

## ***Supporting Information for***

# **Conjugated Microporous Copolymer Networks with Enhanced Gas Adsorption**

Miao Yu, Xiaoyan Wang, Xiao Yang, Yang Zhao, Jia-Xing Jiang\*

*School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, 710062, Shaanxi, P. R.*

*China*

*E-mail: [jiaxing@snnu.edu.cn](mailto:jiaxing@snnu.edu.cn)*

## **Experimental section**

**Synthesis of CP-CMP2:** DBA (331.5 mg, 2.0 mmol), TBrPy (414.4 mg, 0.8 mmol) and TBrCz (96.6 mg, 0.2 mmol) were used in this polymerization (yield: 83.6%), details as described for **CP-CMP1**. Elemental combustion analysis (%) Calcd for  $(C_{27.2}H_{13.8}N_{0.2})_n$ : C 95.16; H 4.02; N 0.82; Found: C 85.08; H 4.25; N 0.88.

**Synthesis of CP-CMP3:** BDA (331.5 mg, 2.0 mmol), TBrPy (310.8 mg, 0.6 mmol) and TBrCz (193.2 mg, 0.4 mmol) were used in this polymerization (yield: 82.5%). Elemental combustion analysis (%) Calcd for  $(C_{26.4}H_{13.6}N_{0.4})_n$ : C 94.29; H 4.05; N 1.66; Found: C 83.48; H 4.21; N 1.69.

**Synthesis of CP-CMP4:** BDA (331.5 mg, 2.0 mmol), TBrPy (259 mg, 0.5 mmol) and TBrCz (241.5 mg, 0.5 mmol) were used in this polymerization (yield: 82.7%). Elemental combustion analysis (%) Calcd for  $(C_{26}H_{13.5}N_{0.5})_n$ : C 93.83; H 4.06; N 2.11; Found: C 82.37; H 4.09; N 1.93.

**Synthesis of CP-CMP5:** BDA (331.5 mg, 2.0 mmol), TBrPy (207.2 mg, 0.4 mmol) and TBrCz (289.8 mg, 0.6 mmol) were used in this polymerization (yield: 86.9%). Elemental combustion analysis (%) Calcd for  $(C_{25.6}H_{13.4}N_{0.6})_n$ : C 93.37; H 4.07; N

2.56; Found: C 81.94; H 4.24; N 2.39.

**Synthesis of CP-CMP6:** BDA (331.5 mg, 2.0 mmol), TBrPy (103.6 mg, 0.2 mmol) and TBrCz (386.4 mg, 0.8 mmol) were used in this polymerization (yield: 80.3%).

Elemental combustion analysis (%) Calcd for  $(C_{24.8}H_{13.2}N_{0.8})_n$ : C 92.42; H 4.10; N 3.48; Found: C 80.11; H 4.33; N 3.06.

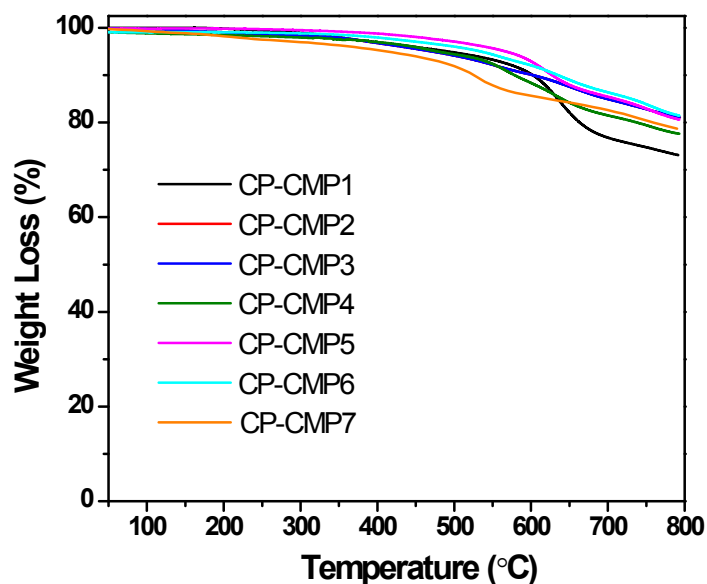
**Synthesis of CP-CMP7:** BDA (331.5 mg, 2.0 mmol) and TBrCz (483 mg, 1.0 mmol) were used in this polymerization (yield: 85.1%). Elemental combustion analysis (%)

Calcd for  $(C_{24}H_{13}N)_n$ : C 91.4, H 4.15, N 4.44; Found: C 77.81; H 4.56; N 3.45.

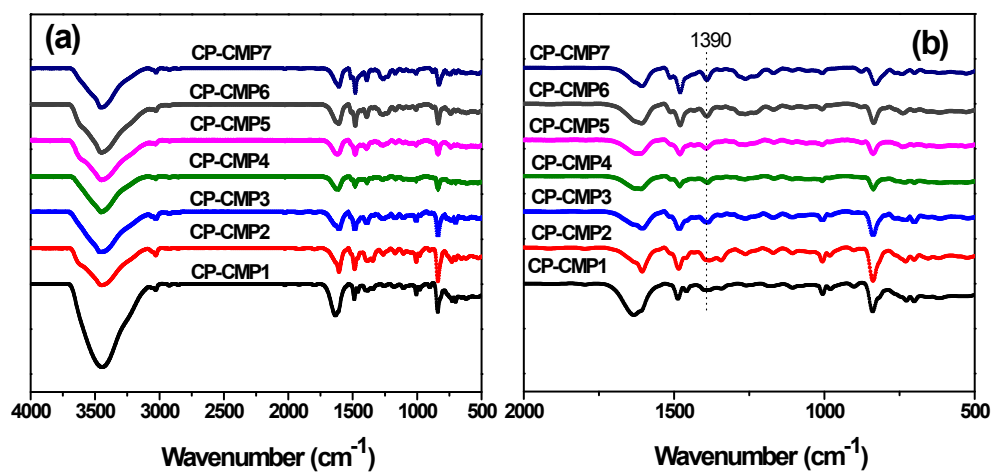
**Table S1.** Surface areas for the copolymer networks from different batch

| Copolymer | 1 <sup>st</sup> batch                                            |                                                                    | 2 <sup>nd</sup> batch                                            |                                                                    | 3 <sup>rd</sup> batch                                            |                                                                    | SD <sub>BET</sub> <sup>c</sup> | SD <sub>Micro</sub> <sup>d</sup> |
|-----------|------------------------------------------------------------------|--------------------------------------------------------------------|------------------------------------------------------------------|--------------------------------------------------------------------|------------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------|----------------------------------|
|           | $S_{\text{BET}}^{\text{a}}$<br>[m <sup>2</sup> g <sup>-1</sup> ] | $S_{\text{Micro}}^{\text{b}}$<br>[m <sup>2</sup> g <sup>-1</sup> ] | $S_{\text{BET}}^{\text{a}}$<br>[m <sup>2</sup> g <sup>-1</sup> ] | $S_{\text{Micro}}^{\text{b}}$<br>[m <sup>2</sup> g <sup>-1</sup> ] | $S_{\text{BET}}^{\text{a}}$<br>[m <sup>2</sup> g <sup>-1</sup> ] | $S_{\text{Micro}}^{\text{b}}$<br>[m <sup>2</sup> g <sup>-1</sup> ] | n=3                            | n=3                              |
| CP-CMP1   | 1191                                                             | 801                                                                | 1079                                                             | 805                                                                | 1091                                                             | 754                                                                | 50 (4.5%)                      | 23 (2.9%)                        |
| CP-CMP2   | 1067                                                             | 796                                                                | 972                                                              | 699                                                                | 998                                                              | 785                                                                | 40 (3.9%)                      | 43 (5.6%)                        |
| CP-CMP3   | 883                                                              | 632                                                                | 964                                                              | 739                                                                | 904                                                              | 627                                                                | 34 (3.7%)                      | 52 (7.8%)                        |
| CP-CMP4   | 1083                                                             | 754                                                                | 960                                                              | 666                                                                | 1039                                                             | 759                                                                | 51 (4.9%)                      | 43 (5.9%)                        |
| CP-CMP5   | 2241                                                             | 1129                                                               | 2142                                                             | 1023                                                               | 2086                                                             | 1016                                                               | 64 (2.9%)                      | 52 (4.9%)                        |
| CP-CMP6   | 1764                                                             | 909                                                                | 1824                                                             | 933                                                                | 1694                                                             | 889                                                                | 53 (3.0%)                      | 21 (2.3%)                        |
| CP-CMP7   | 847                                                              | 699                                                                | 893                                                              | 702                                                                | 904                                                              | 666                                                                | 25 (2.8%)                      | 16 (2.3%)                        |

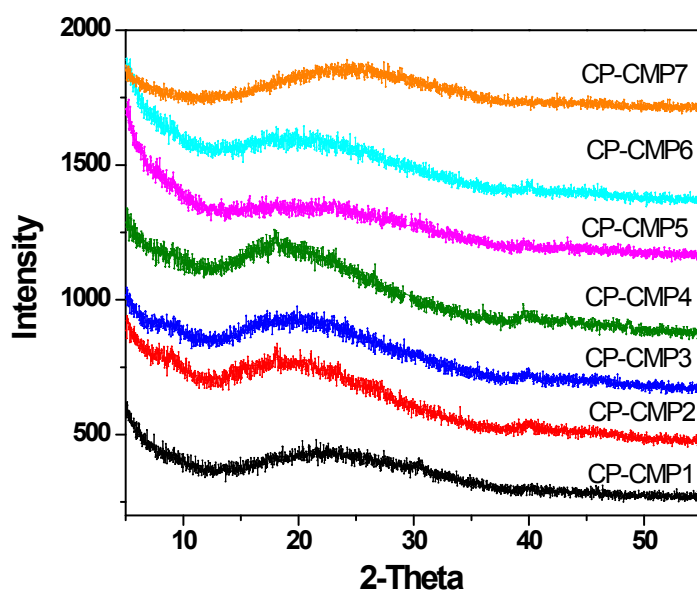
<sup>a</sup> BET Surface area calculated from N<sub>2</sub> adsorption isotherm in the relative pressure ( $P/P_0$ ) range from 0.05 to 0.20 using the Brunauer–Emmett–Teller method, <sup>b</sup> Micropore surface area calculated from the N<sub>2</sub> adsorption isotherm using t-plot method based on the Harkins-Jura Equation, <sup>c</sup> Standard deviation of BET surface area, <sup>d</sup> Standard deviation of micropore surface area (the number in parentheses is relative standard deviation).



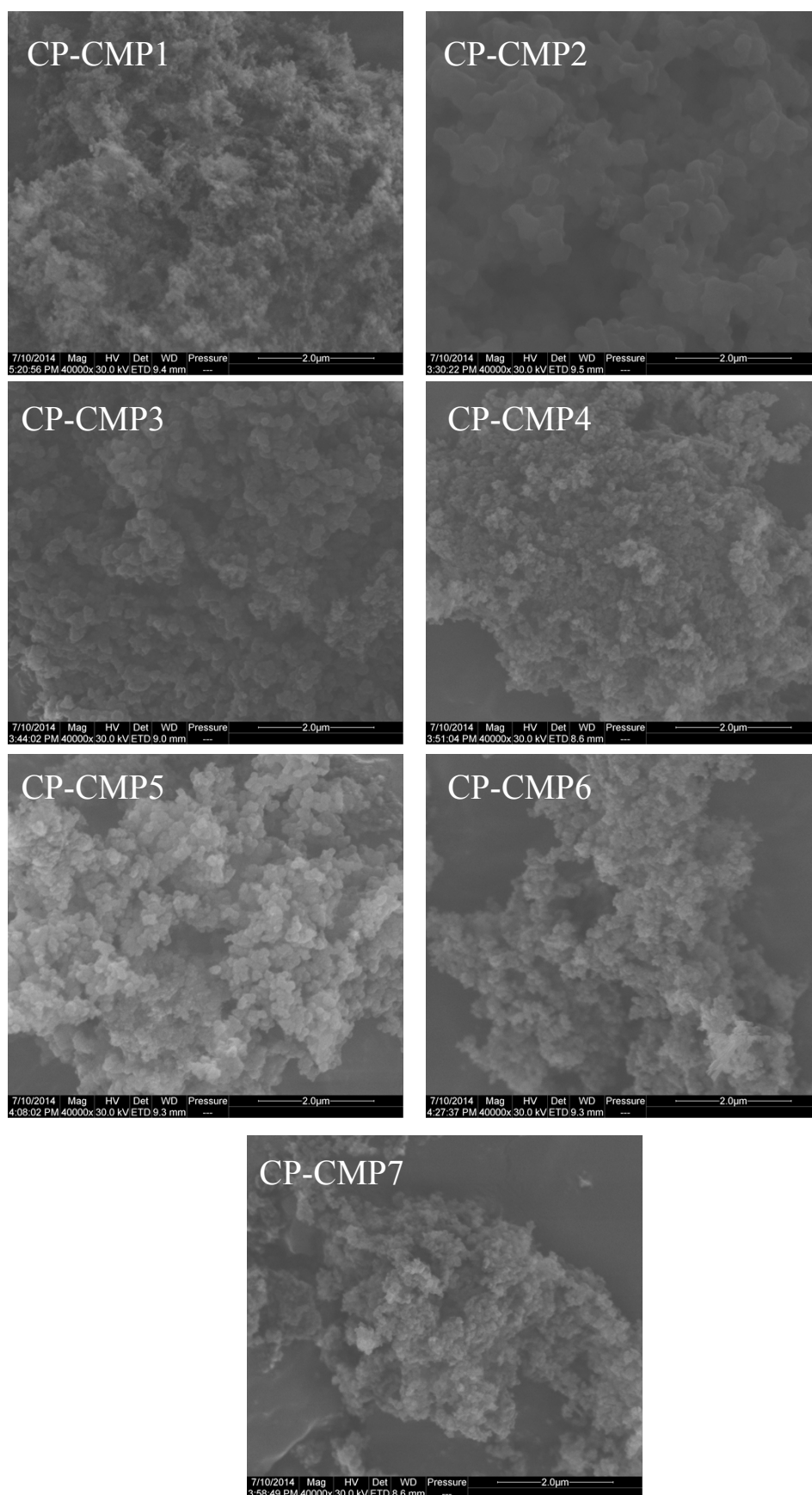
**Figure S1.** Thermogravimetric analysis trace of the copolymer networks under a nitrogen atmosphere with a heating rate of 10 °C/min.



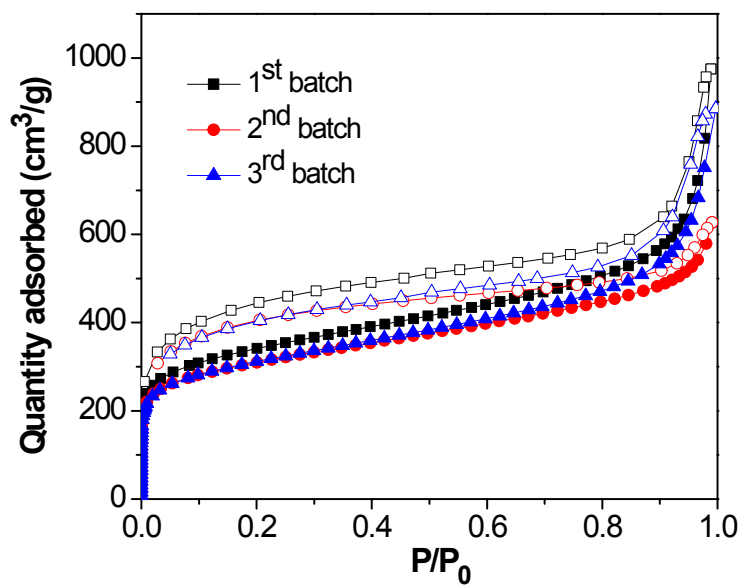
*Figure S2.* FT-IR spectra for the copolymer networks.



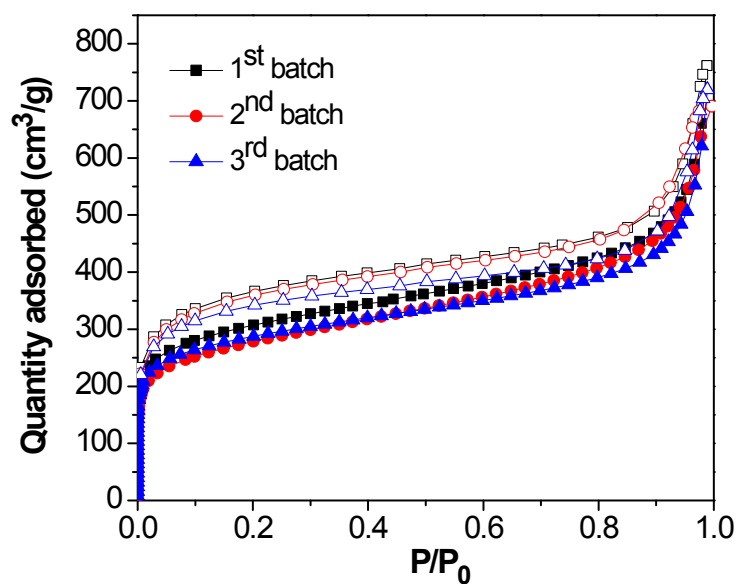
*Figure S3.* Powder XRD patterns of the copolymer networks.



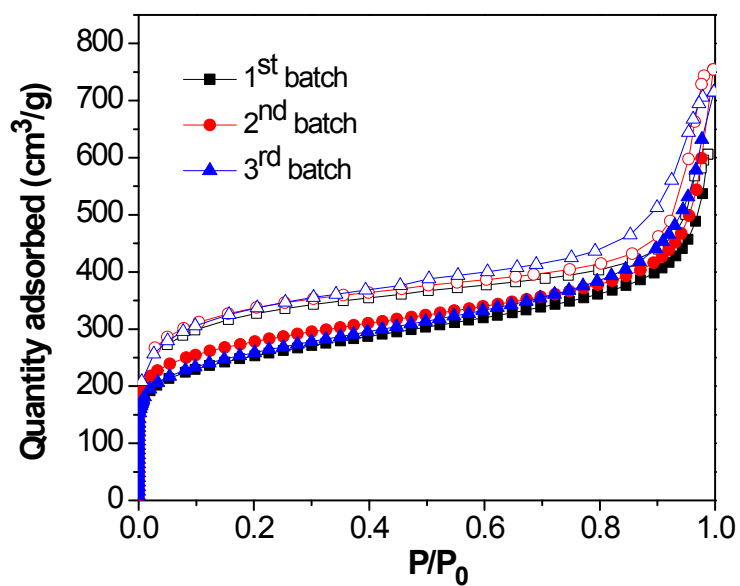
**Figure S4.** Scanning electron microscopy images of the copolymer networks with a scale bar of 2.0  $\mu\text{m}$ .



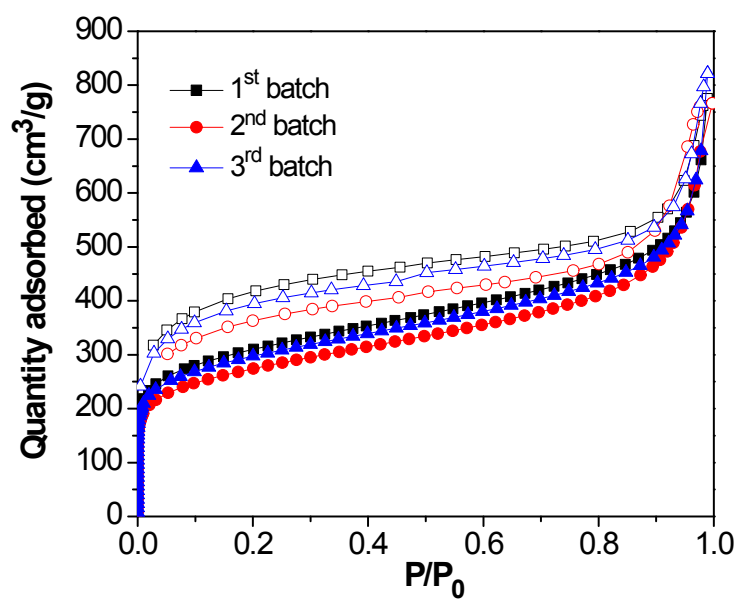
**Figure S5.** Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms for CP-CMP1 produced from different batch.



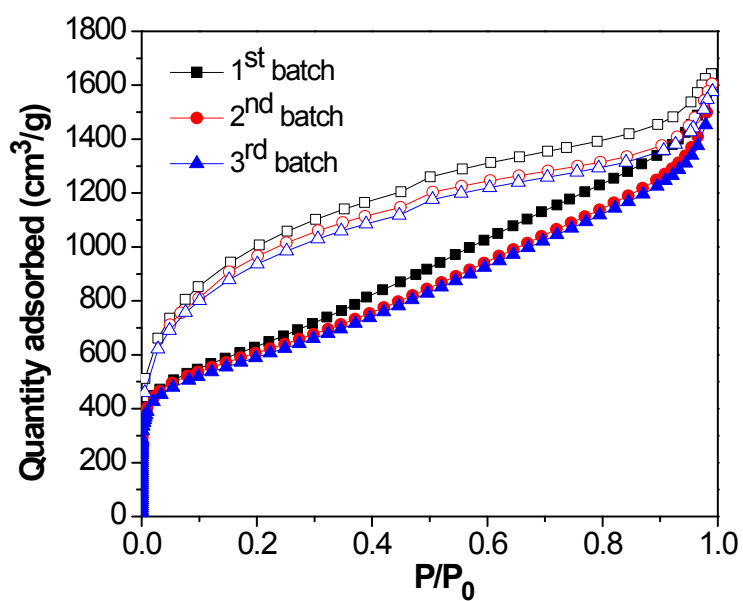
**Figure S6.** Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms for CP-CMP2 produced from different batch.



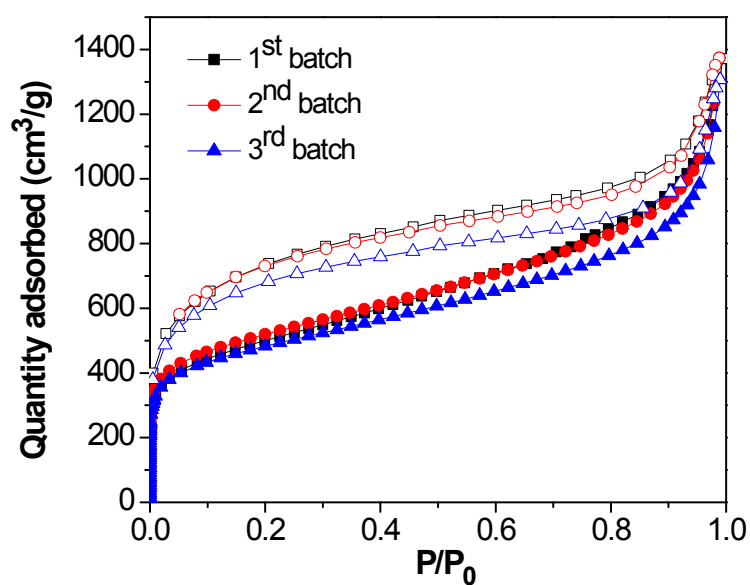
**Figure S7.** Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms for CP-CMP3 produced from different batch.



**Figure S8.** Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms for CP-CMP4 produced from different batch.

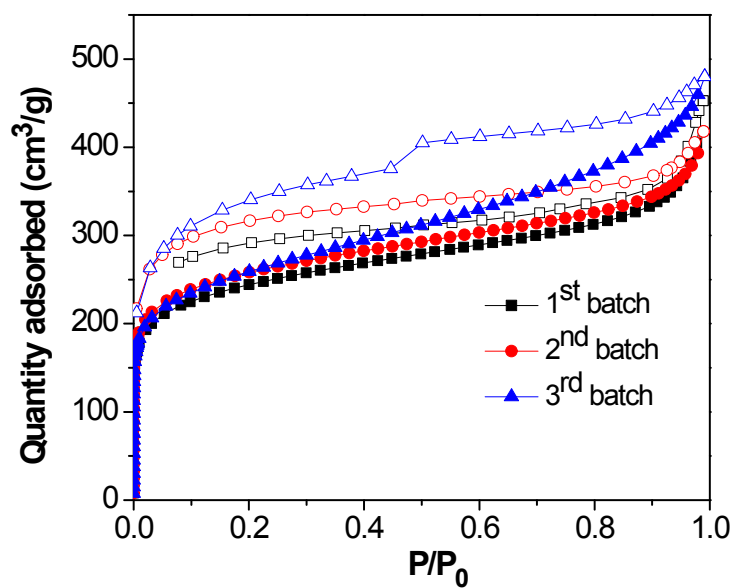


**Figure S9.** Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms for CP-CMP5 produced from different batch.

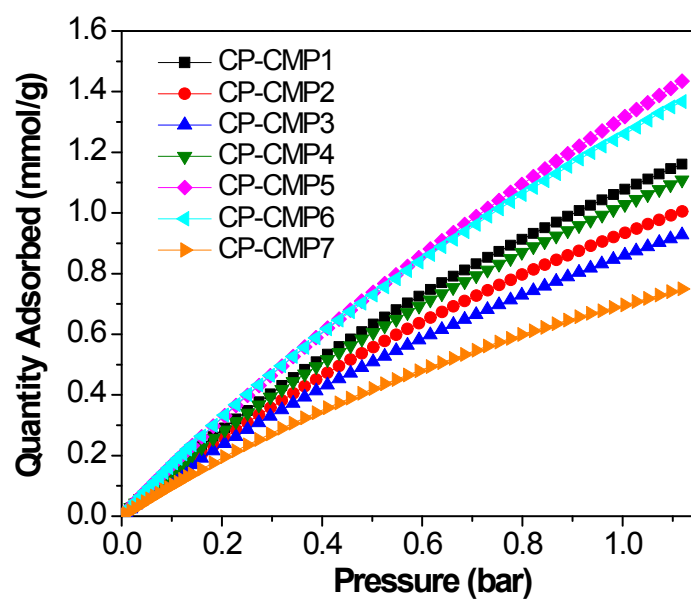


**Figure S10.** Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms for CP-CMP6 produced from different batch.

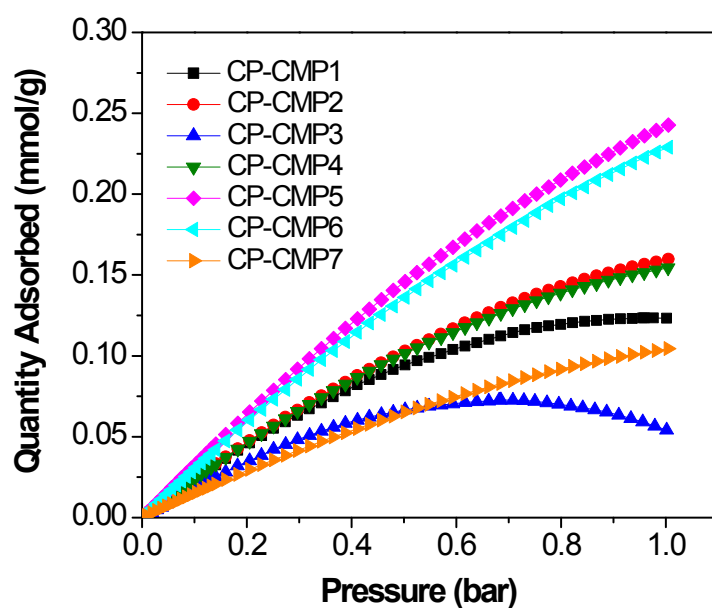




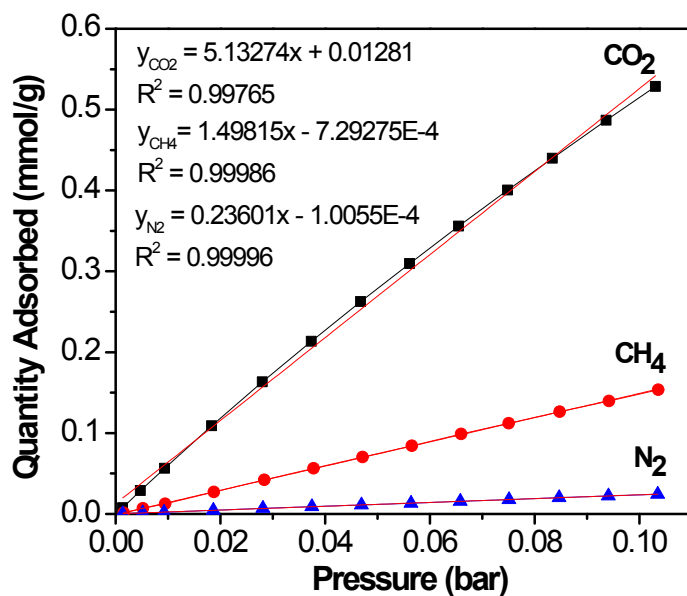
**Figure S11.** Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms for CP-CMP7 produced from different batch.



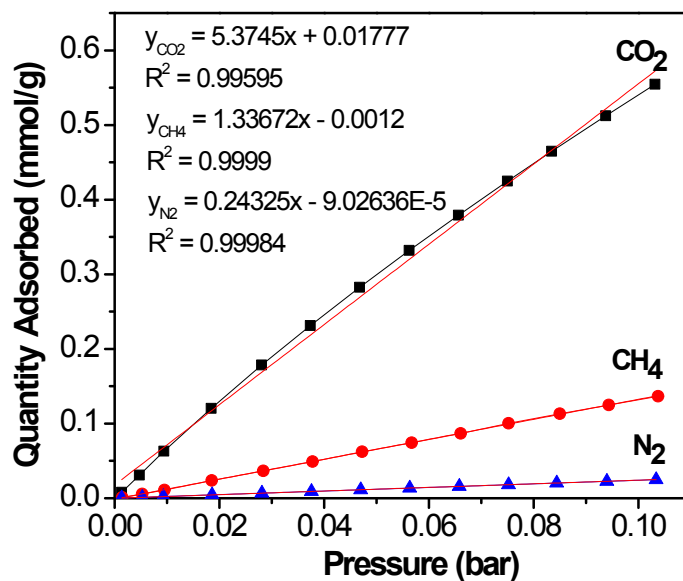
**Figure S12.** CH<sub>4</sub> adsorption isotherms for the copolymer networks collected at 273 K.



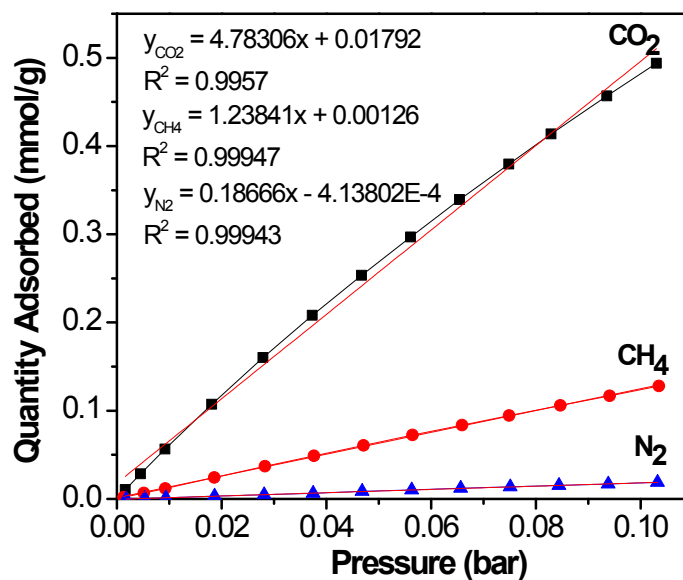
**Figure S13.** N<sub>2</sub> adsorption isotherms for the copolymer networks collected at 273 K.



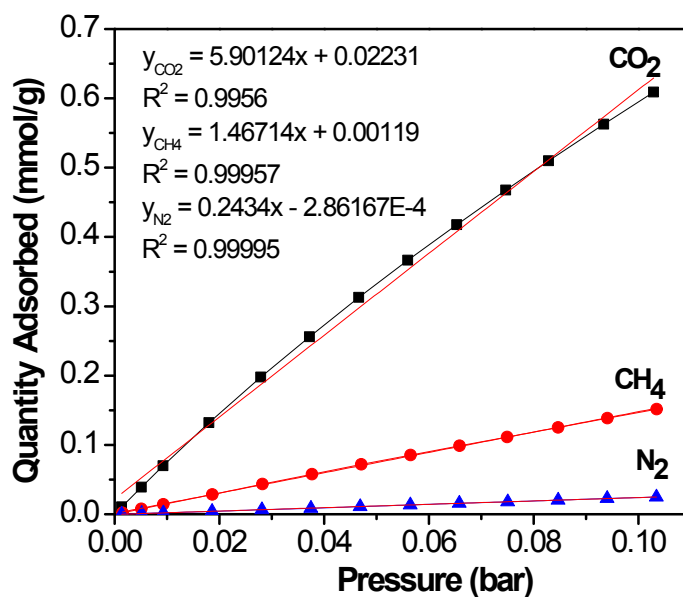
**Figure S14.** Gas adsorption selectivity for CP-CMP1 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.



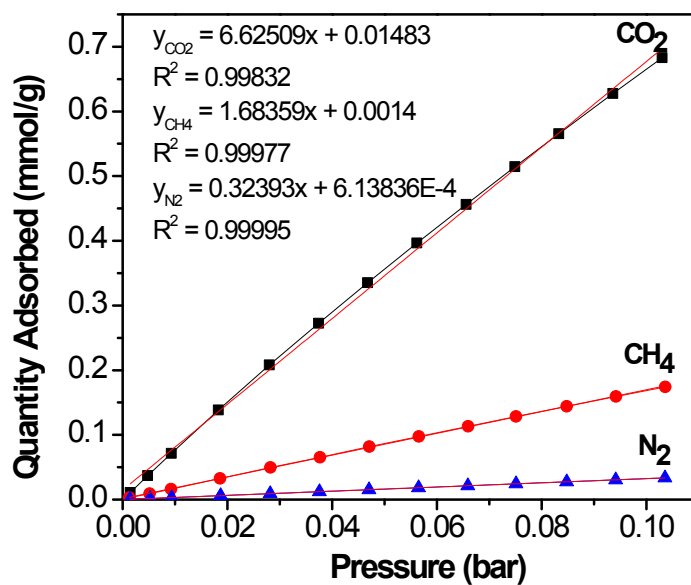
**Figure S15.** Gas adsorption selectivity for the CP-CMP2 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.



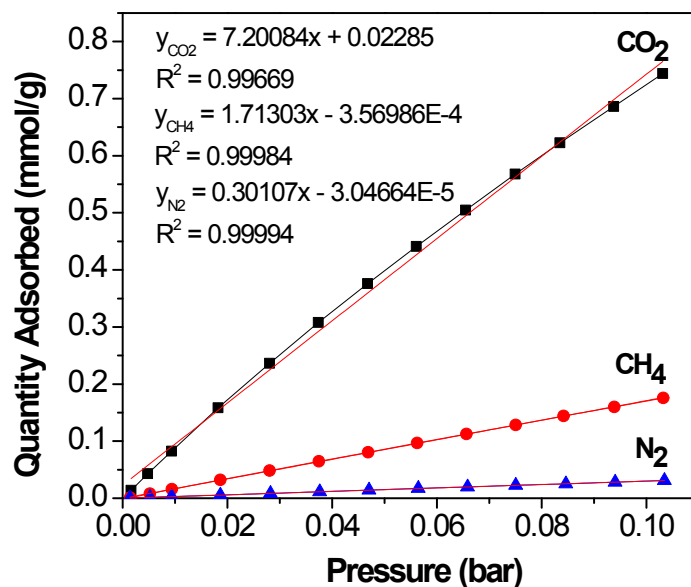
**Figure S16.** Gas adsorption selectivity for the CP-CMP3 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.



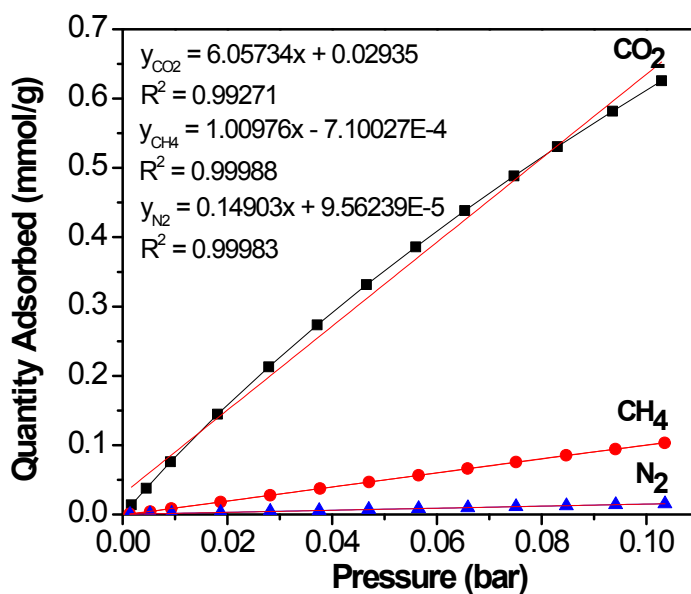
**Figure S17.** Gas adsorption selectivity for the CP-CMP4 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.



**Figure S18.** Gas adsorption selectivity for the CP-CMP5 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.



**Figure S19.** Gas adsorption selectivity for the CP-CMP6 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.



**Figure S20.** Gas adsorption selectivity for the CP-CMP7 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.