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Electronic Supporting Information

Synthesis of thermochemically stable tetraphenyladamantane-based microporous polymers as gas storage materials

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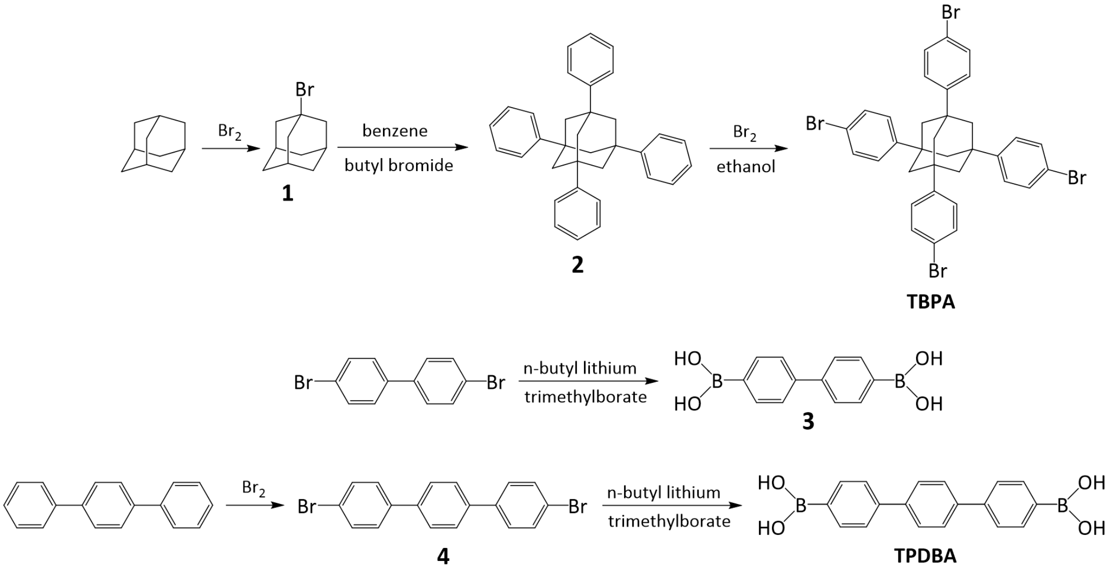
1. Synthetic procedure



Scheme S1. Syntheses route to compounds **1**, **2**, **3**, **4**, **TBPA** and **TPDBA.**

Synthesis of 1,3,5,7-tetrakis(4-bromophenyl)adamantane (TBPA). TBPA was prepared according to the reported procedure.[20] A mixture of 1,3,5,7-tetraphenyladamantane (6.00 g, 13.6 mmol, 1.0 equiv.) and bromine (7.0 ml, 21.7 g, 136 mmol, 10 equiv.) were added under vigorous stirring at room temperature. After stirred for 20 min, the mixture was cooled to -78 ^oC and excess ethanol (60 ml) was added dropwise. And then the mixture was stirred at room temperature overnight. The precipitate was filtered and washed subsequently with saturated aqueous sodium hydrogensulfite solution (50 ml) and water (50 ml), respectively. The obtained white solid was suspended in methanol (50 ml) and stirred for 1h at 40 ^oC. Further purification of the product was recrystallized from chloroform to give an off-white powder (8.92 g, 86.8 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ:7.47 (d,*J*=8.7 Hz, 8H, Ar_mH), 7.32 (d,*J*=8.7 Hz, 8H, Ar_oH), 2.08 (s, 12H, Ad-CH_2);

Synthesis of biphenyl-4,4'-diboronic acid (3).[22] 4,4'-Dibromobiphenyl (1.94 g, 6.21 mmol) was added into a Pyrex ampoule and then the apparatus was evacuated under reduced pressure and backfilled with Ar five times. Then anhydrous tetrahydrofuran (60.0 ml) was added dropwise *via* syringe. After the addition was completed, the resulting solution was stirred for 10min at -78 ^oC. n-butyl lithium (2.5 M in hexane, 18.0 ml, 45.0 mmol) was dropped into the reaction mixture slowly and after stirring another 15 min, the mixture was heated to room temperature. After stirring for 1 h, the mixture was cooled to -78 ^oC again, trimethylborate (4.5 ml, 36.0 mmol) was dropped into the reaction mixture quickly and the mixture was stirred at room temperature for 15 h. Hydrochloric acid (2.0 M, 24.0 ml) was then added to the reaction mixture. After removal of solvent, the residue was dissolved in sodium hydroxide solution (2.0 M, 200 ml) and then filtered. The filtrate was acidified by hydrochloric acid and a white powder was obtained after centrifugation (0.91 g, 60.7 % yield). ^1H NMR (400 MHz, DMSO-d_6) δ:8.10(s, 4H), δ:7.90~7.88(m, 4H), δ:7.67~7.66(m, 4H).

Synthesis of 4,4''-dibromo-*p*-terphenyl (4).[23] In a 500 ml 3-necked flask, 1,3,5-trichlorobenzene (200 ml, 0.9988 mol), *p*-terophenyl (15.0 g, 65.13 mmol) and iodine (150 mg, 0.59 mmol) were added, respectively. After stirred for 10 min at temperature of roughly 25 ^{o}C. Bromine (20.0 ml) were dripped into the flask slowly, and then the mixture was heated to 100 ^{o}C for another 60 min, while being stirring. Then the mixture was cooled to room temperature and an excess of methanol was added to trigger precipitation. The precipitate was filtered and washed with methanol until a white powder were obtained, and the product was dried in *vacuo* (22.86 g, 90.4 % yield, m.p. 319.9~320.2 ^{o}C). ^{1}H NMR (400 MHz, DMSO-d_6) δ:δ:7.87~7.86(m, 4H, $\mathrm{Ar_oH}$), δ:7.79(s, 4H, $\mathrm{Ar_mH}$), δ:7.69~7.68(m, 4H, $\mathrm{Ar_oH}$).

Synthesis of *p*-terphenyl-4,4''-diboronic acid (TPDBA). 4,4''-Dibromo-*p*-terphenyl (1.86 g, 4.80 mmol) were added into a Pyrex ampoule with a stirrer and then the apparatuses were evacuated under reduced pressure and backfilled with Ar five times. Anhydrous tetrahydrofuran (45.0 ml) were added via a syringe. The solutions were then cooled to -78 ^{o}C and n-butyl lithium (2.5 M in hexane, 5.3 ml, 13.05 mmol) were dropped into the reaction mixture slowly. The solutions were warmed up to room temperature. After stirring for 1 h, the mixtures were cooled to -78 ^{o}C again, trimethyl borate (3.0 ml, 24.0 mmol) were dropped into the reaction mixture quickly and the mixtures were stirred at room temperature for 16 h. Hydrochloric acid (2.0 M, 24.0 ml) were then added to the reaction mixtures. After removal of solvents, the residues were dissolved in sodium hydroxide solution (2.0 M, 200 ml) and then filtered. The filtrates were acidified by hydrochloric acid and a white powder was obtained after centrifugation (0.56 g, 36.8 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ:8.10(s, 4H), δ:7.92~7.90(m, 4H, $\mathrm{Ar_oH}$), δ:7.80(s, 4H, $\mathrm{Ar_mH}$), δ:7.71~7.69(m, 4H, $\mathrm{Ar_oH}$).

2. ^{1}H NMR spectrum of TPDBA

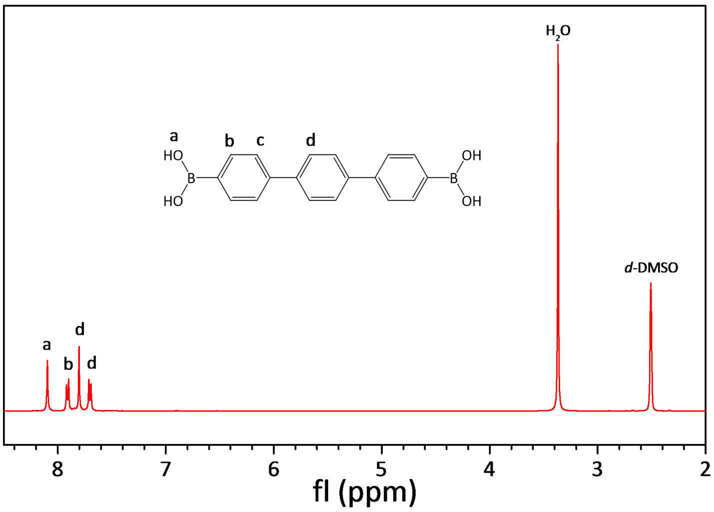


Figure S1. ^{1}H NMR spectrum of TPDBA.

3. XRD-pattern for three MOP-Ad networks

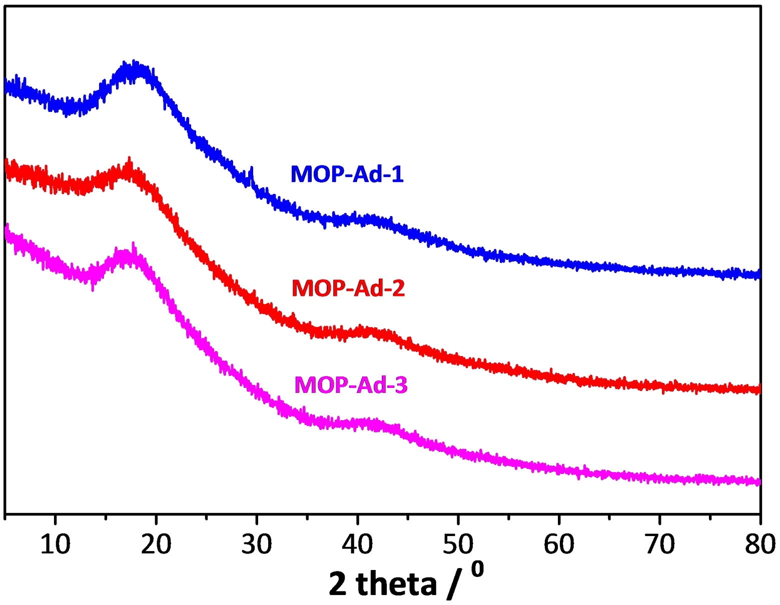


Figure S2. XRD patterns for the three **MOP-Ad** networks.

4. FTIR spectra of MOP-Ad networks after acid and base immersion

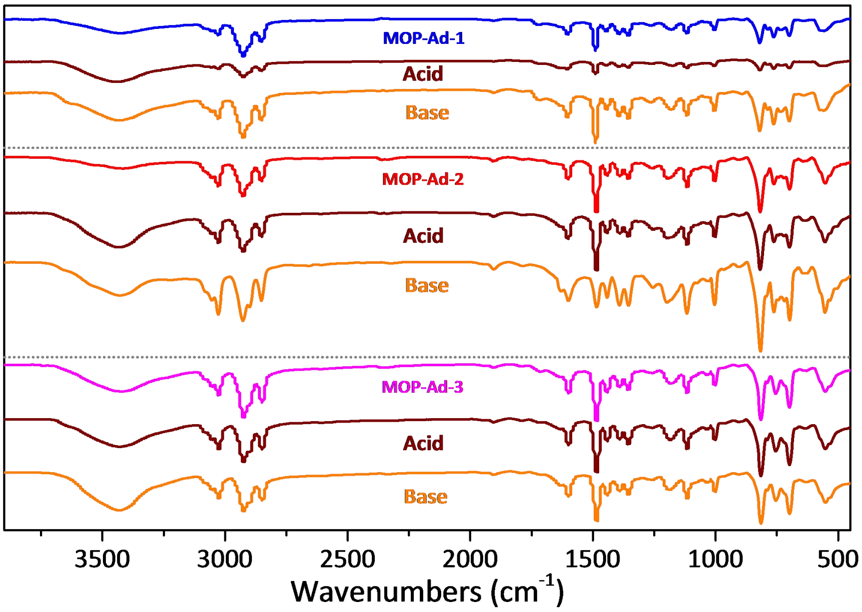


Figure S3. FTIR spectra of **MOP-Ad** networks after hydrochloric acid and sodium hydroxide immersion.

5. ^{13}C CP/MAS NMR spectra of MOP-Ad networks after acid and base immersion

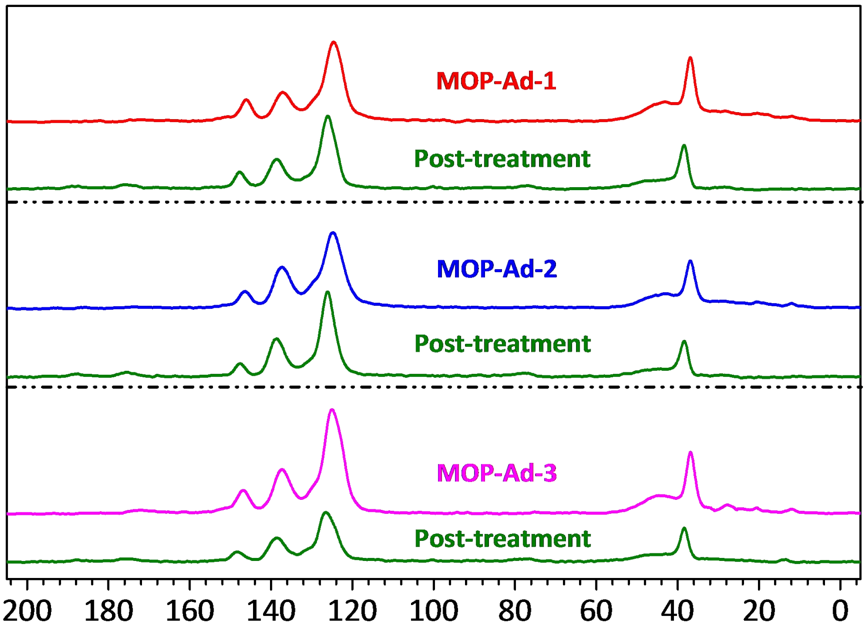


Figure S4. ^{13}C CP/MAS NMR spectra of **MOP-Ad** networks after hydrochloric acid and sodium hydroxide immersion

6. SAXS patterns for MOP-Ad networks

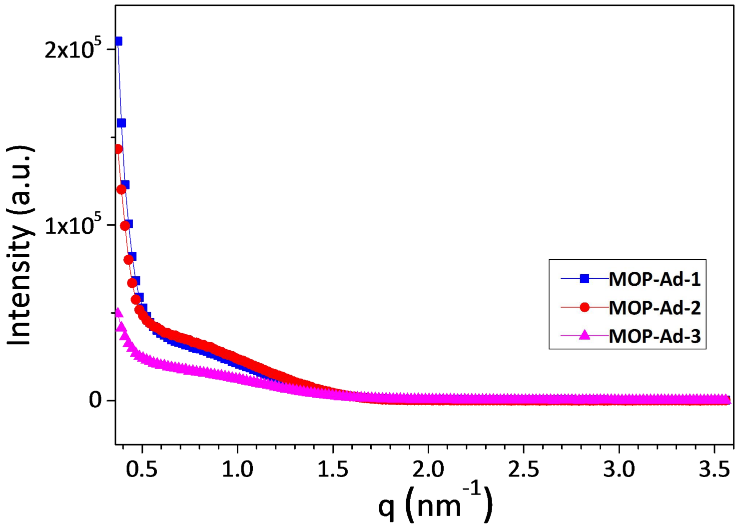


Figure S5. SAXS patterns for the **MOP-Ad** networks.

7. SEM of MOP-Ad networks

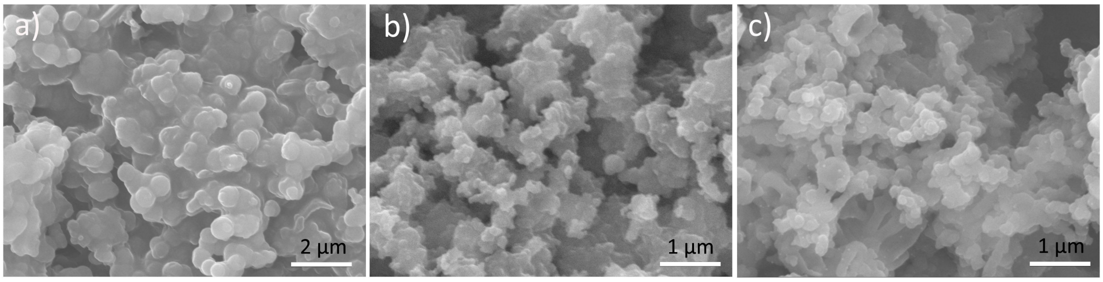
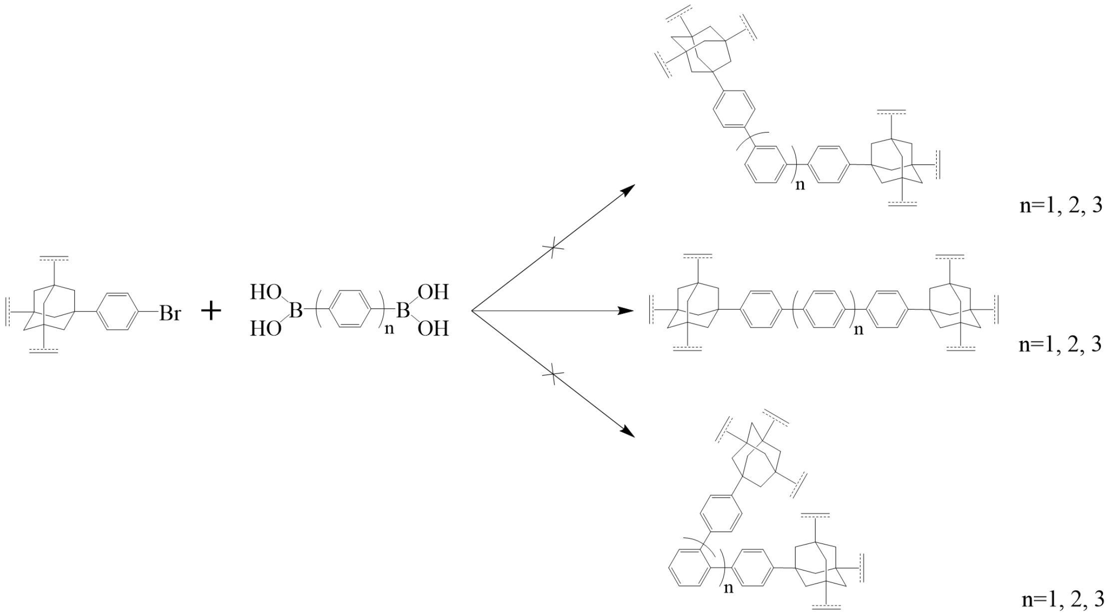


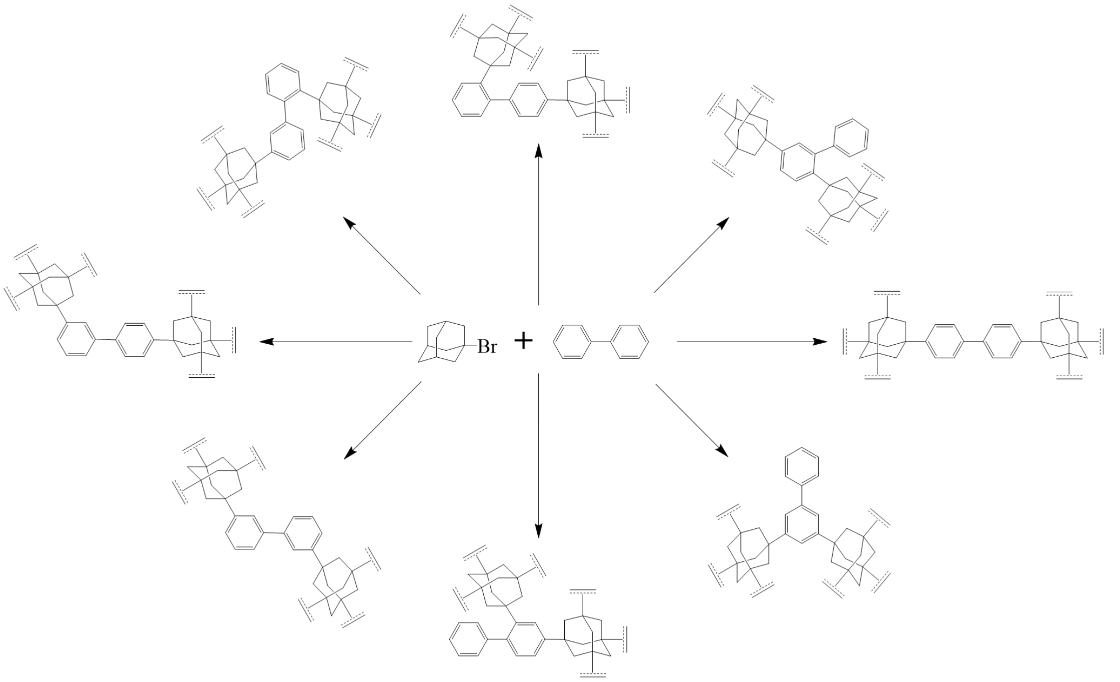
Figure S6. SEM images of **MOP-Ad-1** (a), **MOP-Ad-2** (b) and **MOP-Ad-3** (c).

8. Possible reaction mechanism of the Suzuki coupling reaction for MOP-Ad network production



Scheme S2. The possible reaction mechanism of the Suzuki coupling reaction for the networks reported herein.

9. Possible reaction mechanism of the Friedel-Crafts reaction for network production[16]



Scheme S3. The possible reaction mechanism of the Friedel-Crafts reaction for the networks reported herein.[16]

10. CH_4 adsorption isotherms of MOP-Ad networks

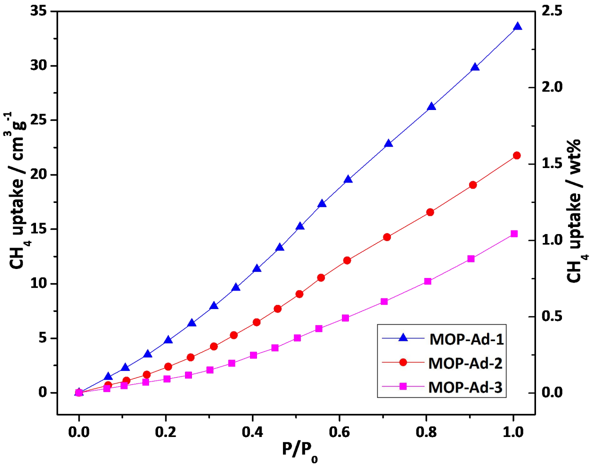


Figure S7. CH_4 adsorption isotherms of **MOP-Ad** networks.

11. Selectivity for MOP-Ad networks

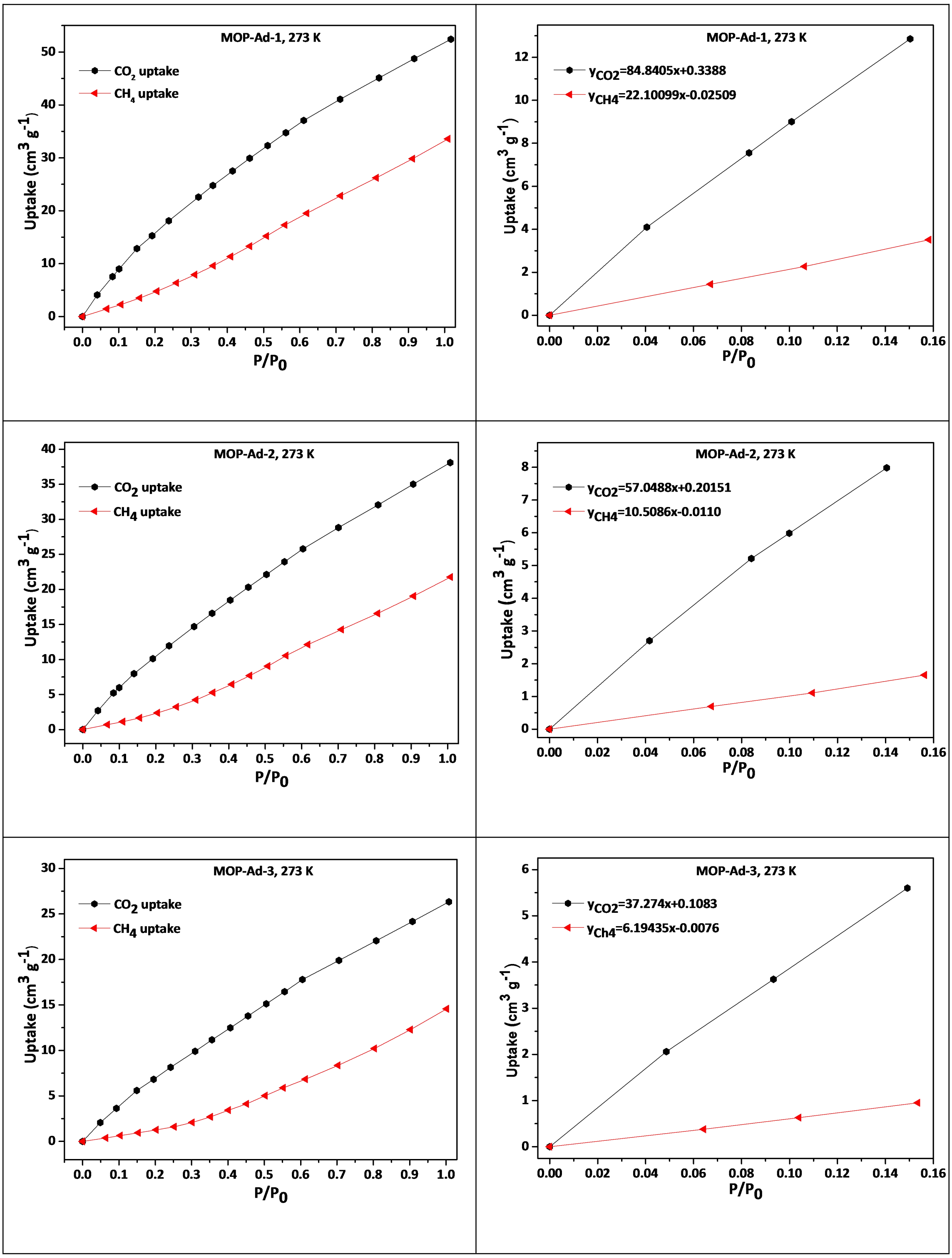


Figure S8. Selectivity for **MOP-Ad** networks.

12. Selectivity for MOP-Ad networks after hydrochloric acid and sodium hydroxide immersion

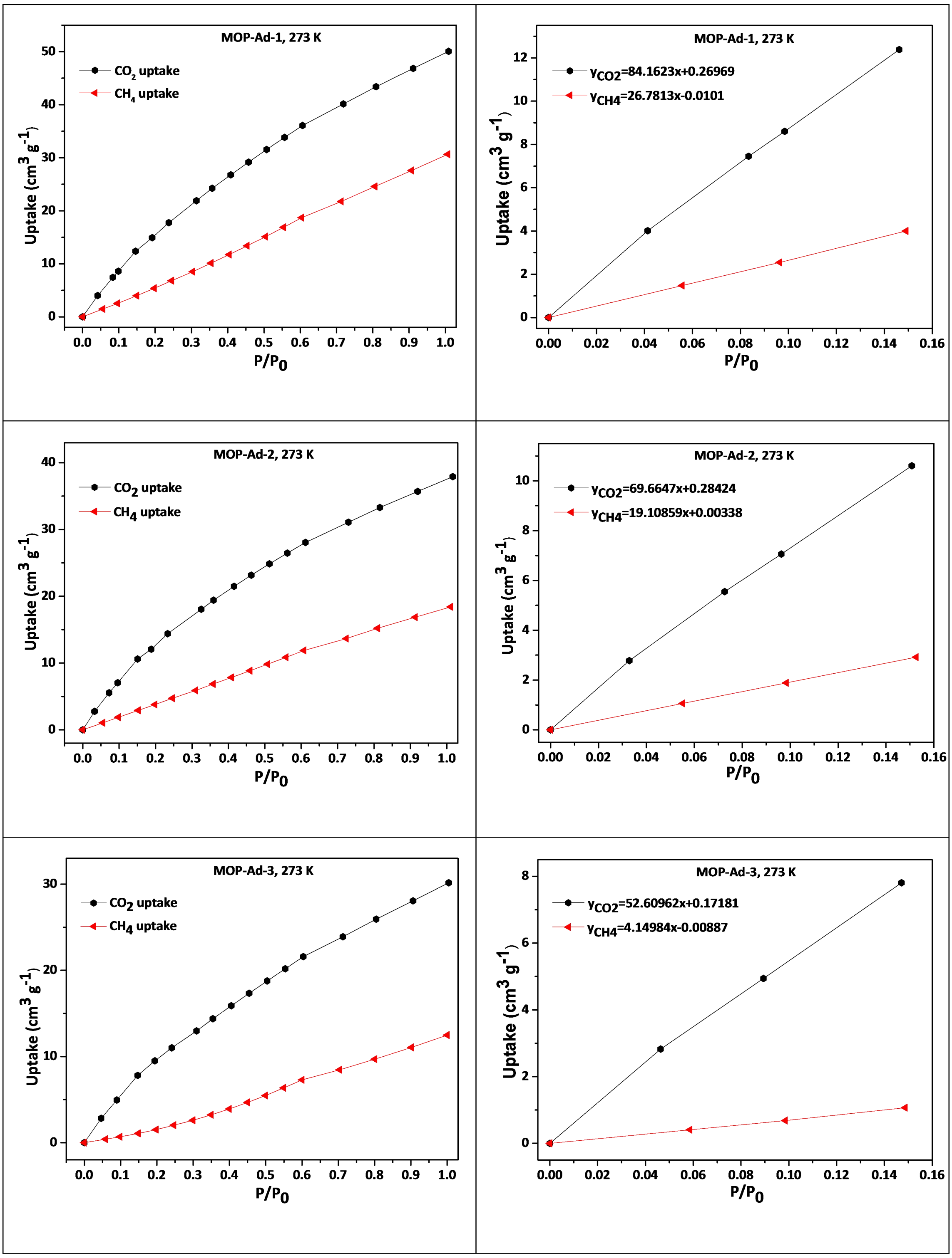


Figure S9. Selectivity for **MOP-Ad** networks after hydrochloric acid and sodium hydroxide immersion.

13. Porosity properties and gas uptake capacities of MOP-Ad networks after hydrochloric acid and sodium hydroxide immersion.

Table S1. Porosity properties and gas uptake capacities of **MOP-Ad** networks after hydrochloric acid and sodium hydroxide immersion.

Samples	CO_2 uptake (wt %)[b]	CH_4 uptake (wt %)[b]	Selectivity[c]
			CO_2/CH_4
MOP-Ad-1	9.8	2.2	3.2
MOP-Ad-2	7.4	1.3	3.7
MOP-Ad-3	5.9	0.9	12.7

[a] Data were obtained at 1.13 bar and 77.3 K.

[b] 1.13 bar and 273.1 K.

[c] Adsorption selectivity based on the Henry’s law.