Supporting Information for

High Surface Area Hypercrosslinked Microporous Organic Polymer Networks Based on Tetraphenylethylene for CO$_2$ Capture

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1. Experimental section

Materials

Tetraphenylethylene (TPE) and 1,1,2,2-tetraphenylethane-1,2-diol (TPD) were purchased from Adamas. Formaldehyde dimethyl acetal (FDA), anhydrous FeCl$_3$, 1,2-dichloroethane (DCE) and other chemicals were obtained from J & K Scientific Ltd. All chemicals were used as received.

Synthesis of hypercrosslinked tetraphenylethylene-containing microporous organic polymer networks

All of the tetraphenylethylene-containing microporous organic copolymer networks were synthesized by Friedel-Crafts alkylation of tetraphenylethylene and / or 1,1,2,2-tetraphenylethane-1,2-diol using a formaldehyde dimethyl acetal external crosslinker promoted by anhydrous FeCl$_3$. All polymerization reactions were carried out at a fixed total molar monomer concentration (50 mmol/L) and a fixed reaction temperature and reaction time (80 ºC/24 h). Both the molar ratios of FeCl$_3$ and FDA to the total monomer were set at 4:1. A typical experimental procedure for **network-1** is given as an example.

Network-1: To the mixture of tetraphenylethylene (1.0 mmol, 0.332 g), FDA (4.0 mmol, 0.304 g) in 20 mL 1,2-dichloroethane, FeCl$_3$ (4.0 mmol, 0.649 g) 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 network polymer was filtered and washed with methanol, distilled water, dichloromethane and acetone successively, until the filtrate was nearly colorless. The further purification of the copolymer 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 brown powder (Yield: 99.5%).

Network-2: tetraphenylethylene (0.8 mmol, 0.266 g), 1,1,2,2-tetraphenylethane-1,2-diol (0.2 mmol, 0.073 g), FDA (4.0 mmol, 0.304 g) in 20 mL 1,2-dichloroethane, $FeCl_3$ (4.0 mmol, 0.649 g) were used in this polymerization (Yield: 99.5%).

Network-3: tetraphenylethylene (0.6 mmol, 0.199 g), 1,1,2,2-tetraphenylethane-1,2-diol (0.4 mmol, 0.147 g), FDA (4.0 mmol, 0.304 g) in 20 mL 1,2-dichloroethane, $FeCl_3$ (4.0 mmol, 0.649 g) were used in this polymerization (Yield: 99.0%).

Network-4: tetraphenylethylene (0.5 mmol, 0.166 g), 1,1,2,2-tetraphenylethane-1,2-diol (0.5 mmol, 0.183 g), FDA (4.0 mmol, 0.304 g) in 20 mL 1,2-dichloroethane, $FeCl_3$ (4.0 mmol, 0.649 g) were used in this polymerization (Yield: 98.9%).

Network-5: tetraphenylethylene (0.4 mmol, 0.133 g), 1,1,2,2-tetraphenylethane-1,2-diol (0.6 mmol, 0.22 g), FDA (4.0 mmol, 0.304 g) in 20 mL 1,2-dichloroethane, $FeCl_3$ (4.0 mmol, 0.649 g) were used in this polymerization (Yield: 98.7%).

Network-6: tetraphenylethylene (0.2 mmol, 0.066 g), 1,1,2,2-tetraphenylethane-1,2-diol (0.8 mmol, 0.293 g), FDA (4.0 mmol, 0.304 g) in 20 mL 1,2-dichloroethane, $FeCl_3$ (4.0 mmol, 0.649 g) were used in this polymerization (Yield: 98.8%).

Network-7: 1,1,2,2-tetraphenylethane-1,2-diol (1.0 mmol, 0.366 g), FDA (4.0 mmol, 0.304 g) in 20 mL 1,2-dichloroethane, $FeCl_3$ (4.0 mmol, 0.649 g) were used in this polymerization (Yield: 98.5%).

Table S1. Elemental analysis for the resulting networks.

Network	Expected C%	Expected H%	Expected O%	Found C%	Found H%
Network-1	94.34	5.66	0	88.15	7.61
Network-2	92.58	5.66	1.76	87.66	7.25
Network-3	90.88	5.67	3.45	86.88	7.81
Network-4	90.05	5.67	4.28	85.10	6.43
Network-5	89.24	5.68	5.08	84.46	6.82
Network-6	87.65	5.69	6.66	85.47	7.62
Network-7	83.20	7.56	9.24	84.54	8.94

2. Characterization
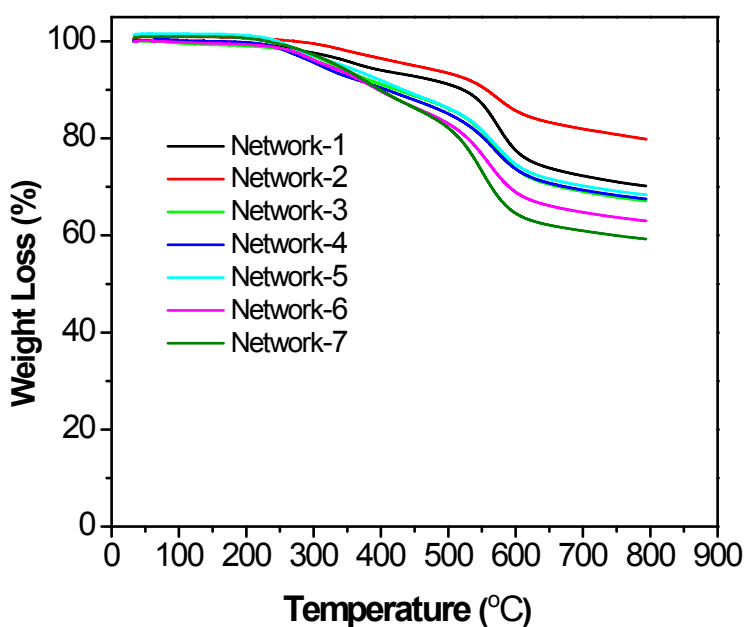
Figure S1. Thermogravimetric analysis of the polymer networks under a nitrogen atmosphere with a heating rate of 10 °C/min.
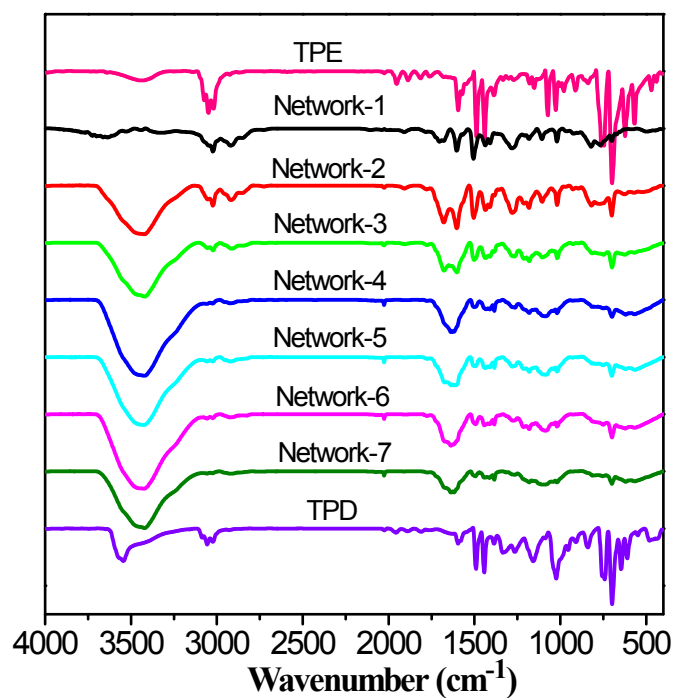
Figure S2. FT-IR spectra of the polymer networks and the monomers of TPE and TPD.
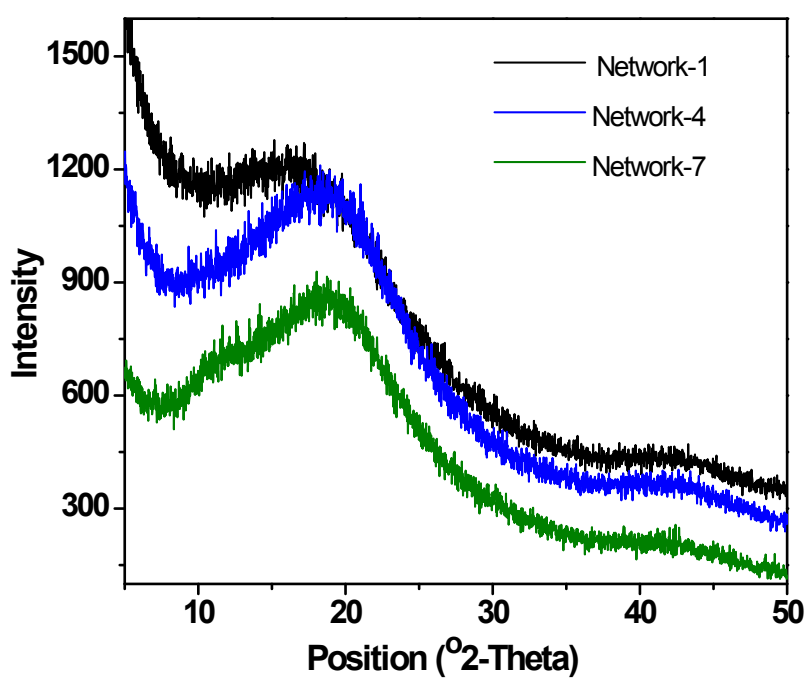
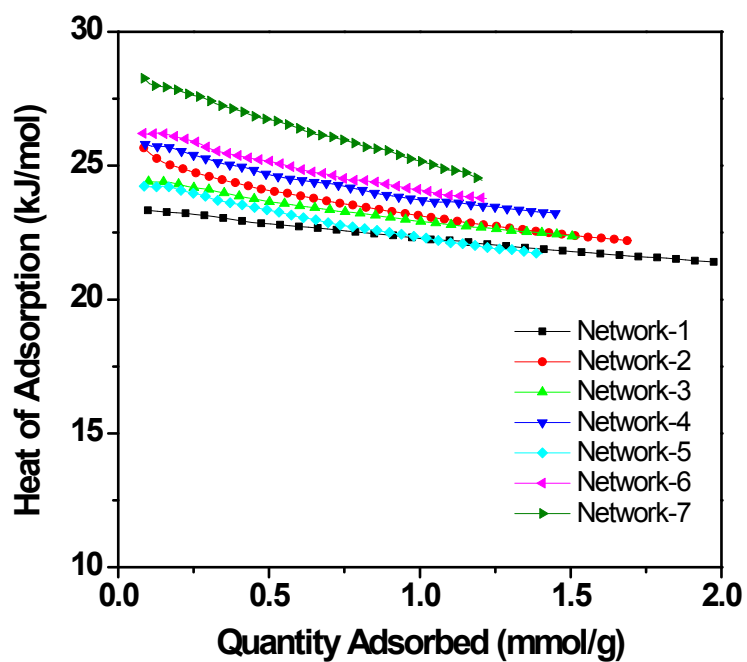***Figure S3***. Examples of powder XRD patterns for network-1, network-4, and network-7.

Figure S4. Isosteric heats of adsorption for CO_2 calculated from the adsorption isotherms collected at 273 K, 283 K and 298 K.
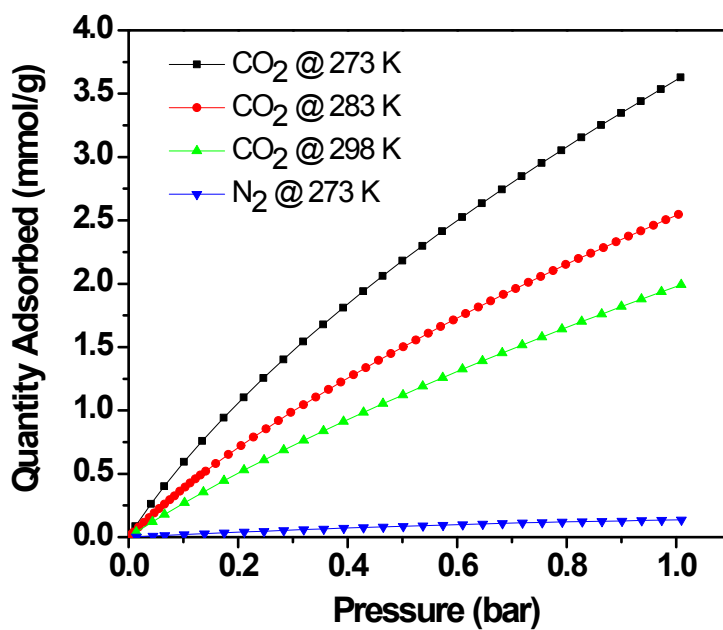

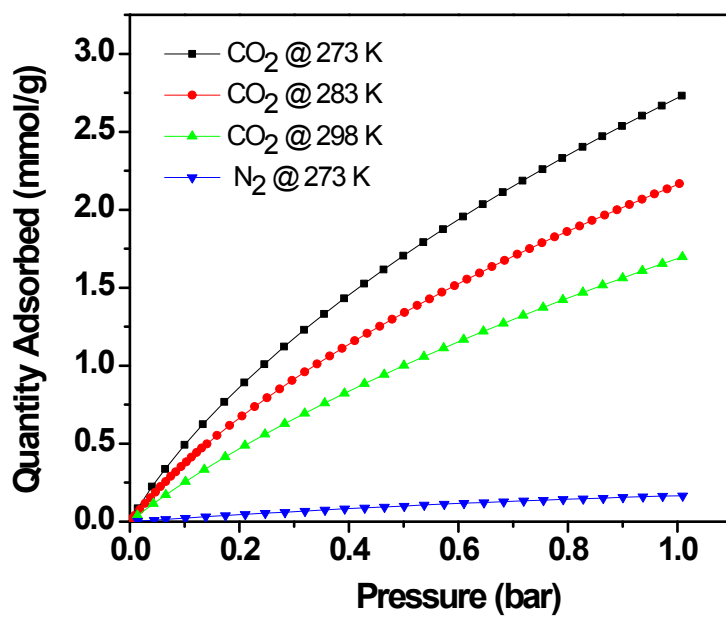***Figure S5***. CO_2 and N_2 sorption capacity for network-1.

Figure S6. CO_2 and N_2 sorption capacity for network-2.
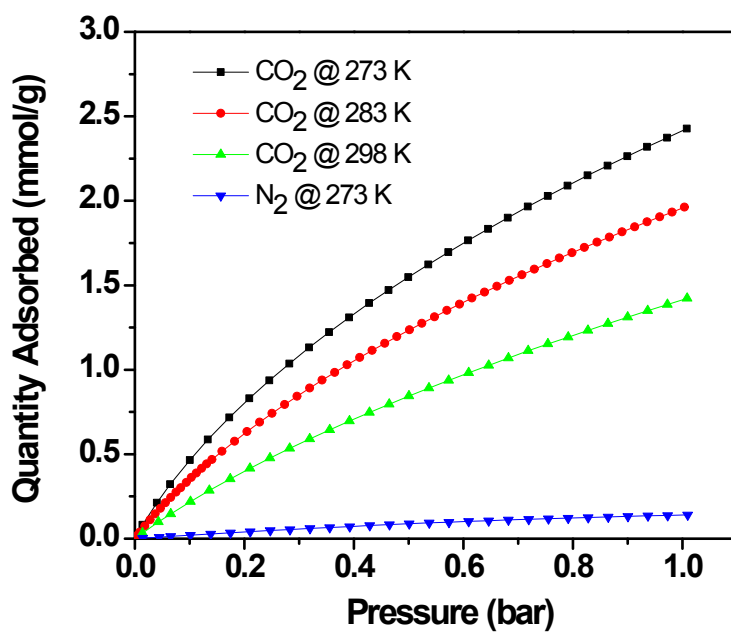
Figure S7. CO_2 and N_2 sorption capacity for network-3.
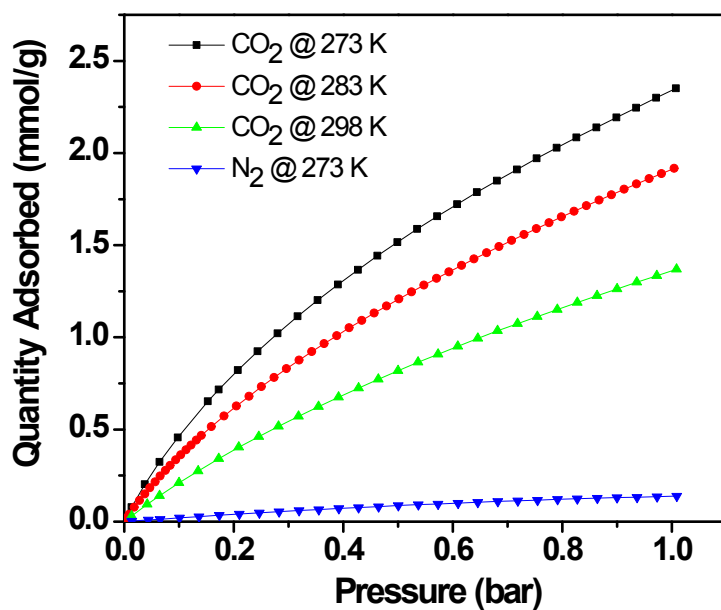
Figure S8. CO_2 and N_2 sorption capacity for network-4.
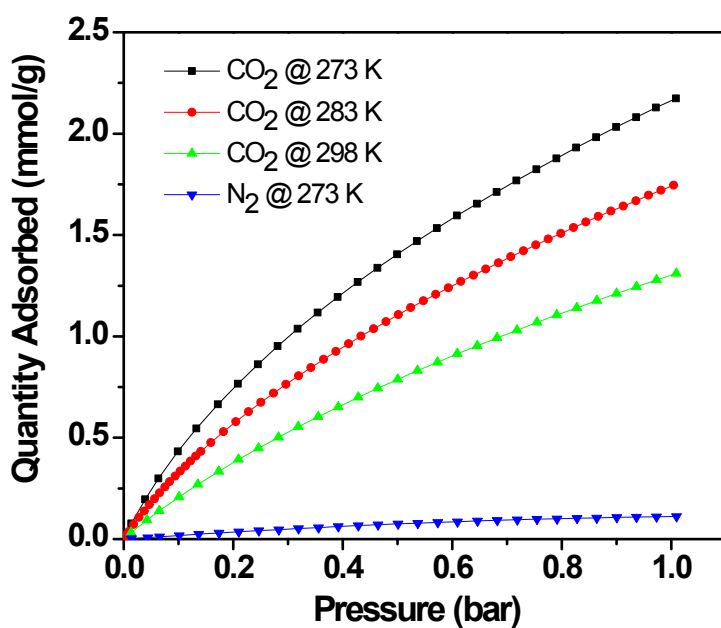
Figure S9. CO_2 and N_2 sorption capacity for network-5.
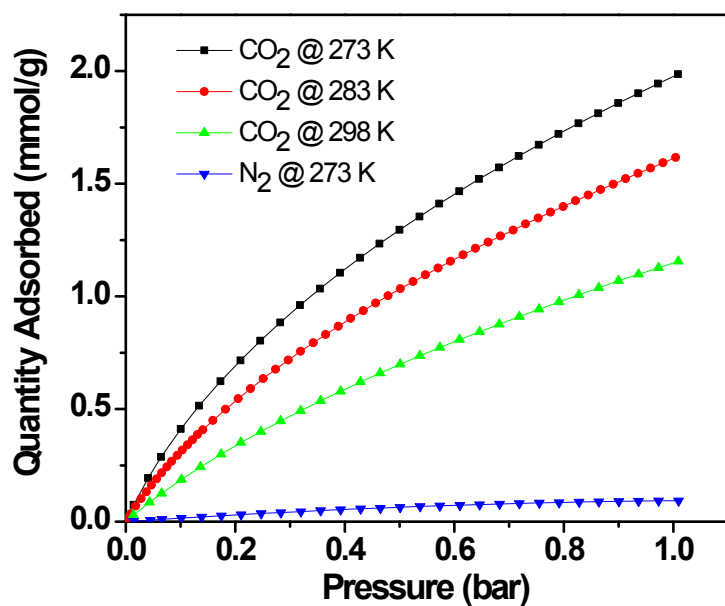
Figure S10. CO_2 and N_2 sorption capacity for network-6.
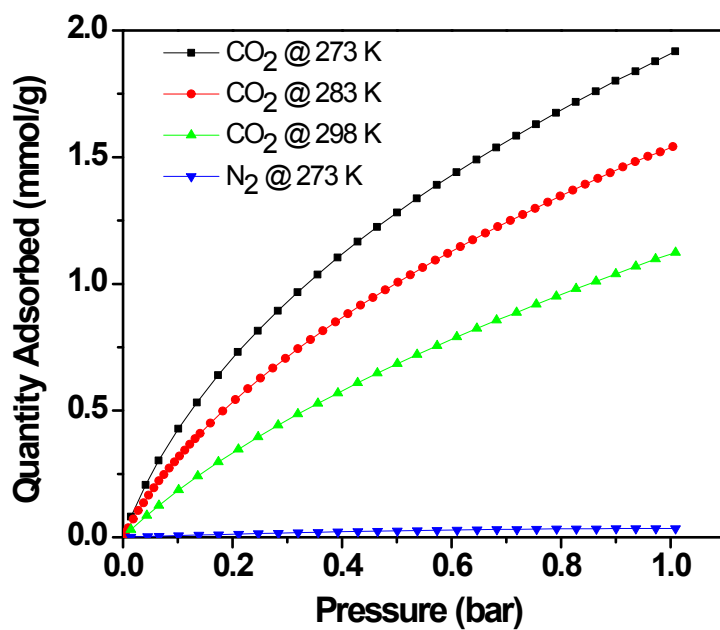
Figure S11. CO_2 and N_2 sorption capacity for network-7.