# Supporting Information

# Conjugated microporous polymer networks with adjustable microstructures for high $CO_2$ uptake capacity and selectivity

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## Section A. Materials and methods

1,3,5-triethynylbenzene and 1,3,5-tri(3,5-dibromophenyl)benzene were purchased from TCI. Tetrakis(triphenylphosphine)palladium(0), copper(I) iodide, tetra(4-bromophenyl)methane and benzene-1,4-dibronic acid were purchased from Aladdin. Diphenyl-1,4-diobronic acid and 1,4-diethynelbenzene were purchased from Energy chemical. All solvents used were purchased from Aladdin.

$^1$H NMR spectra were recorded on Bruker AvanceIII models HD 400NMR spectrometers, where chemical shifts ($\delta$ in ppm) were determined with a residual proton of the solvent as standard. Fourier transform Infrared (FT-IR) spectra were recorded on a Perkin-elmer spectrum one model FT-IR-frontier infrared spectrometer. Solid-state $^{13}$C CP/MAS NMR measurements was recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The samples were prepared by drop-casting a THF suspension onto mica substrate and then coated with gold. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 60° with 0.02° increment. The elemental analysis was carried out on a EuroEA-3000. TGA analysis was carried out using a Q5000IR analyser (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of 5 °C min$^{-1}$ under a nitrogen atmosphere.

Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. BET surface areas were calculated over the relative pressure range 0.05-0.25 $P/P_0$. Nitrogen NLDFT pore size distributions were calculated from the nitrogen adsorption branch using a cylindrical pore size model.

Carbon dioxide sorption isotherms were measured at 298 K and 273 K with a Bel Japan Inc. model BELSORP-max analyzer, respectively. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

Carbon dioxide sorption isotherms were measured at 318 K and 60 bar with a iSorb HP2 analyzer. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

Methane and nitrogen sorption isotherms were measured at 273 K with a Bel Japan Inc. model BELSORP-max analyzer. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

The “wet” experiments were performed at ~50% relative humidity conditions. In order to ensure the samples were fully absorb moisture before beginning analysis, the samples were degassed by the pump at 120 °C for 12 h. Therefore, the micropores are almost empty before exposure to the humidified vapor environment. Then, all the polymer networks were exposed to humidity conditions for 3 days.

## Section B. Synthetic procedures

### Synthesis of *p*-Tetrabromotetraphenylethene (TBTPE) [S1]

Powdered 1,1,2,2-tetraphenylethene (5.00 g, 15.0 mmol) was treated with bromine (7.50 mL, 0.15 mol) and the mixture was kept for 16 h at room temperature.The resulting solid was dissolved in hot toluene (120 mL), concentrated to about 20 mL, and the precipitate was isolated.Purification using flash chromatography on $SiO_2$ (hexanes/$CH_2Cl_2$, 20:1 in vol.) gives TBTPE as a colorless solid (5.94 g) in 61% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.26 (d, 8H), 6.85 (d, 8H).

### Synthesis of 1,1,2,2-tetrakis[4-(trimethylsilylethynyl)phenyl]ethene[S2]

TBTPE (1 g, 1.54 mmol) and $PdCl_2(PPh_3)_2$ (25.2 mg, 0.036 mmol) and CuI (3.6 mg, 0.0185 mmol) were put in to a 100 mL round-bottom flask, then the flask exchanged 3 cycles under vacuum/$N_2$, then added to 50 mL diethylamine. The flask was degassed by freeze-pump-thaw for 3 times, then warmed to R.T., refilled with $N_2$, trimethylsilylacetylene(1 mL, 7.392 mmol) was slowly added via a syringe. The mixture was heated at 50 °C for 15 h. After this the reaction mixture was cooled to room temperature, concentrated to about 10 mL. The crude product was purified by silica gel column chromatography using hexane as eluent. A white solid was obtained (0.61 g, 72% yield). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm): 7.23 (d, 8H), 6.92 (d, 8H), 0.26 (s, 36H).

**Synthesis of 1,1,2,2-tetrakis(4-ethynylphenyl)ethene**[S2]

1,1,2,2-Tetrakis(4-(trimethylsilylethynyl)phenyl)ethene (1.5 g, 2.1 mmol) and THF (40 mL) were placed were put into a 250 mL round-bottom flask. Then, KOH (1.8 g, 32 mmol) dissolved in 40 mL of methanol was added. The mixture was stirred at room temperature overnight. After most of the solvent was evaporated, 100 mL of 1 M aqueous HCl solution was added and the mixture extracted with dichlormethane three times. The organic phases were combined and washed with water and brine and then dried over $MgSO_4$. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using hexane/dichlormethane (100:1 by volume) mixture as eluent. A yellow solid was obtained (0.96 g, 81% yield). $^1$H NMR (400 MHz, $CDCl_3$ ): $\delta$ (ppm) 7.28 (d, 8H), 6.93 (d, 8H), 3.06 (s, 4H).

**Synthesis of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane**[S3]

Tetra(4-bromophenyl)methane (2.04 g, 3.16 mmol), $PdCl_2(PPh_3)_2$ (0.135 g, 0.18 mmol), CuI (0.024 g, 0.125 mmol), and $PPh_3$ (0.1 g, 0.38 mmol) were put into a 250 mL round-bottom flask; then the flask exchanged 3 cycles under vacuum/$N_2$, anhydrous $iPr_2NH$ (30 mL) and trimethylsilylacetylene (2.2 mL, 30.37 mmol) was added via a syringe under the $N_2$. The reaction mixture was brought to reflux at 90°C for 24 h, and then cooled down to room temperature. Solvent was removed in vacuum, and $CHCl_3$ was added to dissolve the residue and filtered through a pad of Celite. The filtrate was washed with dilute $Na_2EDTA$ solution and then dried over anhydrous $Na_2SO_4$; the solution was concentrated, and ethanol was added to obtain tetra(4-trimethylsilyacetylenephenyl)methane as a white solid product (1.37 g, 80% yield).

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.26 (d, 8H), 6.85 (d, 8H), 0.26 (s, 36H).

### Synthesis of tetrakis(4-ethynylphenyl)methane [S3]

NaOH (0.98 g, 24.6 mmol) was dissolved in 10 mL of $CH_3OH$, then added to a solution of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane (1.8 g, 1.2 mmol) in 20 mL of $CH_2Cl_2$, and then stirred for 6 h at room temperature. The reaction mixture was washed with water, and the aqueous phase was extracted with $CH_2Cl_2$, and the combined organic phases were washed with brine, and then dried over anhydrous $Na_2SO_4$. The solution was concentrated, and ethanol was added to the solution. Tetrakis(4-ethynylphenyl)methane was obtained as light yellow solid (1.18 g, 83% yield). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.39 (d, 8H),7.12(d, 8H), δ 3.06 (s, 4H).

### Synthesis of $A_6$CMP-1

Benzene-1,4-diobronic acid (64 mg, 0.38 mmol) and 1,3,5-tri(3,5-dibromophenyl)benzene (100 mg, 0.13 mmol) were put into a 50 mL round-bottom flask, then the flask exchanged 3 cycles under vacuum/$N_2$. Then DMF (8 mL) was added. The solution was further degassed by freeze-pump-thaw for three cycles. Then $K_2CO_3$ (176 mg, 1.28 mol) in 3 mL water and tetrakis(triphenylphesphine)palladium (14.7 mg, 0.013 mol ) in 4 mL DMF were added via a syringe. The reaction was refluxed at 120 °C for 48 h. The solid product was collected by filtration and washed well with THF, methanol, acetone, and water, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give $A_6$CMP-1 as a gray powder (64.5 mg, 94.3 % yield). Elemental Analysis (%) calcd. C 94.45, H 5.55; Found C 94.08, H 4.75.

### Synthesis of $A_6$CMP-2

1,3,5-tri(3,5-dibromophenyl)benzene (100 mg, 0.13 mmol) and 1,4-diethynelbenzene (52.2 mg, 0.4 mmol) were put into a 50 mL round-bottom flask, then the flask exchanged 3 cycles under vacuum/$N_2$. Then DMF (2 mL) and triethylamine (2 mL) ($Et_3N$) were added. The solution was further degassed by freeze-pump-thaw for three cycles. The reaction was heated to 120 °C, when the solution had reached this temperature, a slurry of tetrakis(triphenylphesphine)palladium (18.3 mg, 0.016 mmol) in 1 mL DMF and copper(I) iodide (6 mg, 0.03 mmol) in 1 mL $Et_3N$ was added and the reaction was kept at 120 °C for 48 h. The solid product was collected by filtration and washed well with THF, methanol, acetone, and water, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give $A_6$CMP-2 as a brownish black powder (78.7 mg, 87.7 % yield). Elemental Analysis (%) calcd. C 95.08, H 4.82; Found C 93.84, H 4.66.

### Synthesis of $A_6$CMP-3

Diphenyl-1,4-diobronic acid (93 mg, 0.38 mmol) and 1,3,5-tri(3,5-dibromophenyl)benzene (100 mg, 0.13 mmol) were put into a 50 mL round-bottom flask, then the flask exchanged 3 cycles under vacuum/$N_2$. Then DMF (8 mL) was added. The solution was further degassed by freeze-pump-thaw for three cycles. Then $K_2CO_3$ (176 mg, 1.28 mol) in 3 mL water and tetrakis(triphenylphesphine)palladium (14.7 mg, 0.013 mol ) in 4 mL DMF were added via a syringe. The reaction was refluxed at 120 °C for 48 h. The solid product was collected by filtration and washed well with THF, methanol, acetone, and water, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give $A_6$CMP-3 as a gray powder (90.5 mg, 92.6 % yield). Elemental Analysis (%) calcd. C 94.55, H 5.45; Found C 93.08, H 4.83.

### Synthesis of $A_6$CMP-4

1,3,5-tri(3,5-dibromophenyl)benzene (130 mg, 0.17 mmol) and 1,3,5-triethynylbenzene (50 mg, 0.33 mmol) were put into a 50 mL round-bottom flask, then the flask exchanged 3 cycles under vacuum/$N_2$. Then DMF (2 mL) and triethylamine (2 mL) ($Et_3N$) were added. The solution was further degassed by freeze-pump-thaw for three cycles. The reaction was heated to 120 °C, when the solution had reached this temperature, a slurry of tetrakis(triphenylphesphine)palladium (23.0 mg, 0.02 mmol) in 1 mL DMF and copper(I) iodide (6.0 mg, 0.03 mmol) in 1 mL $Et_3N$

was added and the reaction was kept at 120 °C for 48 h. The solid product was collected by filtration and washed well with THF, methanol, acetone, and water, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give $A_6$CMP-4 as a brownish black powder (90.8 mg, 91.8 % yield). Elemental Analysis (%) calcd. C 97.46, H 2.54; Found C 95.28, H 3.68.

### Synthesis of $A_6$CMP-5

1,3,5-tri(3,5-dibromophenyl)benzene (68.4 mg, 0.09 mmol) and 1,1,2,2-tetrakis(4-ethynylphenyl)ethane (50 mg, 0.13 mmol) were put into 50 mL round-bottom flask, then the flask exchanged 3 cycles under vacuum/$N_2$. Then DMF (2 mL) and triethylamine ($Et_3N$) (2 mL) were added. The solution was further degassed by freeze-pump-thaw for three cycles. The reaction was heated to 120 °C, when the solution had reached this temperature, a slurry of tetrakis(triphenylphesphine)palladium (14.4 mg, 0.01 mmol) in 1 mL DMF and copper(I) iodide (3 mg, 0.02 mmol) in 1 mL $Et_3N$ was added and the reaction was kept at 120 °C for 48 h. The solid product was collected by filtration and washed well with THF, methanol, acetone, and water, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give $A_6$CMP-5 as a brownish black powder (73.7 mg, 97.2 % yield). Elemental Analysis (%) calcd. C 96.19, H 3.81; Found: C 93.87, H 4.67.

### Synthesis of $A_6$CMP-6

1,3,5-tri(3,5-dibromophenyl)benzene (112 mg, 0.14 mmol) and tetrakis(4-ethynylphenyl)methane (100 mg, 0.21 mmol) were put into a 50 mL round-bottom flask, then the flask exchanged 3 cycles under vacuum/$N_2$. Then DMF (2 mL) and triethylamine ($Et_3N$) (2 mL) were added. The solution was further degassed by freeze-pump-thaw for three cycles. The reaction was heated to 120 °C, when the solution had reached this temperature, a slurry of tetrakis(triphenylphesphine)palladium (14.4 mg, 0.01 mmol) in 1 mL DMF and copper(I) iodide (3.1 mg, 0.02 mmol) in 1 mL $Et_3N$

was added and the reaction was kept at 120 °C for 48 h. The solid product was collected by filtration and washed well with THF, methanol, acetone, and water, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give $A_6$CMP-6 as a brownish black powder (127.4 mg, 89.7 % yield). Elemental Analysis (%) calcd. C 96.10, H 3.88; Found C 94.64, H 4.35.

**Synthesis of $A_6$CMP-7**

1,5-cycloocatadiene (0.2 mL, 1.8 mmol, dried over $CaH_2$) was added to a solution of bis(1,5-cyclooctadiene )nickel (0) (440 mg, 1.6 mmol) and 2,2’-bipyridyl (250 mg, 1.6 mmol) in dehydrated THF (8 mL), and the mixture was heated to 70 °C for 1 h. Then 1,3,5-tri(3,5-dibromophenyl)benzene (160 mg, 0.20 mmol) was added to the resulting purple solution, and the reaction was stirred at 80 °C for 48 h. After cooling to room temperature, HCl (6 M, 4 mL) was added to the mixture. The solid product was collected by filtration and washed well with water, ethanol, and acetone, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol, and THF for 24 h, respectively, to give $A_6$CMP-7 as a gray powder (57.9 mg, 94.2 % yield). Elemental Analysis (%) calcd. C 95.08, H 4.92; Found C 93.75, H 5.41.

## Section C. FT-IR spectral profiles

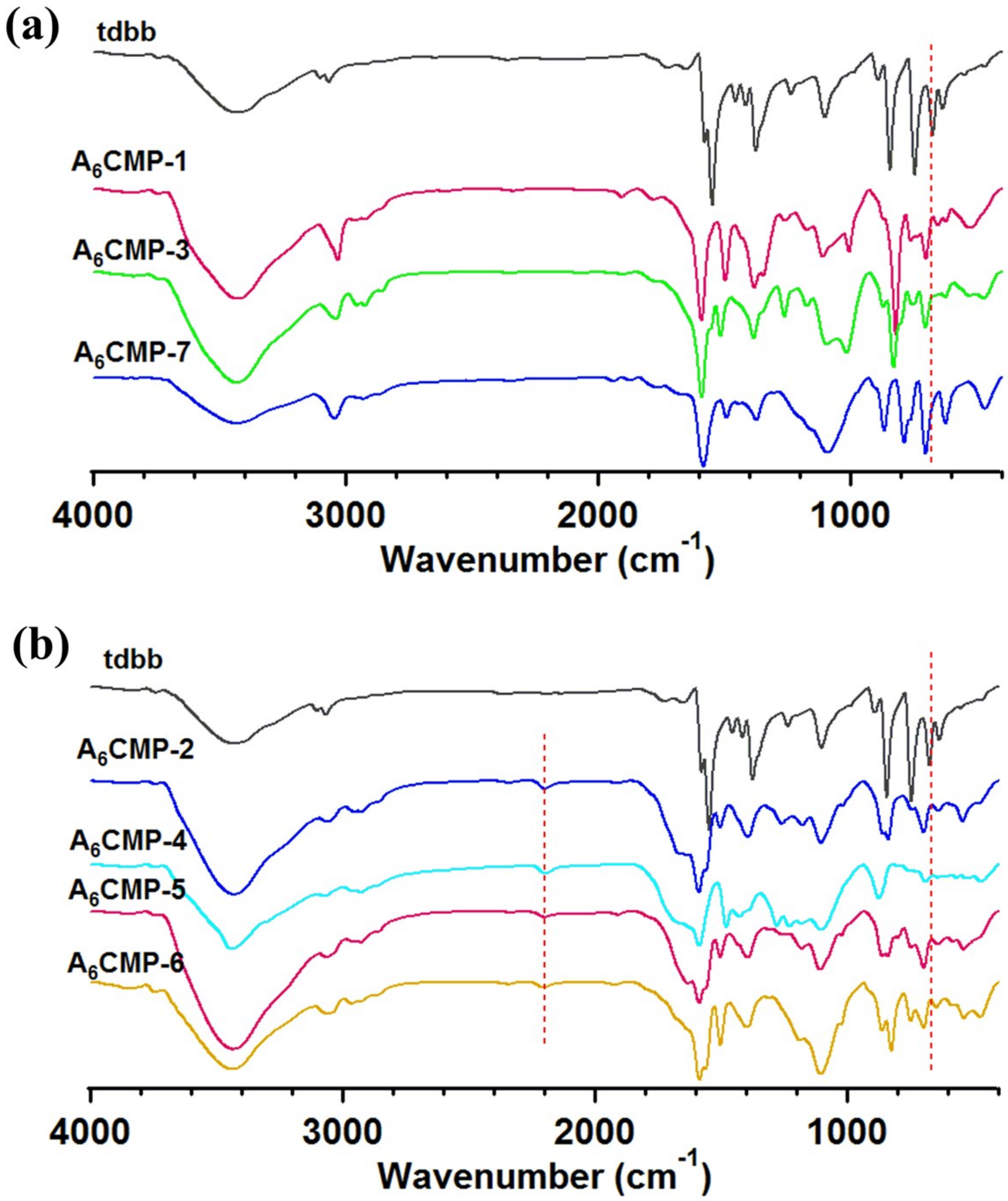
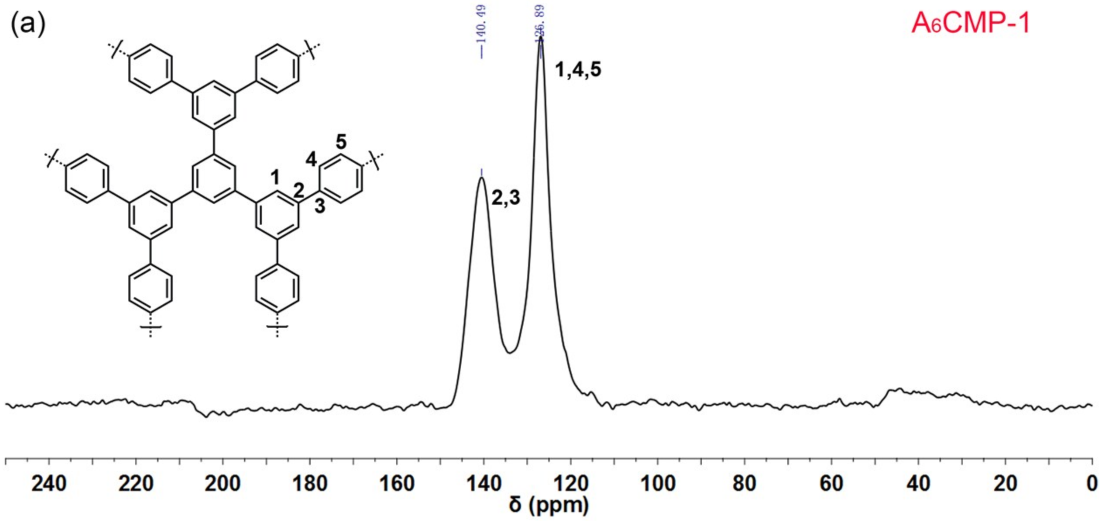
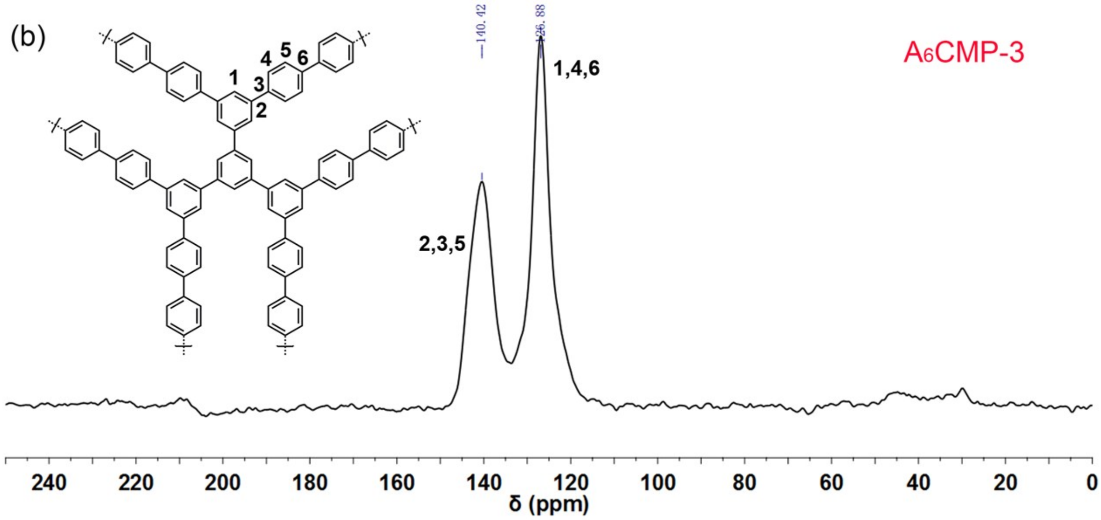
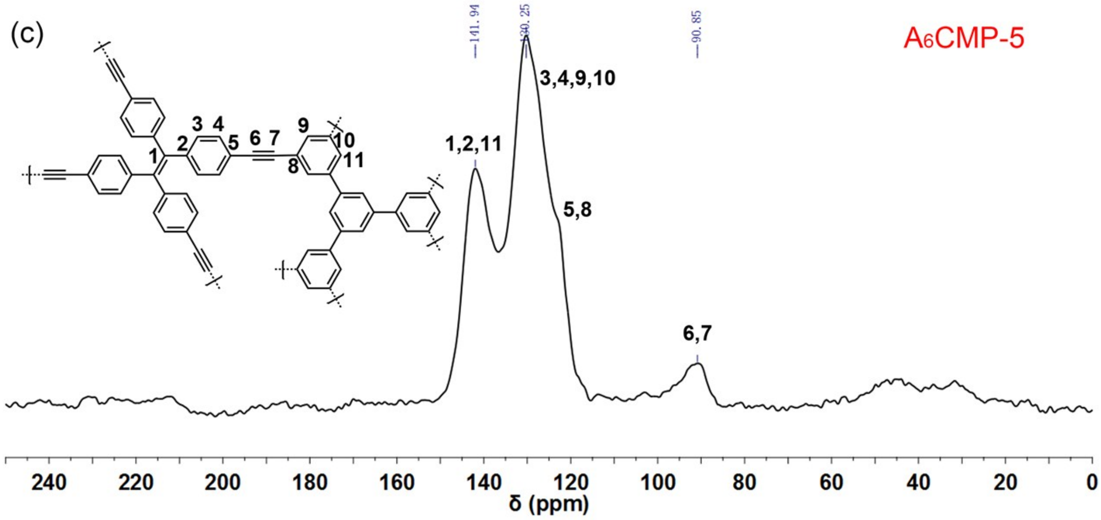


**Fig. S1** IR spectra of 1,3,5-tri(3,5-dibromophenyl)benzene (tdbb), and polymers $A_6$CMP-1–7.

## Section D. The solid-state $^{13}$CCP-MAS NMR







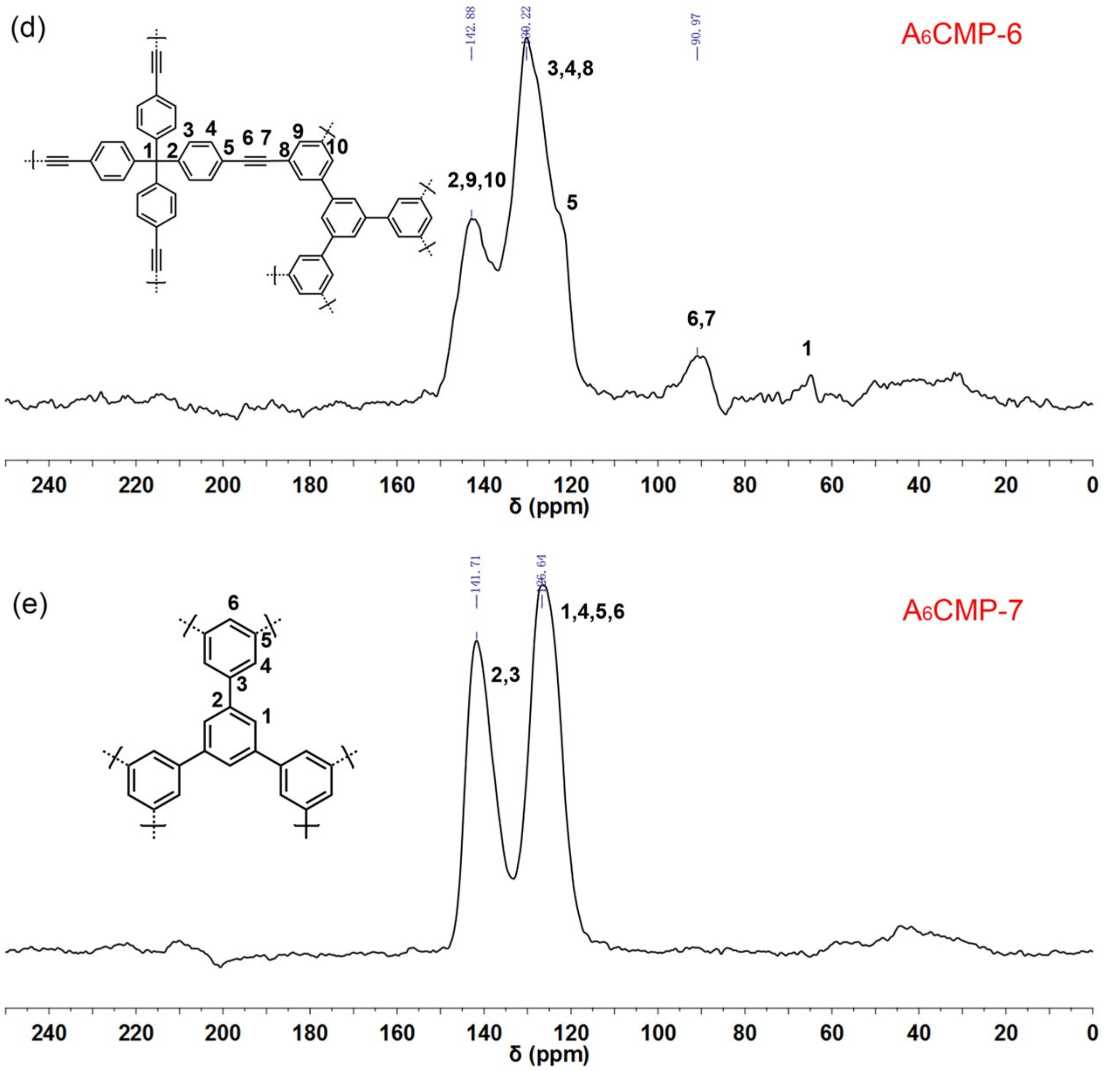


Fig. S2 The solid-state $^{13}C$ CP-MAS NMR of polymers.

## Section E. Thermal stability

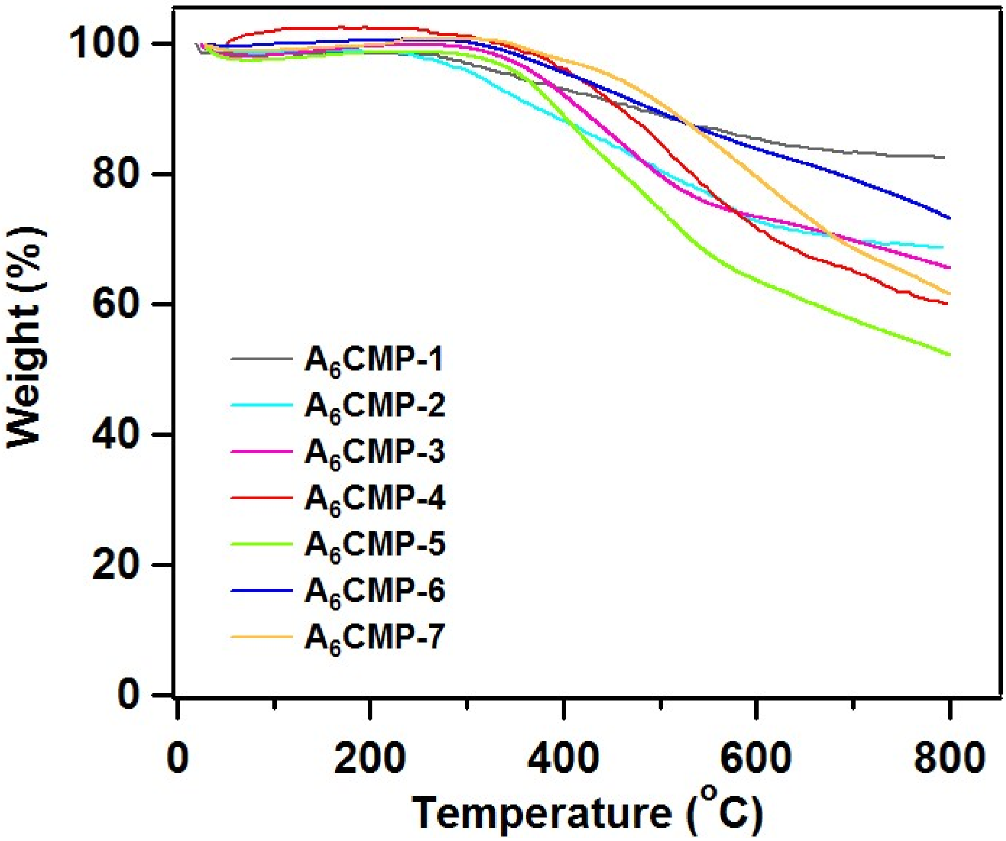


**Fig. S3** Thermal stability of $A_6$CMP-1–7.

## Section F. Powder X-ray diffraction patterns

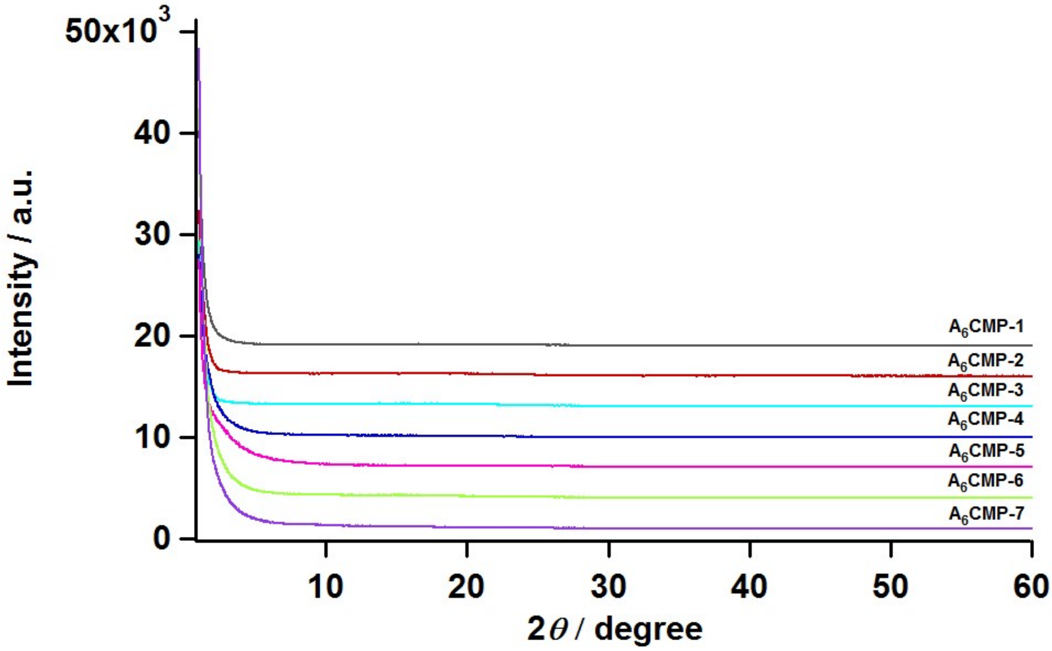


**Fig. S4** Powder X-ray diffraction profiles of $A_6$CMP -1–7.

## Section G. HR-TEM images

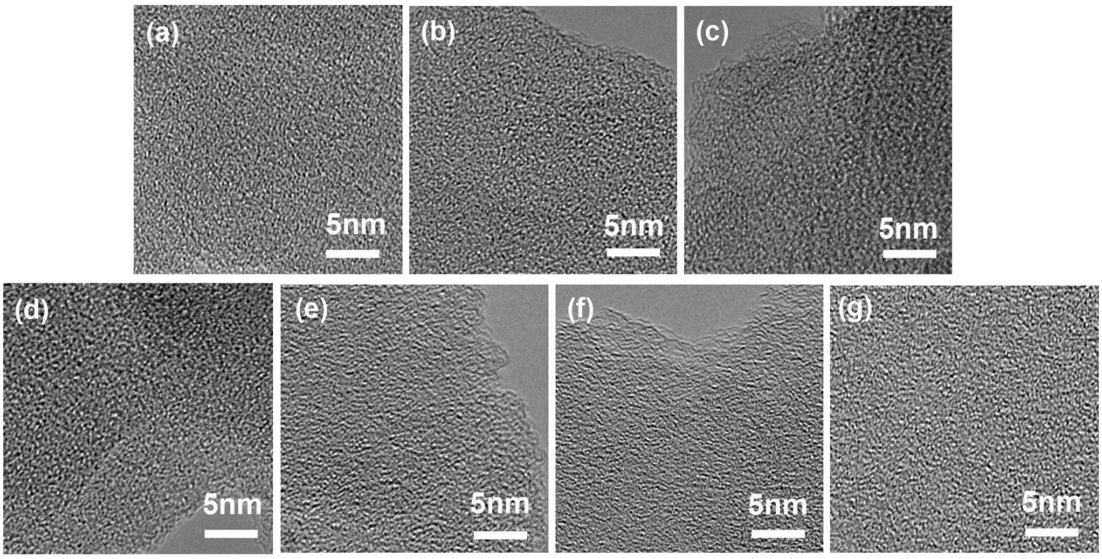


**Fig. S5** HR-TEM images of (a) $A_6$CMP-1, (b) $A_6$CMP-2, (c) $A_6$CMP-3, (d) $A_6$CMP-4, (e) $A_6$CMP-5, (f) $A_6$CMP-6, and (g) $A_6$CMP-7.

## Section H. $CO_2$ adsorption isotherms

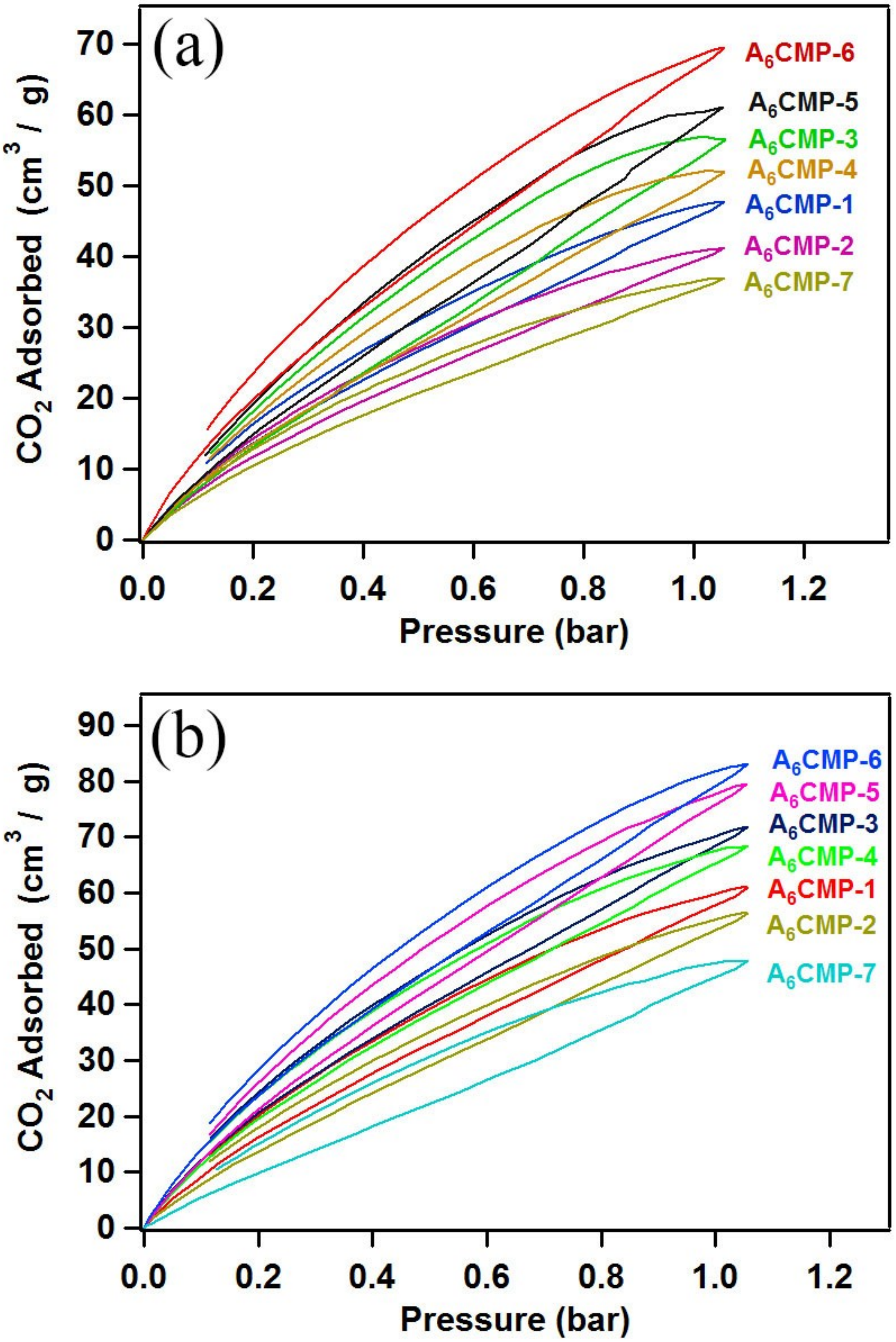


**Fig. S6** $CO_2$ adsorption isotherms of the $A_6$CMPs collected at (a) 298 K and (b) 273 K.

## Section I. The $CO_2$ uptake of CMPs under wet conditions

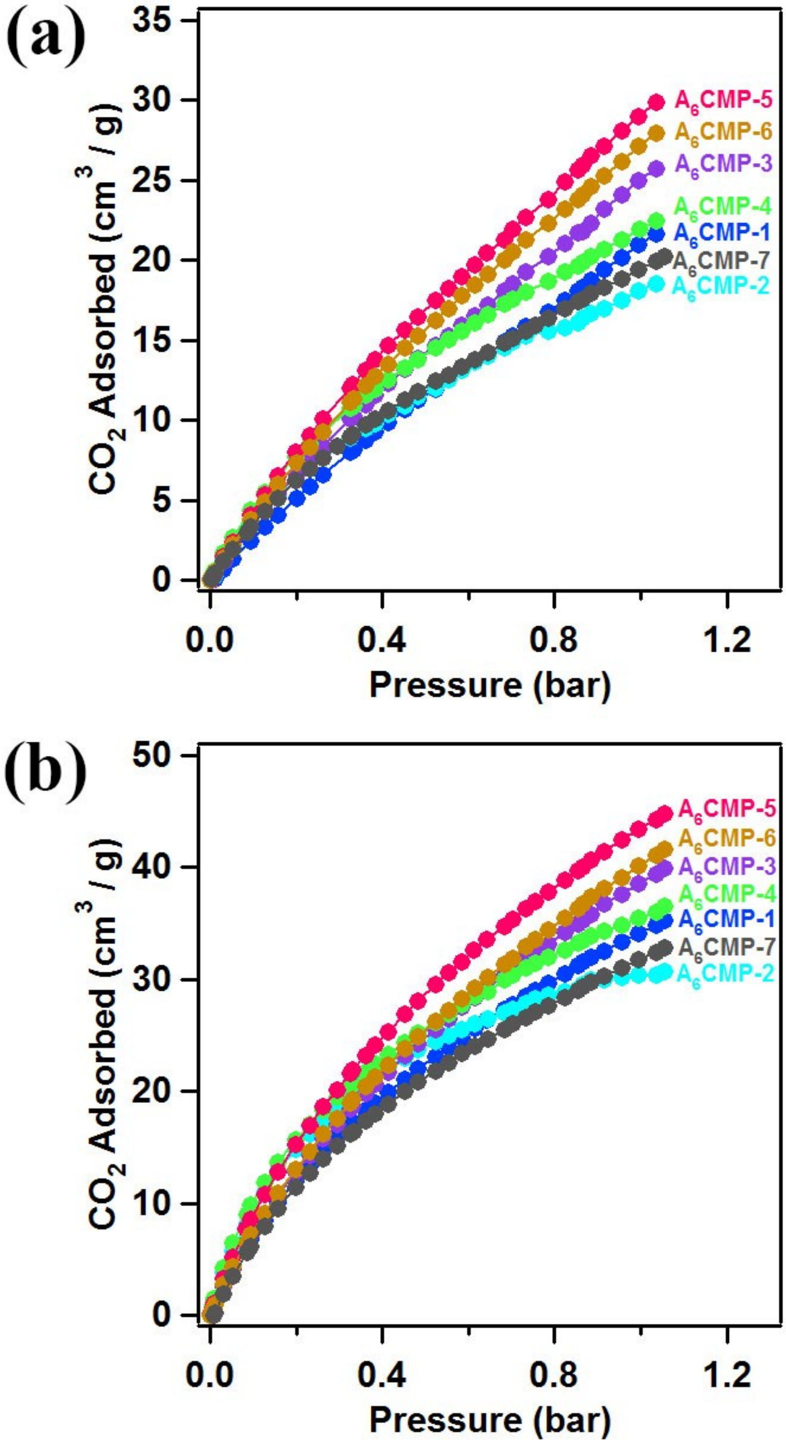


**Fig. S7** The $CO_2$ uptake of $A_6$CMPs under wet conditions (a) at 298 K and 1.0 bar, and (b) at 273 K and 1.0 bar.

## Section J. $CO_2$, $CH_4$, and $N_2$ adsorption capacity

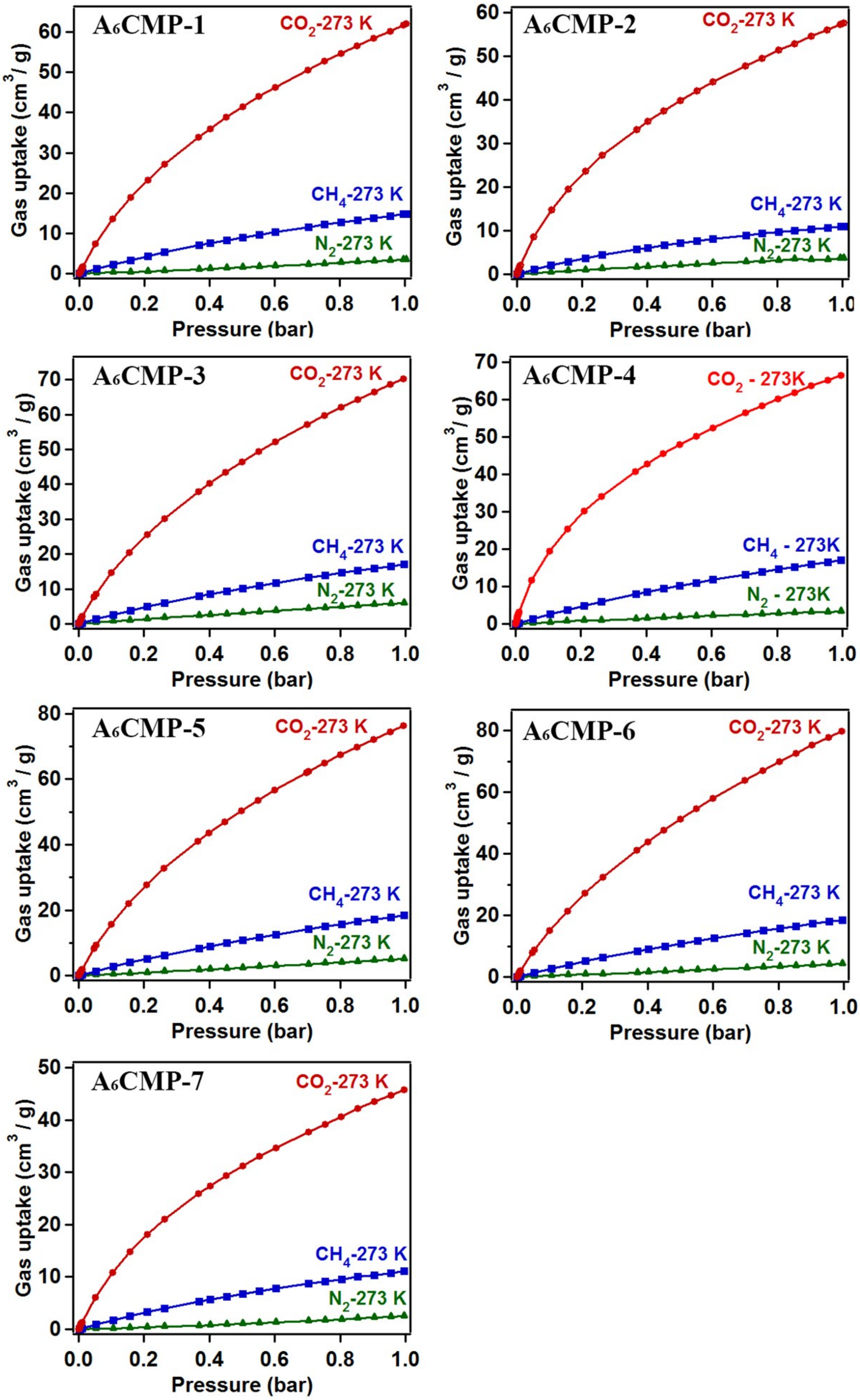


**Fig. S8** $CO_2$, $CH_4$, and $N_2$ adsorption isotherms of $A_6CMPs$ at 273 K.

## Section K. Corresponding data of gas selectivity analyses

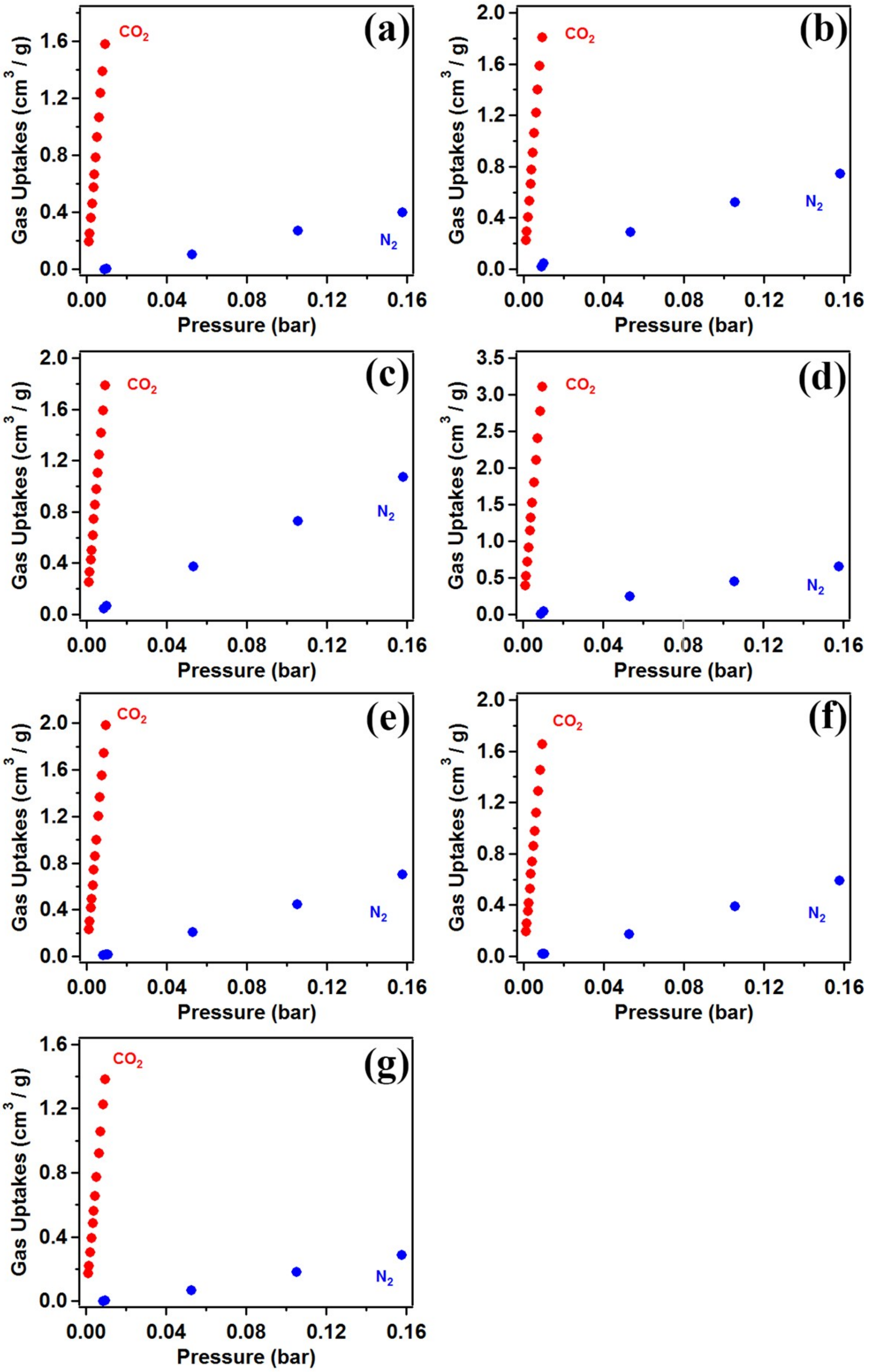


**Fig. S9** CO$_2$/N$_2$ initial slope selectivity studies for A$_6$CMP-1 (a), A$_6$CMP-2 (b), A$_6$CMP-3 (c), A$_6$CMP-4 (d), A$_6$CMP-5 (e), A$_6$CMP-6 (f), and A$_6$CMP-7 (g) at 273 K.

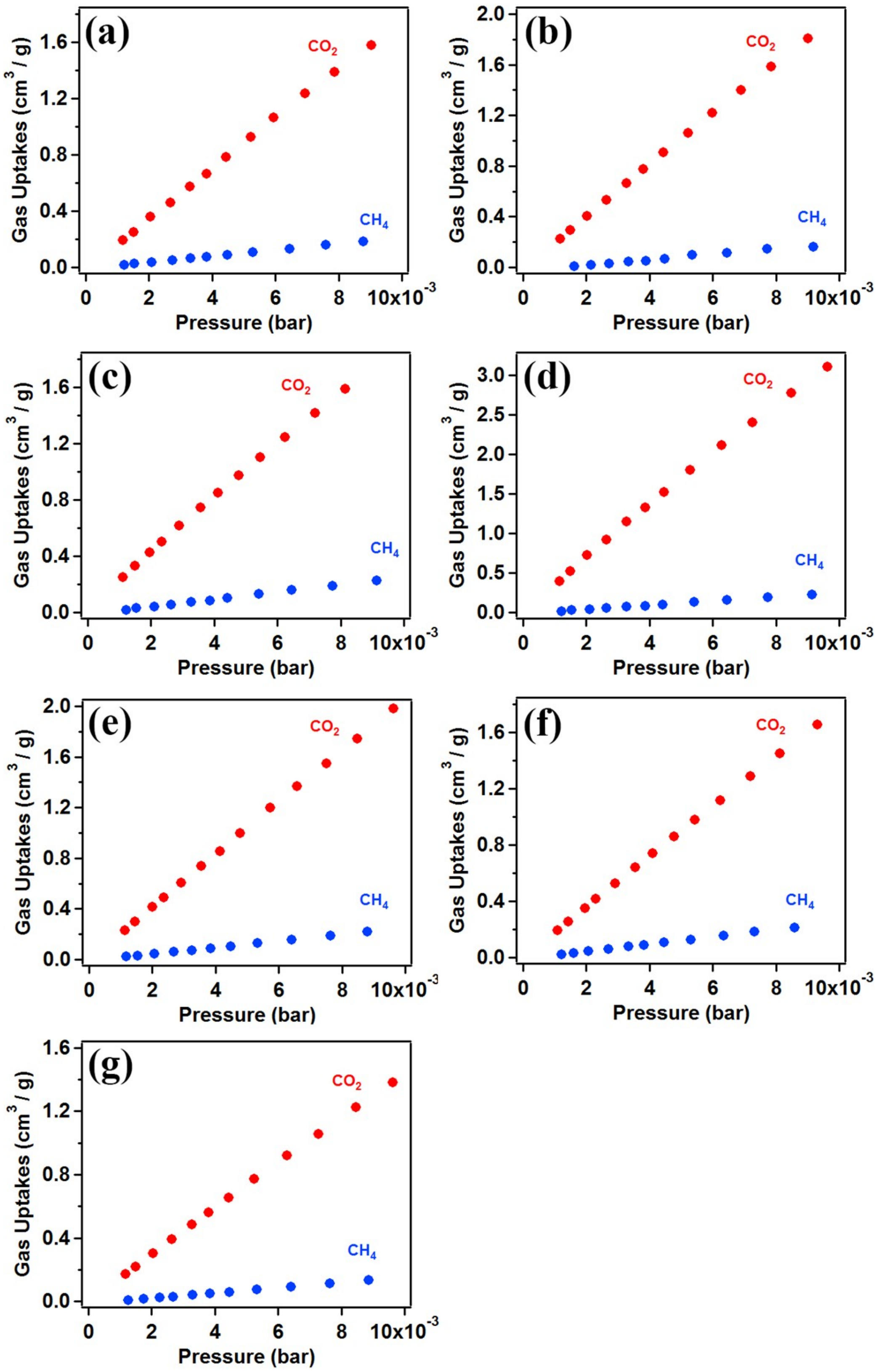


**Fig. S10** $CO_2$/$CH_4$ initial slope selectivity studies for A$_6$CMP-1 (a), A$_6$CMP-2 (b), A$_6$CMP-3 (c), A$_6$CMP-4 (d), A$_6$CMP-5 (e), A$_6$CMP-6 (f), and A$_6$CMP-7 (g) at 273 K.

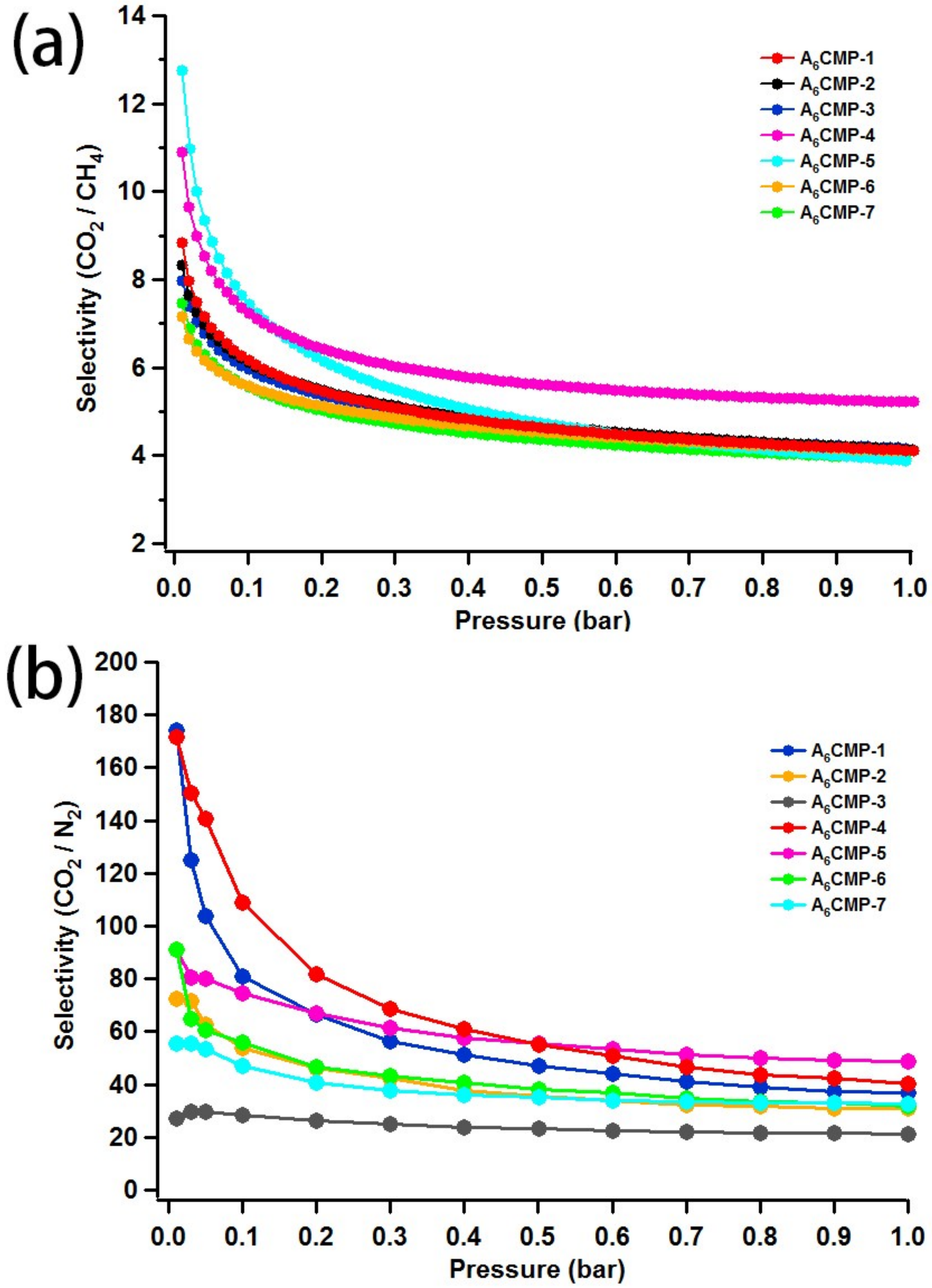


**Fig. S11** (a) $CO_2/CH_4$ selectivity of $A_6CMP$ for a molar ratio of 50/50 at 273 K, (b) $CO_2/N_2$ selectivity of $A_6CMP$ for a molar ratio of 15/85 at 273 K.

**Table S1. Porosity properties and gas uptake for the polymers**

| CMPs | $S_{BET}$[a] ($m^2/g$) | $S_{micro}$[b] ($m^2/g$) | $V_{total}$[c] ($cm^3/g$) | $S_{micro}$ /$S_{BET}$ | d (nm) | $CO_2/N_2$[d] selectivity at 273 K | $CO_2/CH_4$[d] selectivity at 273 K | $CO_2/N_2$[e] selectivity at 273 K | $CO_2/CH_4$[e] selectivity at 273 K |
|---|---|---|---|---|---|---|---|---|---|
| **$A_6$CMP-1** | 740 | 438 | 1.27 | 0.59 | 0.70 | 41.2 | 4.7 | 44 | 6.6 |
| **$A_6$CMP-2** | 640 | 382 | 0.67 | 0.59 | 0.56 | 32.1 | 4.7 | 28 | 6.6 |
| **$A_6$CMP-3** | 1042 | 638 | 1.34 | 0.61 | 0.64 | 21.2 | 4.4 | 19.3 | 5.5 |
| **$A_6$CMP-4** | 960 | 582 | 1.24 | 0.61 | 0.51 | 48.9 | 5.8 | 47 | 7.5 |
| **$A_6$CMP-5** | 1110 | 689 | 1.57 | 0.62 | 0.64 | 36.9 | 5.3 | 31.6 | 7.2 |
| **$A_6$CMP-6** | 1115 | 800 | 0.70 | 0.72 | 0.46 | 32.8 | 4.2 | 30 | 5.4 |
| **$A_6$CMP-7** | 571 | 307 | 0.97 | 0.54 | 0.65 | 31 | 4.1 | 24 | 5.1 |

[a] Surface area calculated by the BET method; [b] Micropore area and micropore volume determined by the *t*-plot method; [c] Total pore volume at $P/P_0 \sim 0.995$. [d] Selectivity was calculated by IAST method for $CO_2/N_2$ (at mole ratio of 15/85 ) and $CO_2/CH_4$ (at mole ratio of 50/50) at 273 K. [e] Selectivity was calculated by Henry law at 273 K.

**Table S2. The $CO_2$ uptakes at 1.0 bar of CMPs**

| **Polymers** | Dried at 298 K ($cm^3$ / g) | Humidified at 298 K ($cm^3$ / g) | Dried at 273 K ($cm^3$ / g) | Humidified at 273 K ($cm^3$ / g) |
|---|---|---|---|---|
| **$A_6$CMP-1** | 52 | 21 | 62 | 35 |
| **$A_6$CMP-2** | 44 | 18 | 57 | 30 |
| **$A_6$CMP-3** | 57 | 26 | 71 | 40 |
| **$A_6$CMP-4** | 54 | 23 | 66 | 36 |
| **$A_6$CMP-5** | 62 | 30 | 77 | 45 |
| **$A_6$CMP-6** | 70 | 28 | 81 | 42 |
| **$A_6$CMP-7** | 38 | 20 | 46 | 33 |

## Section L. Supporting references

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