

Electronic supplementary information (ESI) for

Microporous spiro-centered poly(benzimidazole) networks: preparation, characterization, and gas sorption properties

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Synthesis of 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrone

The monomer 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (100 mg) was suspended in ethanol (10.0 mL). To the suspension, a mixture of concentrated nitric acid (1.00 mL) and glacial acetic acid (1.00 mL) was added slowly while the temperature was kept at 0–5 °C. The mixture was stirred at room temperature for 24 h. The tetrone product was then collected by filtration and washed with water and ethanol. After dried at 80 °C in a vacuum oven, a brown solid was obtained (72 % yield). M.p.: >300 °C; ¹H NMR (400 MHz, *d*⁶-DMSO): δ (ppm) 6.36 (s, 2H, Ar-*H*), 6.33 (s, 2H, Ar-*H*), 2.28 (dd, *J* = 13.2 Hz, *J* = 35.6 Hz, 4H, -CH₂-), 1.31 (s, 12H, -CH₃).

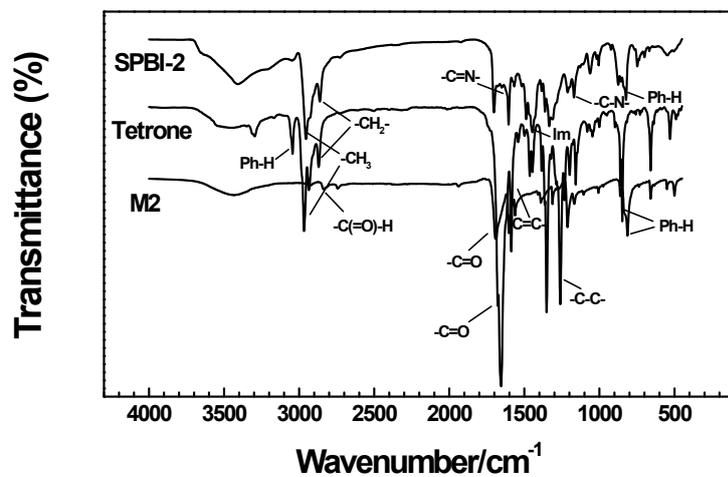


Fig. S1. FT-IR spectra of 4,4'-biphenyldicarboxaldehyde, tetrone monomer, and **SPBI-2**.

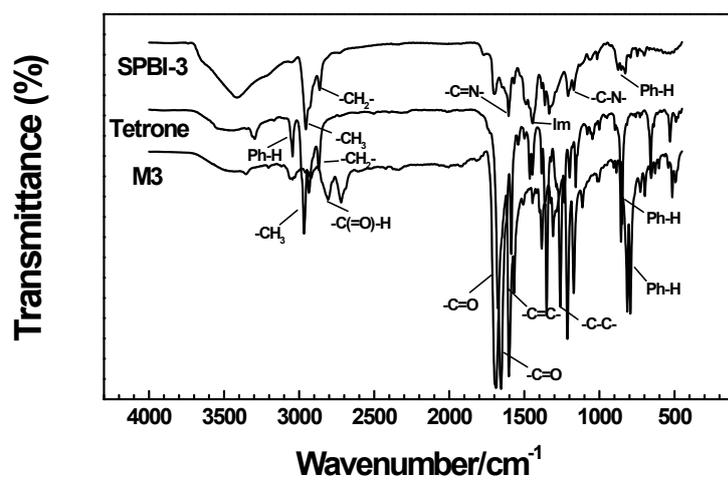


Fig. S2. FT-IR spectra of 1,3,5-tris(4-formylphenyl)benzene, tetrone monomer, and **SPBI-2**.

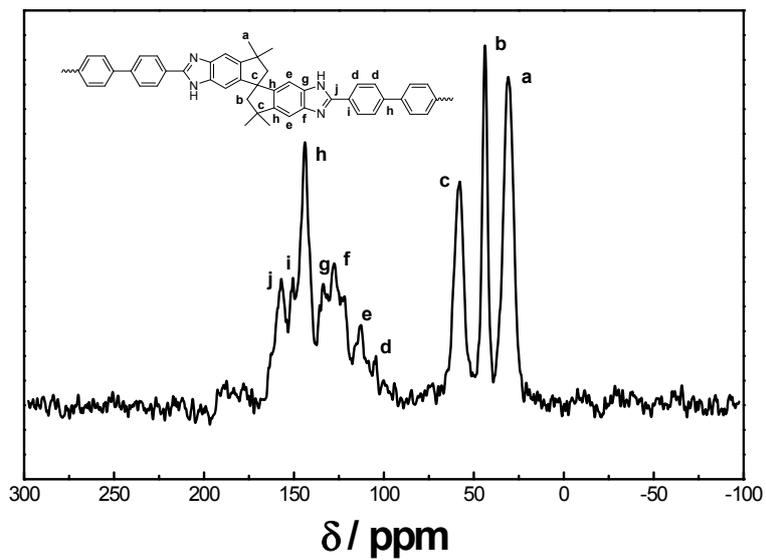


Fig. S3. Solid-state ^{13}C CP/MAS spectrum of **SPBI-2** recorded at the MAS rate of 5 Hz.

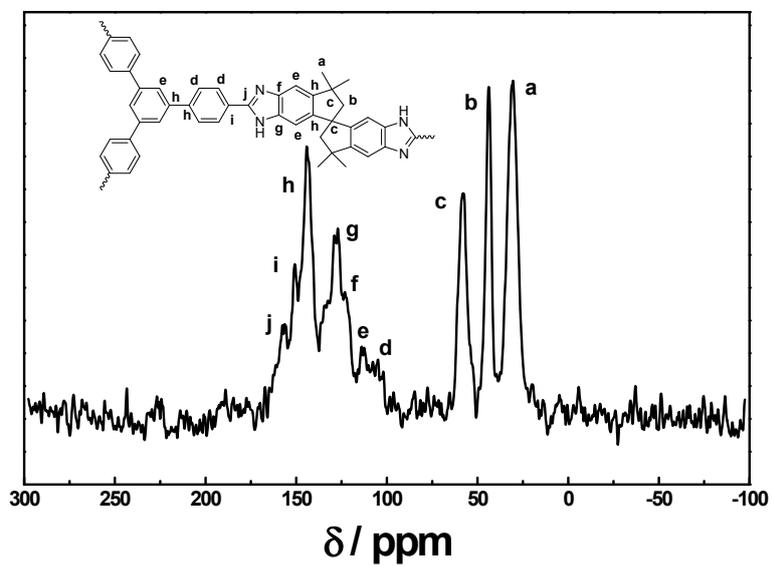


Fig. S4. Solid-state ^{13}C CP/MAS spectrum of **SPBI-3** recorded at the MAS rate of 5 Hz.

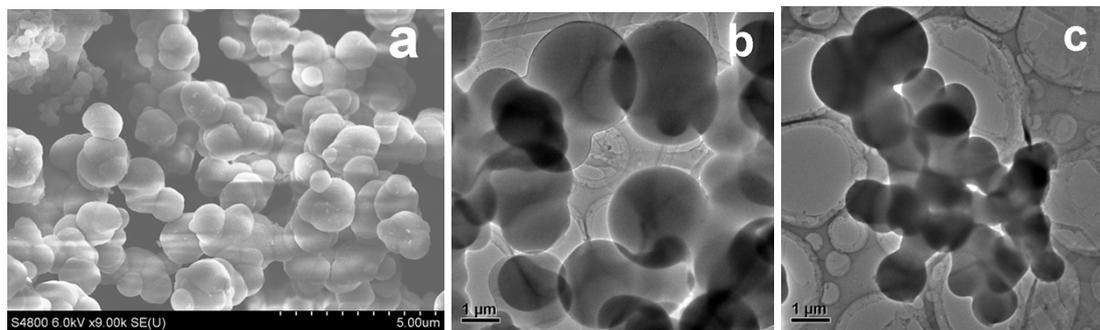


Fig. S5. SEM (a) and TEM (b and c) images of SPBI-1 (b), SPBI-2 (c), and SPBI-3 (a)