphenyl)benzene (**M4**), **APOP-4**, and model compound (**MC**).

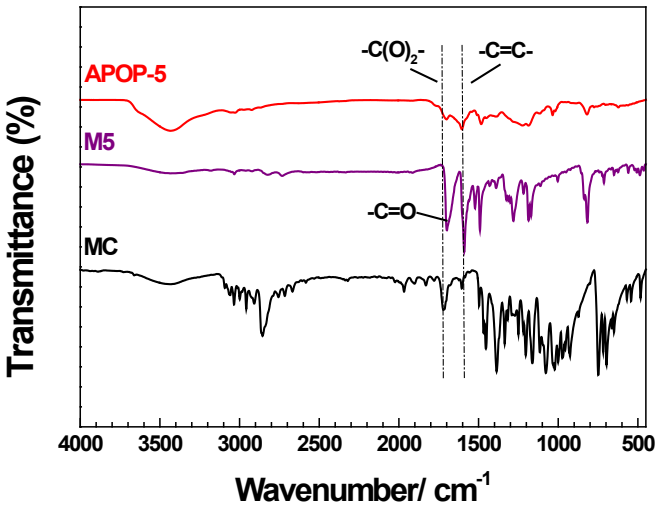


Fig. S10 FT-IR spectra of tri(4-formylbiphenyl)amine (**M5**), **APOP-5**, and model compound (**MC**).

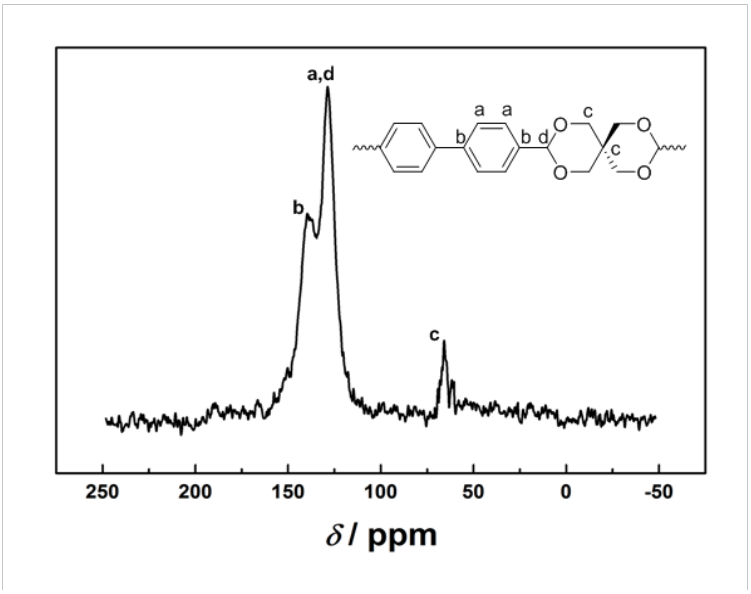


Fig. S11 Solid-state ^{13}C CP/MAS NMR spectrum of **APOP-2** recorded at the MAS rate of 5 kHz.

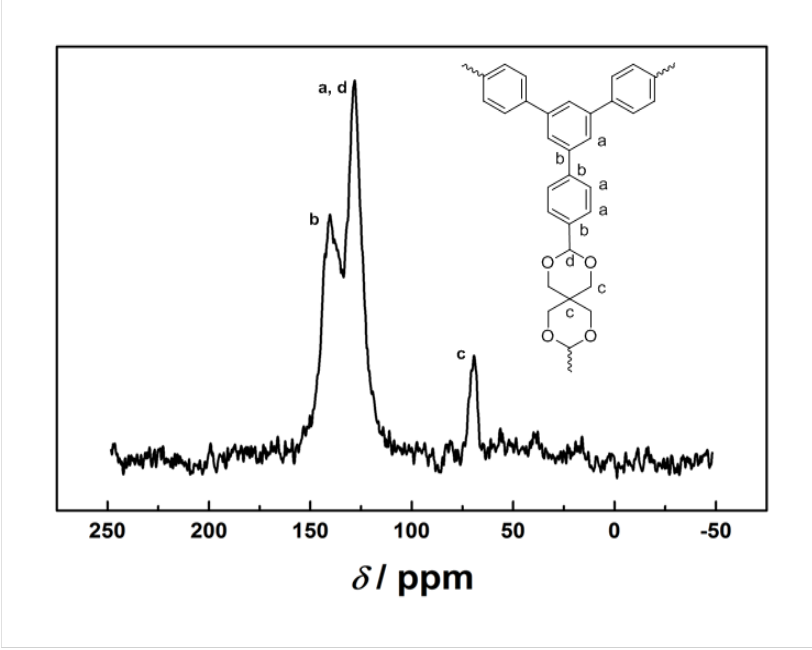


Fig. S12 Solid-state ^{13}C CP/MAS NMR spectrum of **APOP-3** recorded at the MAS rate of 5 kHz.

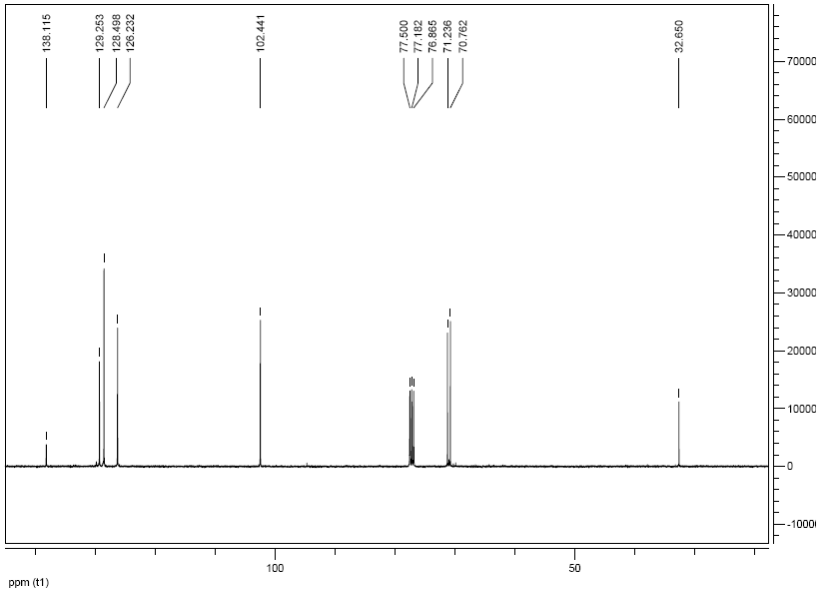


Fig. S13 Liquid ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of model compound dibenzalpenlpentaerythritol.

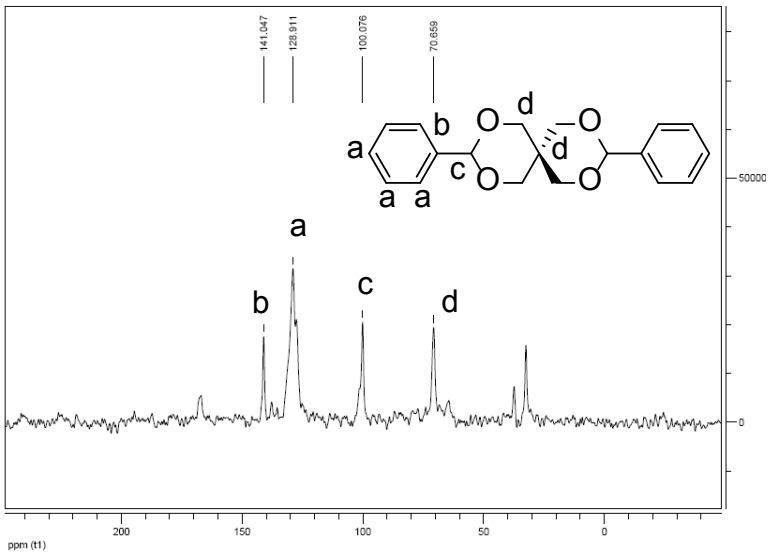


Fig. S14 Solid-state ^{13}C CP/MAS NMR spectrum of model compound dibenzalpenlpentaerythritol recorded at the MAS rate of 5 kHz.

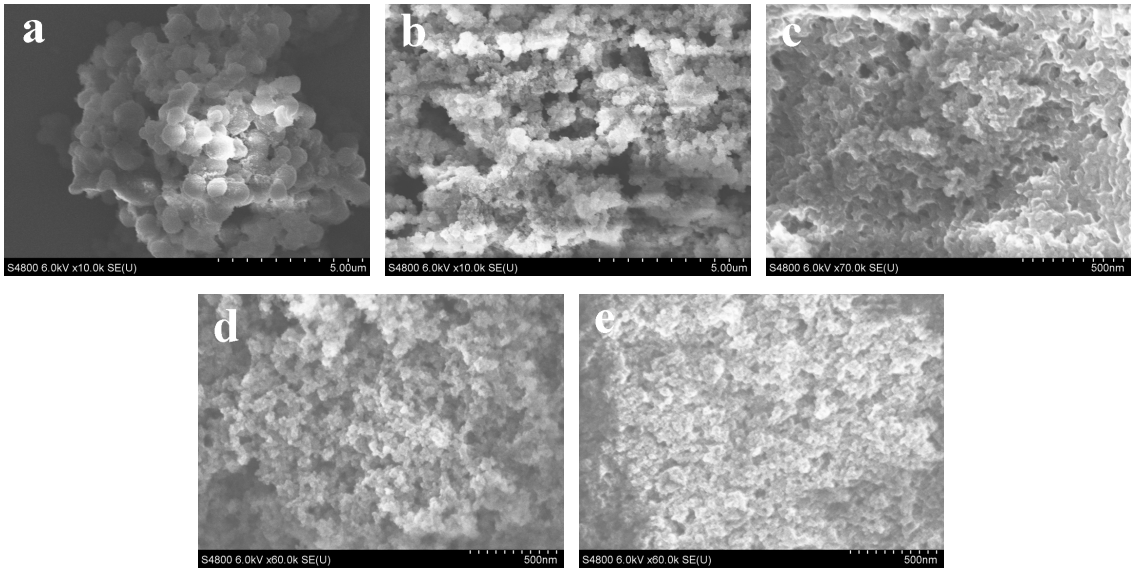


Fig. S15 SEM images of **APOP-1** (a), **APOP-2** (b), **APOP-3** (c), **APOP-4** (d), and **APOP-5** (e).

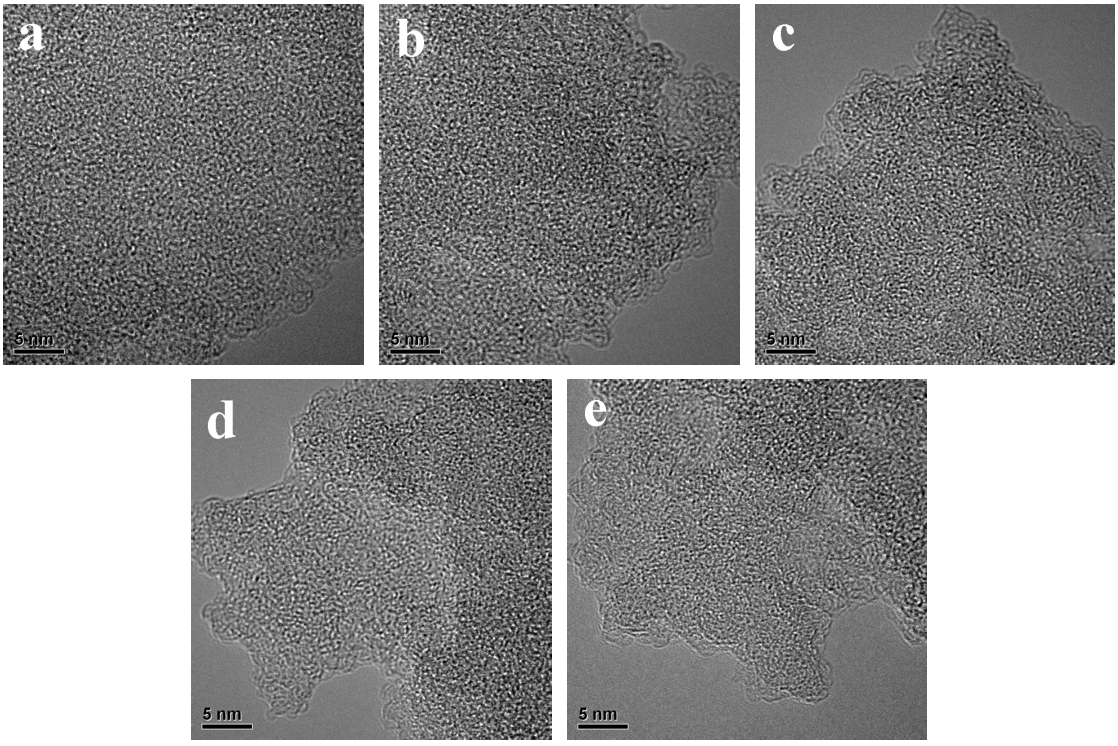
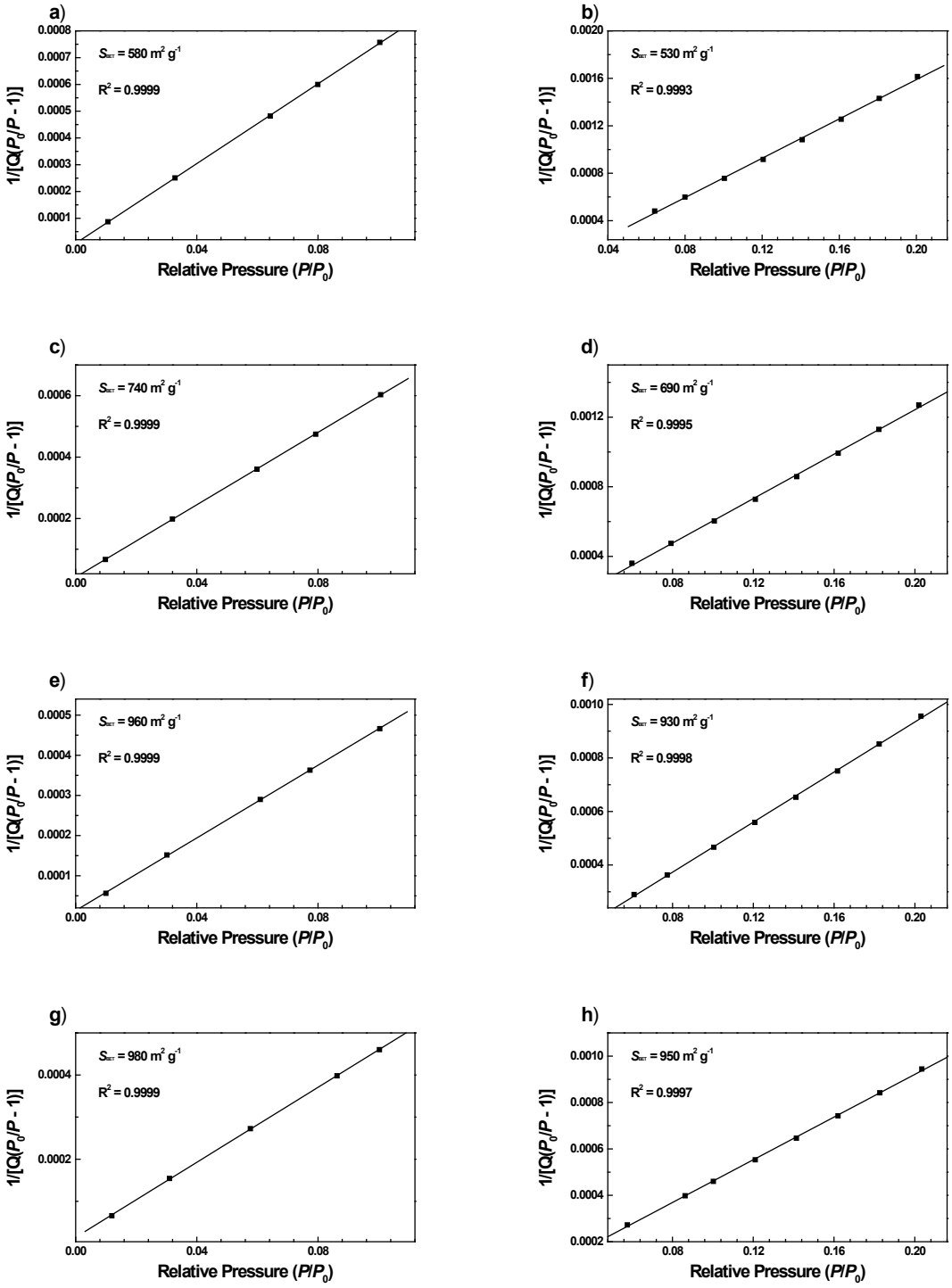


Fig. S16 HR-TEM images of **APOP-1** (a), **APOP-2** (b), **APOP-3** (c), **APOP-4** (d), and **APOP-5** (e).



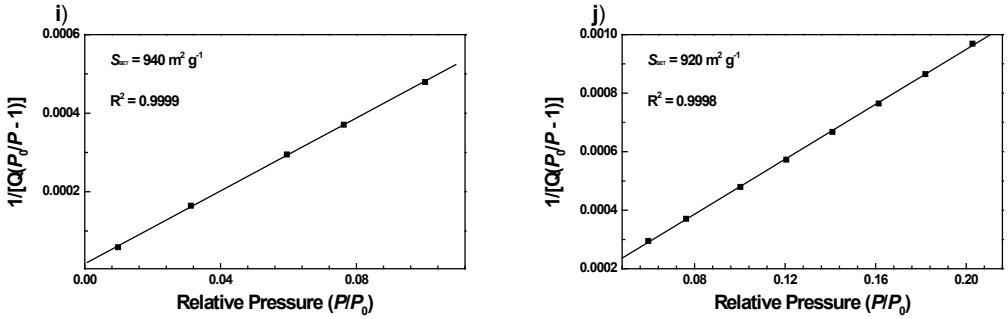


Fig. S17 BET specific surface area plots for **APOP-1** (a and b), **APOP-2** (c and d), **APOP-3** (e and f), **APOP-4** (g and h) and **APOP-5** (i and j) calculated over different relative pressure ranges: P/P_0 = 0.01–0.10 (a, c, e, g, and i) and P/P_0 = 0.05–0.20 (b, d, f, h, and j), respectively.

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

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

[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.