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富羧酸基团的共轭微孔聚合物：结构单元对孔隙和气体吸附性能的影响

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Carboxyl-Enriched Conjugated Microporous Polymers: Impact of Building Blocks on Porosity and Gas Adsorption

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Section A Synthetic procedures

Synthesis of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane [S1]

Tetra(4-bromophenyl)methane (2.04 g, 3.16 mmol), $PdCl_2(PPh_3)_2$ (0.135 g, 0.18 mmol), CuI (0.024g, 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 heated at 80℃ 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 (86% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.26 (d, 8H), 6.85 (d, 8H), 0.26 (s, 36H).

Synthesis of tetrakis(4-ethynylphenyl)methane [S1]

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 (68.7% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, 8H), 7.12 (d, 8H), δ 3.06 (s, 4H) .

Synthesis of CMP@1

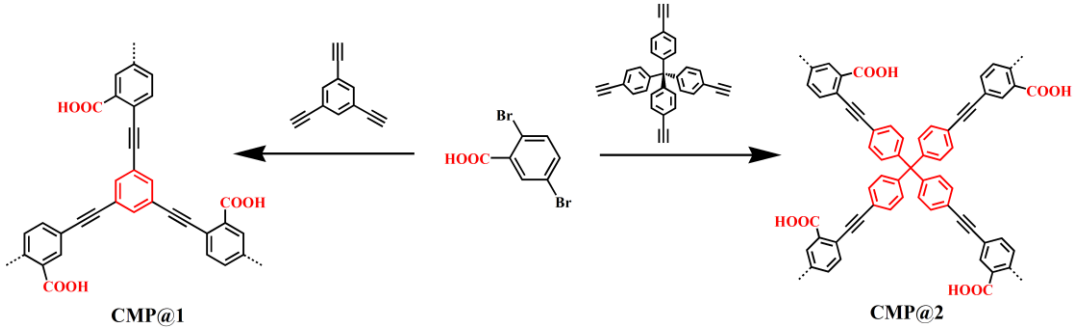
1,3,5-Triethynylbenzene (50 mg, 0.33 mmol) and 2,5-diobromobenzoic acid (92.4 mg, 0.33 mmol) were put into a 50 mL round-bottom flask, the flask exchanged 3 cycles under vacuum/N_2. Then added to 2 mL DMF and 2 mL triethylamine, the flask was degassed by three freeze–pump–thaw cycles, purged with N_2. When the solution had reached reaction temperature, a slurry of tetrakis(triphenylphosphine)palladium (0) (23.11 mg, 0.02 mmol) in the 1 mL DMF and copper (I) iodide (4.8 mg, 0.025 mmol) in the 1 mL Et_3N was added and the reaction was stirred at 120 ℃ under nitrogen for 48 h. The solid product was collected by filtration and washed well with hot

reaction solvent for 4 times 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 CMP@1 as yellow solid in 92%. Elemental Analysis (%) Calcd. (Actual value for an infinite 2D polymer) C 78.11, H 2.96. Found: C 74.84, H 2.04.

Synthesis of CMP@2

Tetrakis(4-ethynylphenyl)methane (104 mg, 0.25 mmol) and 2,5-diobromobenzoic acid (92.4 mg, 0.33 mmol) were put into a 50 mL round-bottom flask, the flask exchanged 3 cycles under vacuum/N_2. Then added to 2 mL DMF and 2 mL triethylamine, the flask was degassed by three freeze–pump–thaw cycles, purged with N_2. When the solution had reached reaction temperature, a slurry of tetrakis(triphenylphosphine)palladium (0) (23.11 mg, 0.02 mmol) in the 1 mL DMF and copper (I) iodide (4.8 mg, 0.025 mmol) in the 1 mL Et_3N was added and the reaction was stirred at 120 ℃ under nitrogen for 48 h. The solid product was collected by filtration and washed well with hot reaction solvent for 4 times 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 CMP@2 as olivine solid in 87%. Elemental Analysis (%) Calcd. (Actual value for an infinite 2D polymer), C 82.06, H 3.59. Found: C 79.92, H 2.88.

Section B Schematic representation



Scheme S1 Schematic representation of synthesis of CMP@1 and CMP@2.

Section C HR-TEM images

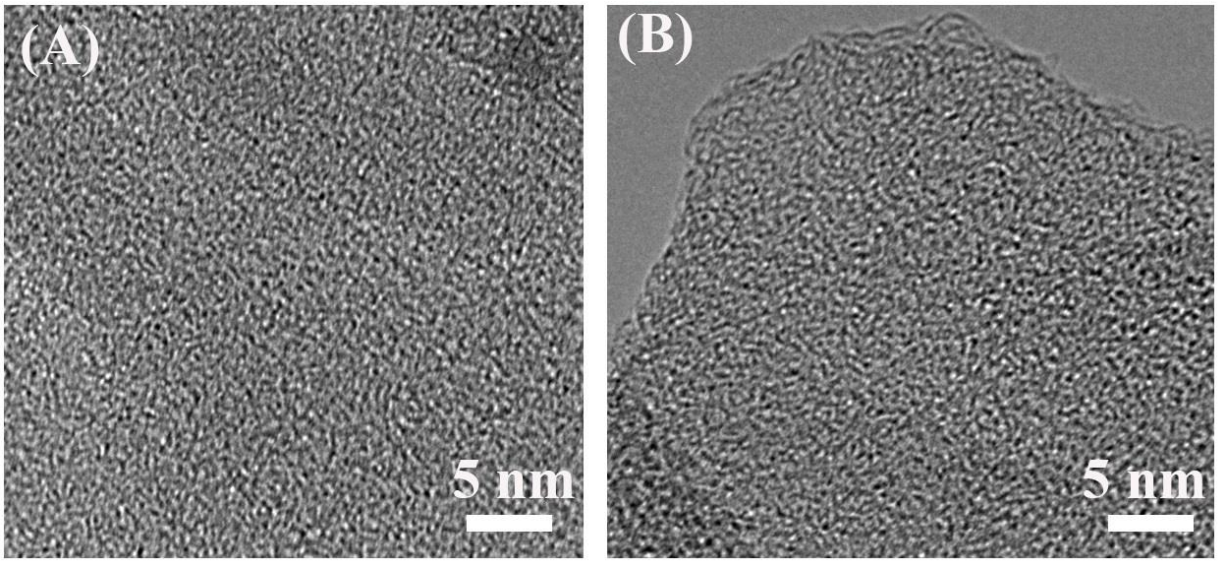


Fig.S1 HR-TEM images of (A) CMP-COOH@1 and (B) CMP-COOH@2.

Section D Powder X-ray diffraction patterns

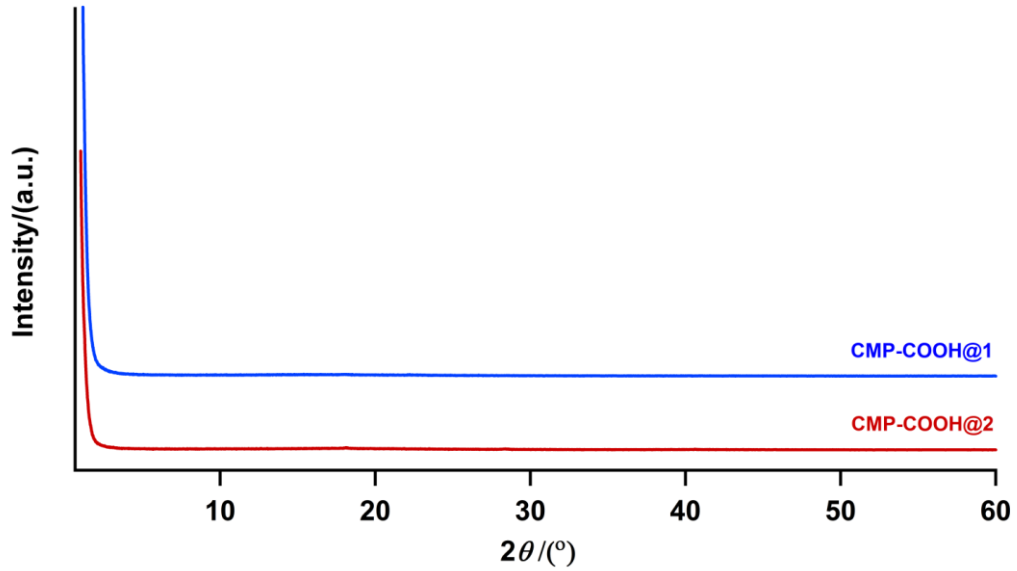


Fig.S2 Powder X-ray diffraction profiles of CMP-COOH@1 and CMP-COOH@2.

Section E TGA curves

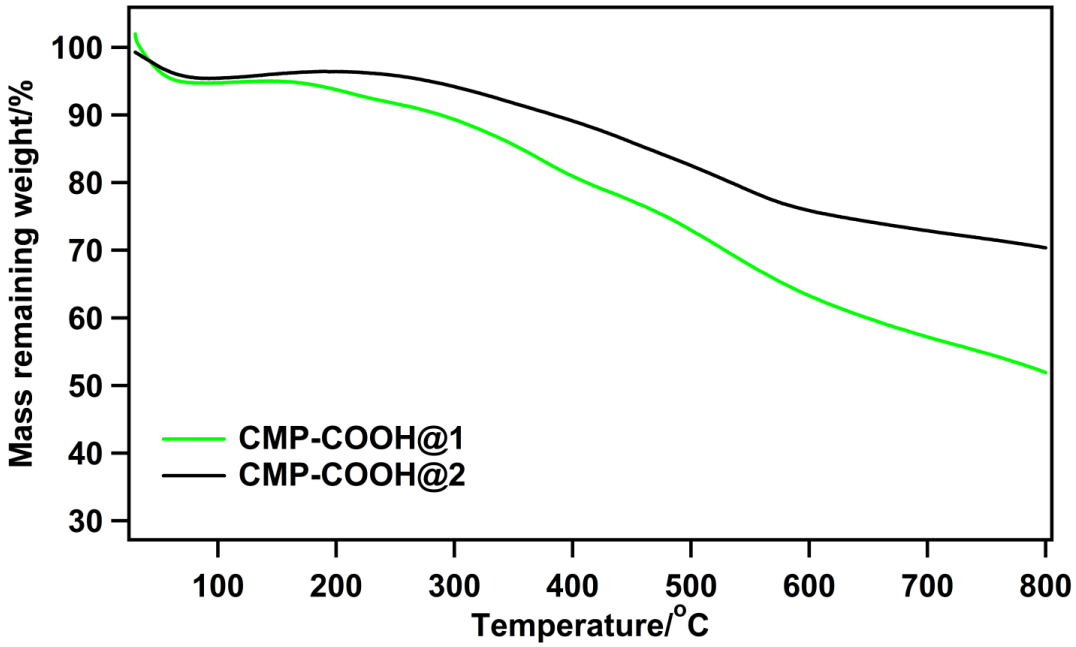


Fig.S3 TGA curves of CMP-COOH@1 and CMP-COOH@2.

Section F Electronic absorbance spectra

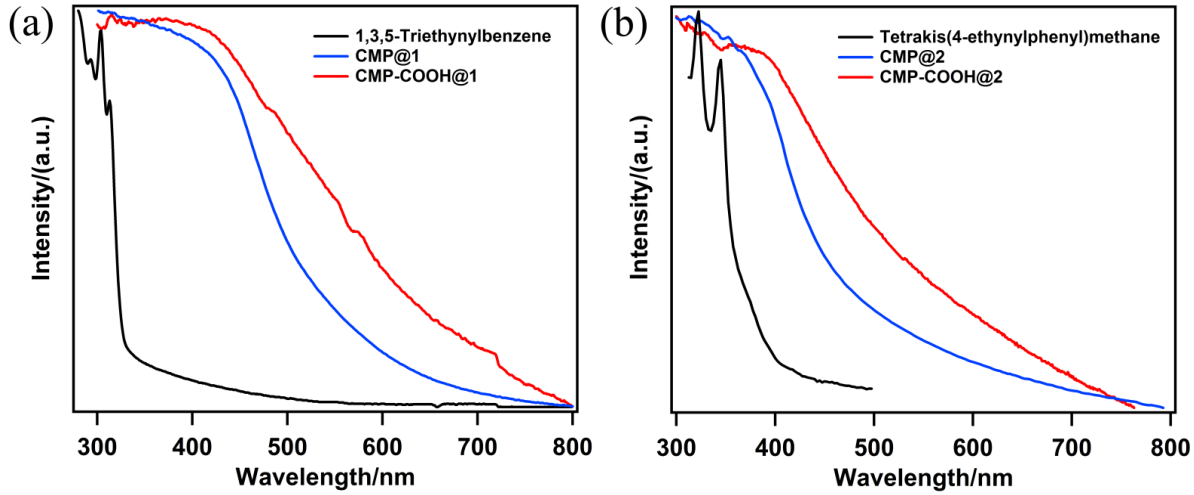


Fig.S4 Electronic absorbance spectra of (a) CMP@1 and CMP-COOH@1, and (b) CMP@2 and CMP-COOH@2.

Section G Pore property

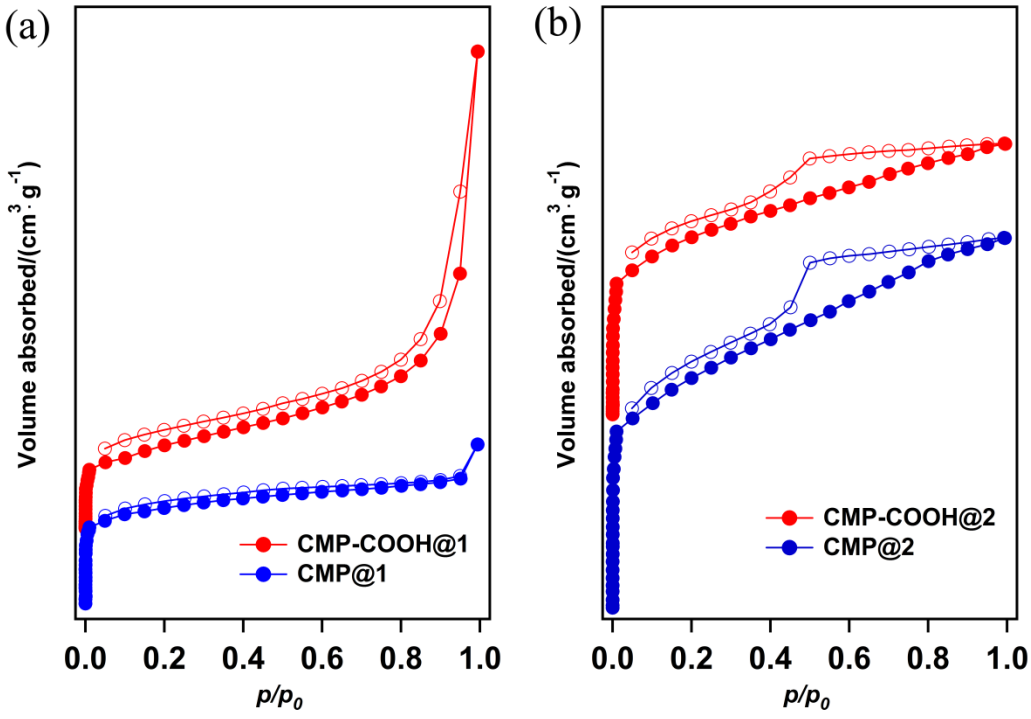


Fig.S5 Nitrogen sorption curves of CMP polymers.

filled circles: adsorption, open circles: desorption, STP = standard temperature pressure.

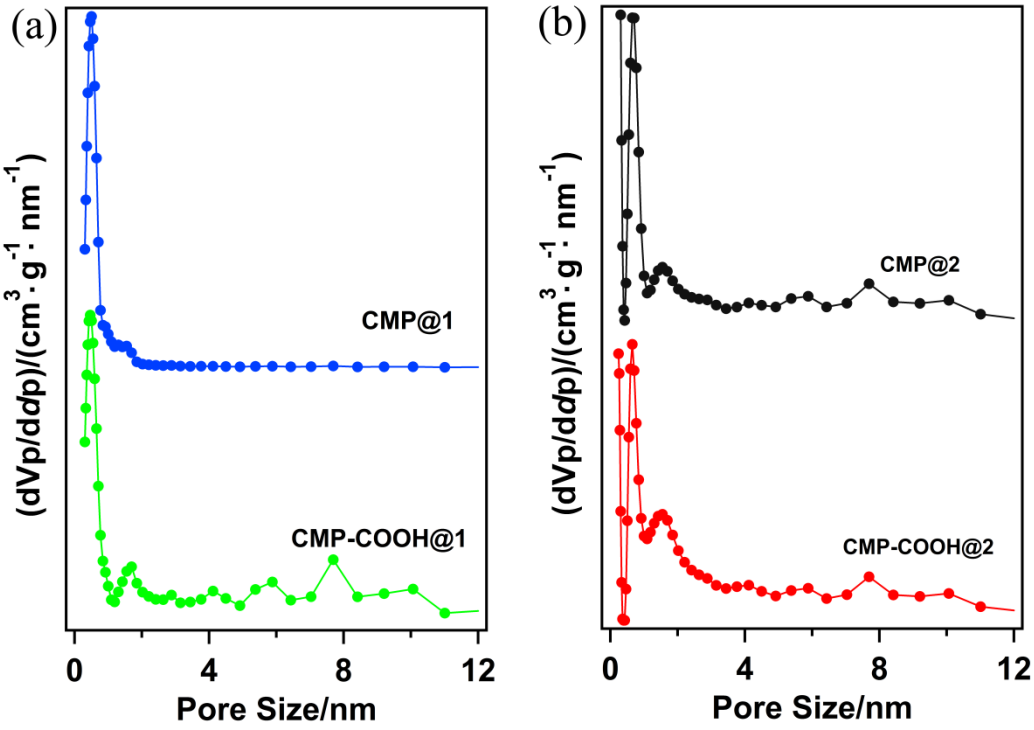


Fig.S6 Pore size distribution of CMP polymers.

Section H Gas adsorption isotherms

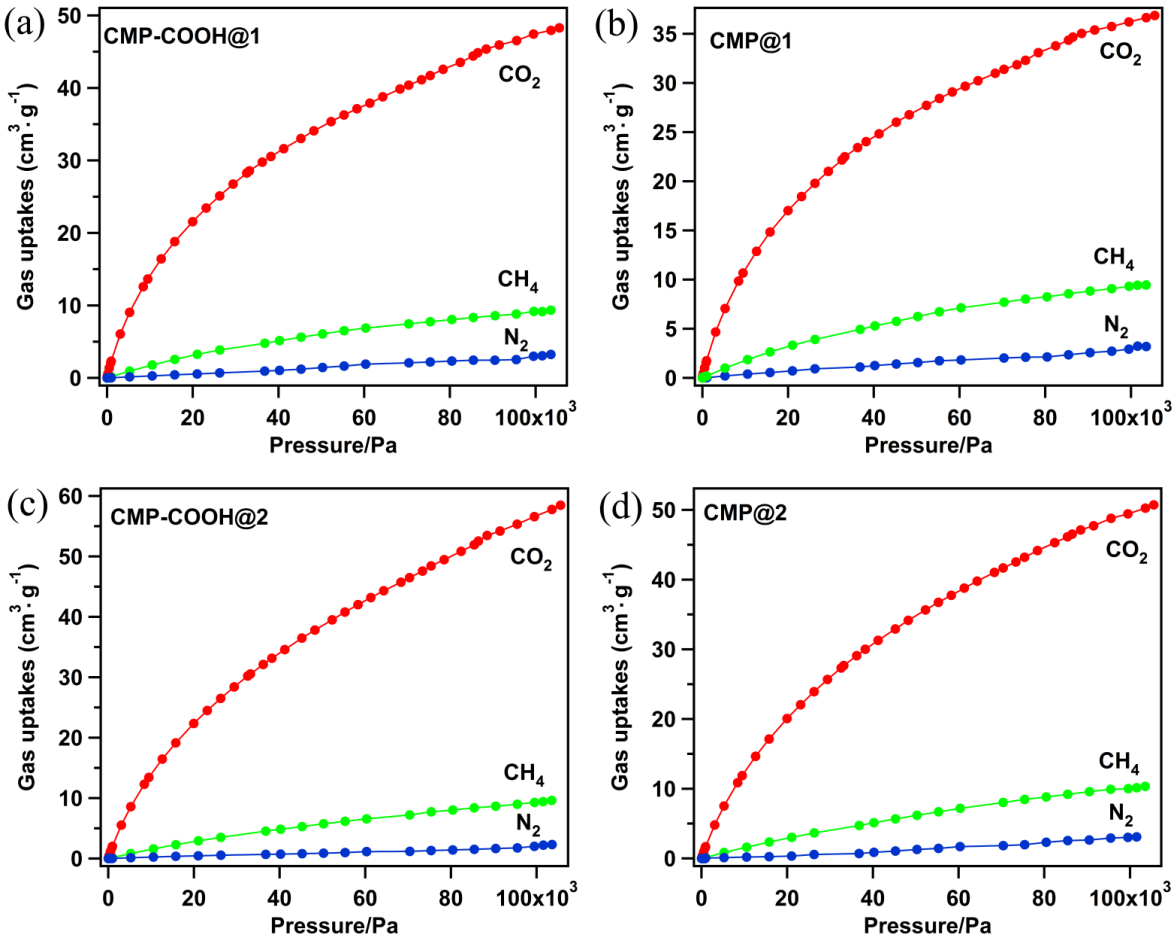


Fig.S7 Gas adsorption isotherms of polymers CMP-COOH@1 (a), CMP@1 (b), CMP-COOH@2 (c), and CMP@2 (d) at 273 K and 1.05 × 10^5 Pa.

Section I Corresponding data of gas selectivity analyses

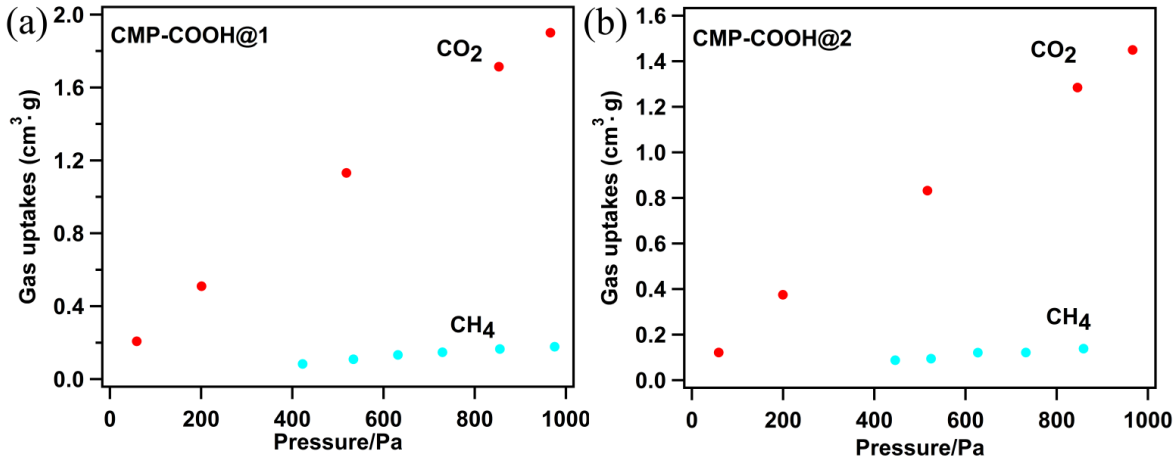


Fig.S8 CO_2/CH_4 initial slope selectivity studies for CMP-COOH@1 (a) and CMP-COOH@2 (b) at 273 K.

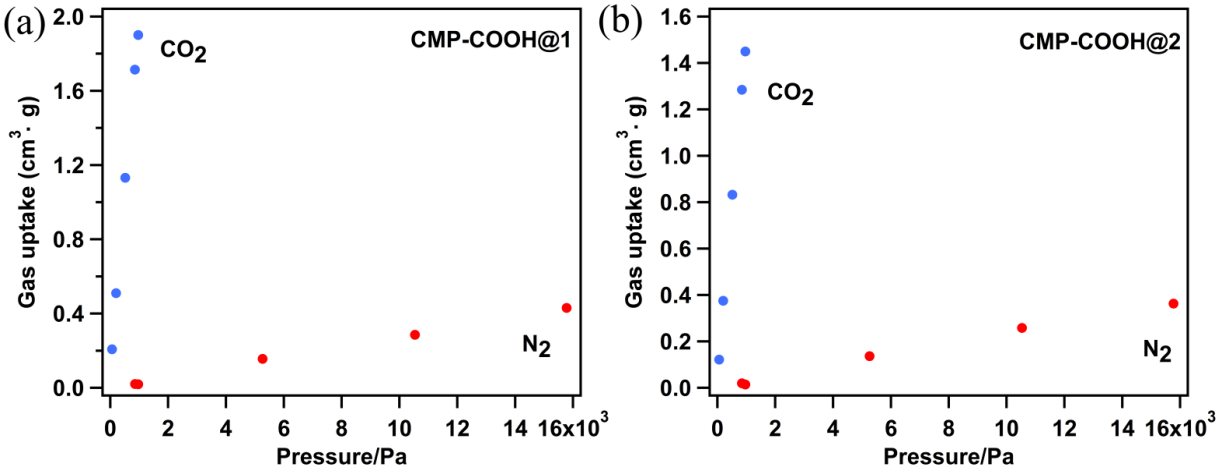


Fig.S9 CO_2/N_2 initial slope selectivity studies for CMP-COOH@1 (a) and CMP-COOH@2 (b) at 273 K.

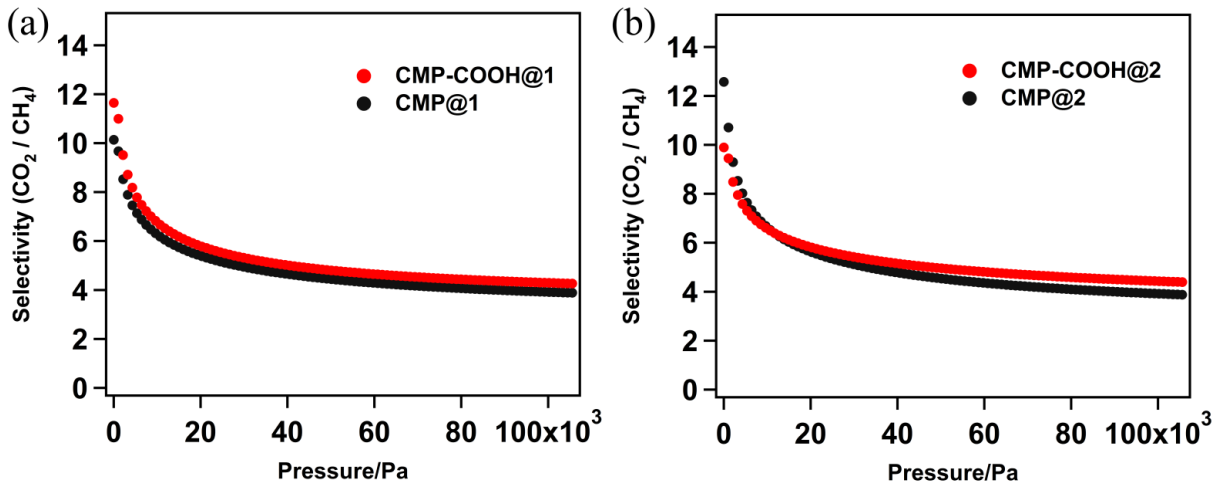


Fig.S10 (a) CO_2/CH_4 selectivity of CMP-COOH@1 and CMP@1 for a molar ratio of 50/50 at 273 K, (b) CO_2/CH_4 selectivity of CMP-COOH@2 and CMP@2 for a molar ratio of 50/50 at 273 K.

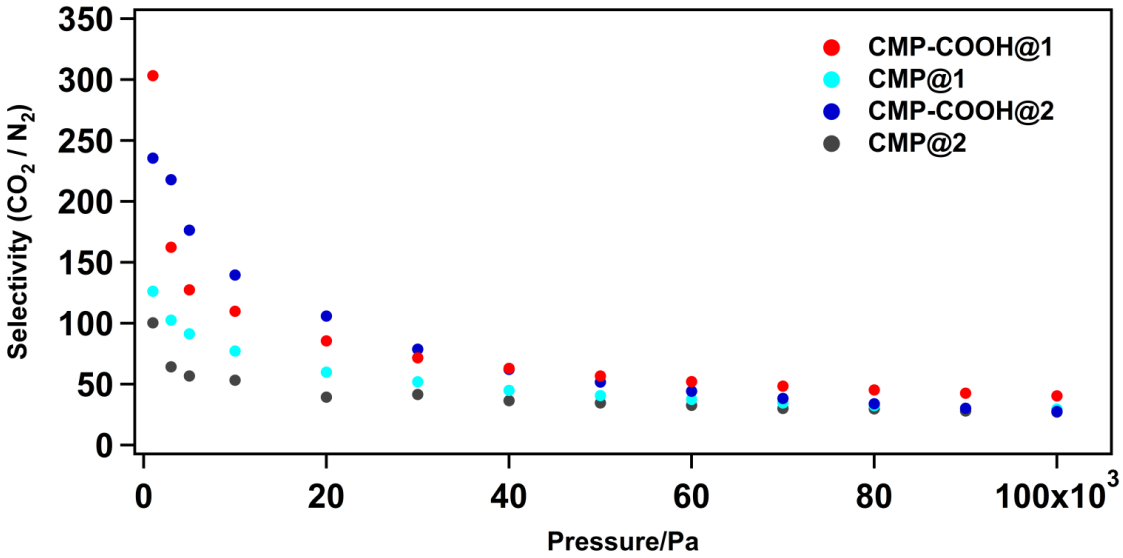


Fig.S11 (a) CO_2/N_2 selectivities of carboxylic polymers for a molar ratio of 15/85 at 273 K.

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

Polymers	S_{BET} (m^2/g)[a)]	S_{Micro} (m^2/g)[b)]	S_{Micro} / S_{BET} (%)	V_{Total} (cm^3/g)[c)]	V_{Micro} (cm^3/g)[d)]	V_{Micro}/ V_{Total} (%)	CO_2 uptake (mmol/g)[e)]	Selectivity[f)] CO_2/N_2	Selectivity[f)] CO_2/CH_4
CMP-COOH@1	835	424	50.8%	0.77	0.49	63.6%	2.17	45.4	5.5
CMP@1	979	531	54.2%	0.55	0.41	74.5%	1.66	32.1	4.7
CMP-COOH@2	765	400	52.3%	0.83	0.58	69.9%	2.63	37.8	5.2
CMP@2	876	523	59.8%	0.59	0.52	88.1%	2.28	30.5	4.1

(a) Specific surface area calculated from the adsorption branch of the nitrogen adsorption−desorption isotherm using the BET method; (b) Micropore surface area calculated from the adsorption branch of the nitrogen adsorption−desorption isotherm using the *t*-plot method; (c) Total pore volume at $p/p_0 = 0.99$; (d) The micropore volume derived from the *t*-plot method; (e) Adsorption capacity were obtained at 1.05 bar and 273 K; (f) Adsorption selectivity based on the IAST method at 273 K and 1.05 bar.

Section J. Supporting references

(1) Li, P. Z.; Wang, X. J.; Liu, J.; Lim, J. S.; Zou, R.; Zhao, Y. *J. Am. Chem. Soc*. **2016,** *138*, 2142.