Supporting Information for

Hypercrosslinked Microporous Polymers Based on Carbazole for Gas Storage and Separation

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Experimental Sections

Carbazole, 1,4-diiodobenzene, 1,10-phenanthroline, 1,3,5-tribromobenzene, 18-crown-6, potassium carbonate, copper iodide, DMPU, N,N-dimethylformamide, and other chemicals were purchased from Aldrich or J&K and used as received.

The monomers of 1,4-bis(carbazol-9yl)benzene (M**1**)[S1] and 1,3,5-tri(9H-carbazol-9-yl)benzene (M**2**)[S2] were synthesized according to the literatures.

Synthesis of the hypercrosslinked microporous polymer network of FCBCz

To the mixture of 1,4-bis(carbazol-9yl)benzene (0.408 g, 1.0 mmol) and FDA (0.304 g, 4.0 mmol) in 20 mL 1,2-dichloroethane, anhydrous $FeCl_3$ (0.649 g, 4.0 mmol) was added at room temperature. The mixture was heated to 80 °C and stirred for 24 h under a nitrogen atmosphere and then cooled down to room temperature. The precipitated polymer network was filtered and washed with methanol, distilled water, dichloromethane, and acetone successively, until the filtrate was nearly colorless. Further purification of the network was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C to give brown powder (Yield: 452 mg, 98.26%). Elemental combustion analysis (%) calcd. for FCBCz $(C_{34}H_{24}N_2)_n$: C 88.70, H 5.22, N 6.09; Found: C 75.83, H 5.65, N 4.66.

Synthesis of the hypercrosslinked microporous polymer network of FCTCz

To a mixture of 1,3,5-tri(9H-carbazol-9-yl)benzene (0.573 g, 1.0 mmol), FDA (0.456 g, 6.0 mmol) in 20 mL 1,2-dichloroethane, anhydrous $FeCl_3$ (0.974 g, 6.0 mmol) was added at room temperature. The mixture was heated to 80 °C and stirred for 24 h under a nitrogen atmosphere. The mixture was then cooled down to room temperature and the precipitated polymer network was filtered and washed with methanol, distilled water, dichloromethane, and acetone successively, until the filtrate was nearly colorless. Further purification of the network was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C to give dark green powder (Yield: 634 mg, 97.39%). Elemental combustion analysis (%) calcd. for FCTCz $(C_{48}H_{33}N_3)_n$: C 88.48 , H 5.07, N 6.45; Found: C 78.05, H 5.48, N 5.53.

FT-IR Spectroscopy

The polymer sample was ground with KBr and then pressed into transparent pellet. FT-IR spectra were collected in transmission on a Tensor 27 FT-IR spectrometer (Bruker) at room temperature.

Thermogravimetric Analysis

The thermal properties of the polymer networks were evaluated using a thermogravimetric analysis (TGA)–differential thermal analysis instrument (Q1000DSC+LNCS+FACS Q600SDT) over the temperature range from 30 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C /min.

Powder X-ray diffraction measurements

Powder X-ray diffraction measurements (PXRD) was carried out on X-ray Deffractometer (D/Max-3c).

Scanning Electron Microscopy

The polymer morphology was carried out on an environmental scanning electron microscope (FEI, Quanta 200).

Gas Sorption

Surface areas and pore size distributions were measured by nitrogen adsorption at 77.3 K using a Micromeritics ASAP 2420-4 volumetric adsorption analyzer. The surface areas were calculated in the relative pressure (*P/Po*) range from 0.05 to 0.20. Pore size distributions and micropore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory (NL-DFT). Samples were degassed at 120 °C for 15 h under vacuum (10^{-5} bar) before analysis.

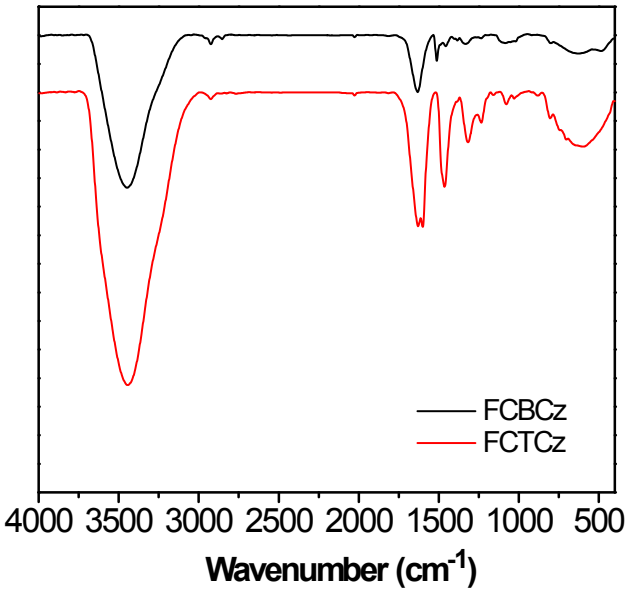

Fig. S1. FT-IR spectra for the polymer networks.

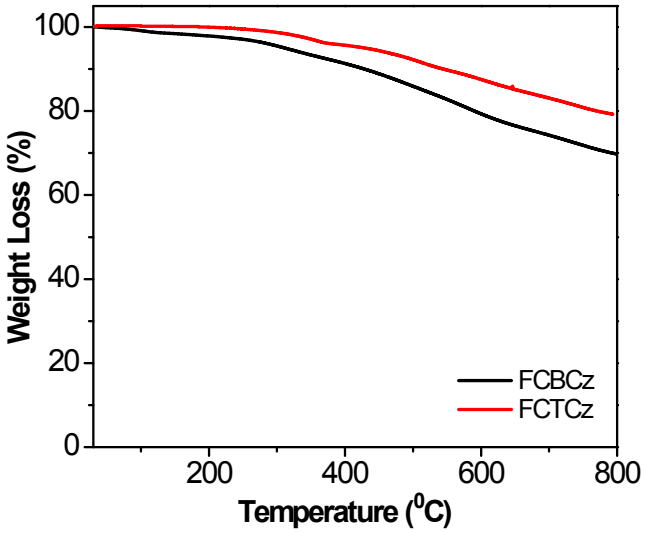

Fig. S2. Thermogravimetric analysis trace of the polymer networks under a nitrogen atmosphere with a heating rate of 10 °C/min.

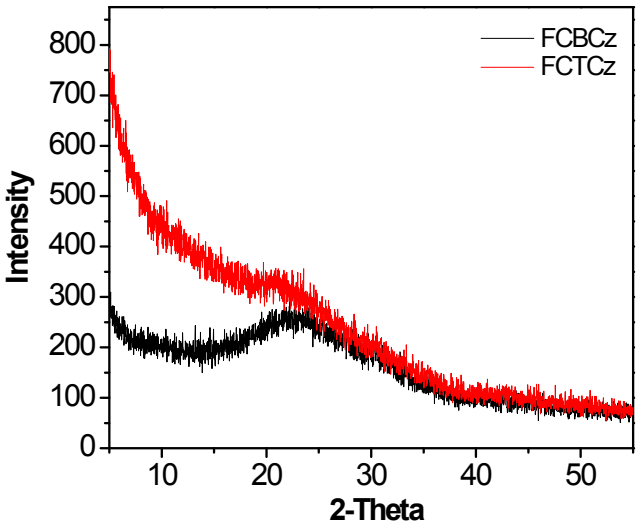

Fig. S3. Powder XRD patterns for the polymer networks.

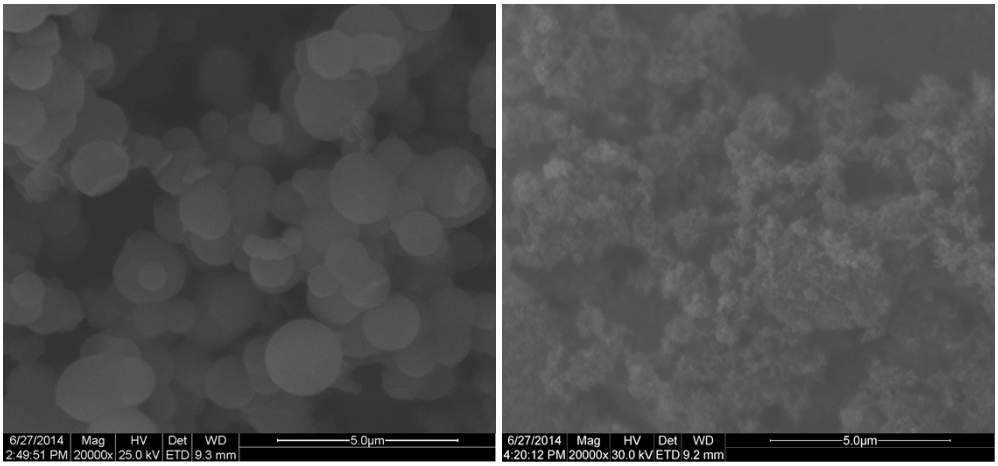

Fig. S4. Scanning electron microscopy (SEM) images for FCBCz (left) and FCTCz (right) with a scale bar of 5.0 µm.

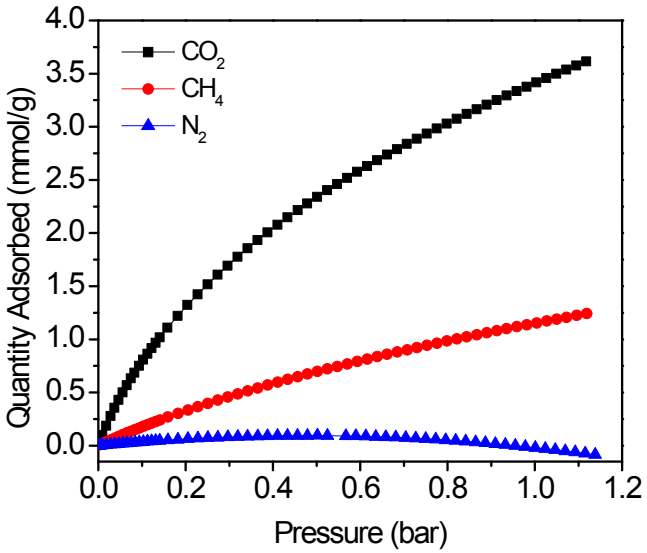

Fig. S5. CO_2, N_2 and CH_4 adsorption isotherms of FCBCz collected at 273 K.

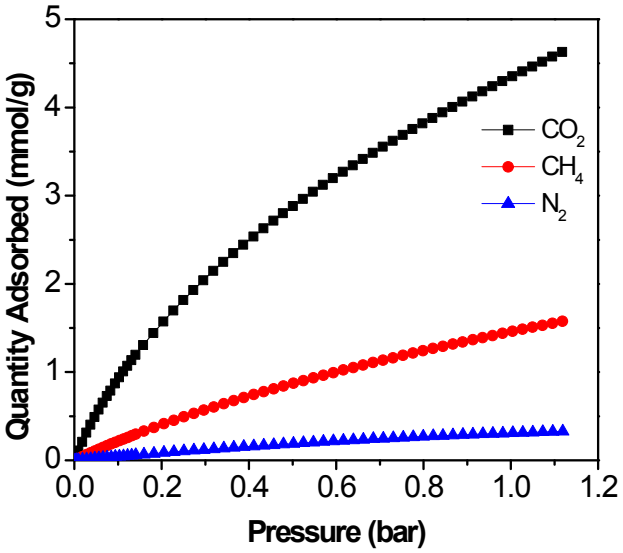

Fig. S6. CO_2, N_2 and CH_4 adsorption isotherms of FCTCz collected at 273 K.

References

[S1] H. P. Shi, J. X. Dai, L. W. Shi, M. H. Wang, L. Fang, S. M. Shuang, C. Dong, *Chem. commun.,* 2012, **48**, 8586.

[S2] Q. Chen, M. Luo, P. Hammershoj, D. Zhou, Y. Han, B. W. Laursen, C. G. Yan, B. H. Han, *J. Am. Chem. Soc.,* 2012, **134**, 6084.