

Supporting Information

Facile synthesis of tetraphenylethene-based conjugated microporous polymers as absorbents for CO₂ and organic vapor uptake

Chang Xu,^a Yiang Zhu,^b Chan Yao,^a Wei Xie,^a Guangjuan Xu,^a Shuran Zhang,^a Yanning Zhao ^{a*}
and Yanhong Xu^{a,c*}

^aKey Laboratory of Preparation and Applications of Environmental Friendly Materials, Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education (Jilin Normal University), Ministry of Education, Changchun, 130103, China.

Email: ynzhaos27@163.com; xuyh198@163.com

^bSchool of Environmental Studies, China University of Geosciences, Lumo Road 388, Wuhan, Hubei Province, China.

^cSchool of School of Chemistry and Environmental Engineering, the Collaborative Innovation Center of Optical Materials and Chemistry, Changchun University of Science and Technology, Changchun, 130022, China.

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Section A. Materials and methods

Pyromellitic dianhydride (PMDA) and 1,3,5-Trimethylbenzene was purchased from Aladdin. 3,3',4,4'-biphenyltetracarboxylic dianhydride (BTDA), 1-Methyl-2-pyrrolidinone (NMP) and isoquinoline was purchased from Macklin. 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) was purchased from Energy Chemical.

Fourier transform Infrared (FT-IR) spectra were recorded on a Perkin-elmer model FT-IR-frontier infrared spectrometer. 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 for SEM by drop-casting a tetrahydrofuran 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 $2\theta = 1.5^\circ$ up to 60° with 0.02° increment. 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. The solid UV-visible analyzer was used for shimadzu UV-3600. For the UV test, the blank sample test is first carried out with the solid barium sulfate powder as the background, and then the holder with solid samples of CMPs was mounted onto the window of the integration sphere.

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. The Saito-Foley (SF) method was applied for the estimation of pore size and pore size distribution.

Section B. Synthetic procedures

Synthesis of TPE-NH₂

TPE-NH₂ was synthesized according to a previously published procedure^{S1}. 1,1,2,2-Tetraphenylethane (3 g, 9 mmol) was added in small portions to a mixture of acetic acid (30 mL) and fuming nitric acid (30 mL) that was precooled by ice bath. Then the ice bath was removed and the reaction mixture was stirred at room temperature for 3 h. The light-yellow precipitation was obtained by pouring the mixture into ice water (300 g). After filtration and recrystallization from 1,4-dioxane, light yellow crystals were obtained as 1,1,2,2-tetrakis(4-nitrophenyl)ethane in 50% yield. Raney nickel (2 g) and hydrazine monohydrate (670 mg, 13.4 mmol) were added carefully to the solution of THF (10 mL) containing 1,1,2,2-tetrakis(4-nitrophenyl)ethane (525 mg, 1 mmol). Subsequently, the reaction mixture was heated to reflux for 2 h. After cooling, the nickel was filtered off and the filtrate was evaporated under reduced pressure to obtain a light-yellow solid in 68% yield. ¹H NMR (400 MHz, DMSO) δ (ppm): 7.17 (d, 8H), 6.46 (d, 8H), 4.0 (s, 8H).

Synthesis of CMP@1

A Pyrex tube was charged with PMDA (21.8 mg, 0.1 mmol) and TPE-NH₂ (19.6 mg, 0.05 mmol) in a mixed solution of NMP (0.2 mL), mesitylene (1.0 mL), and isoquinoline (0.02 mL). The tube was snap frozen at 77 K (LN₂ bath) and evacuated to vacuum, then the tube was sealed with a flame. The reaction mixture was heated at 160 °C for 5 days to afford a yellow precipitate which was isolated by filtration over a medium glass frit and washed with anhydrous tetrahydrofuran (THF, 20.0 mL). The product was immersed in anhydrous THF (20.0 mL) for 8 h, during which the activation solvent was decanted and freshly replenished four times. The solvent was removed under vacuum at 85 °C to afford CMP@1 as a yellow powder (35.6 mg, 86%).

Synthesis of CMP@2-3

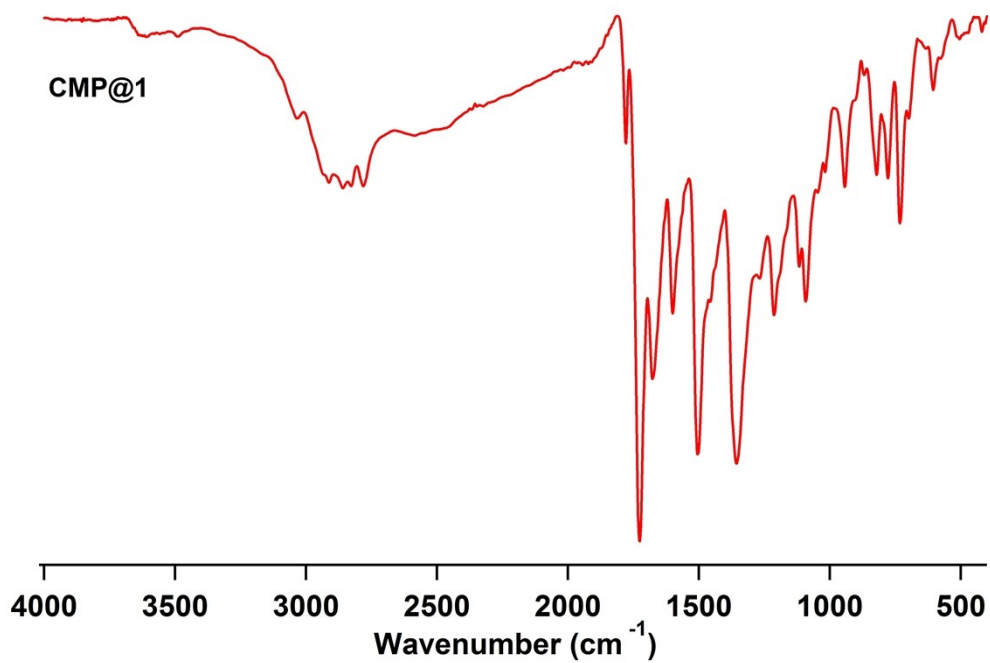
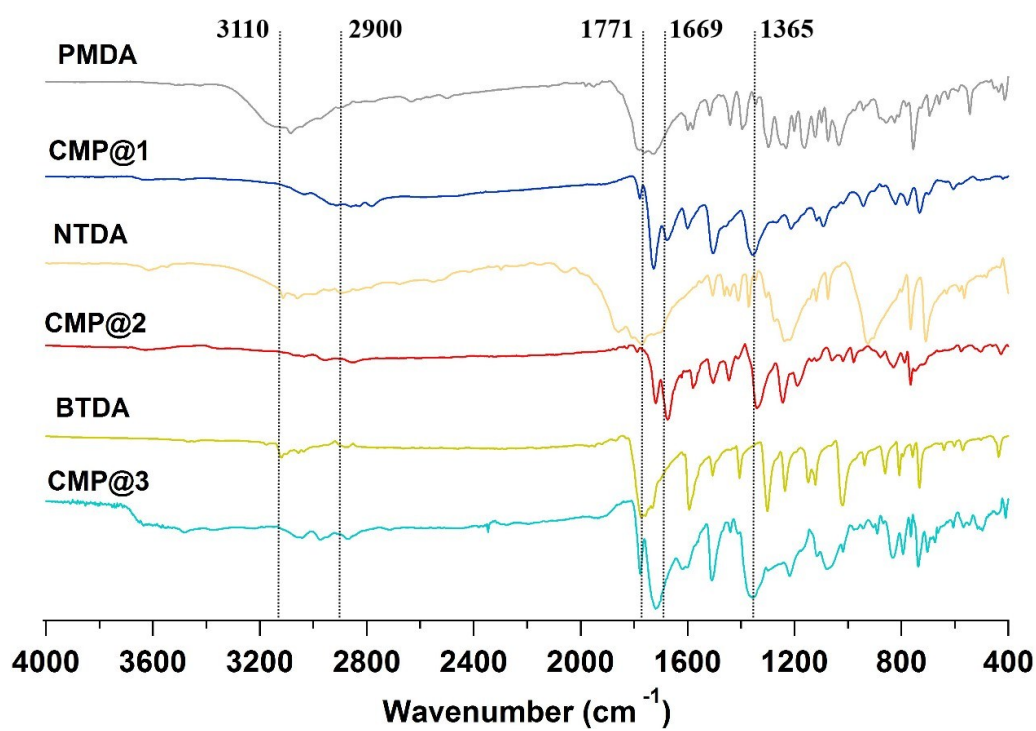
Similar synthetic procedure to CMP@1, NTDA (26.8 mg, 0.1 mmol) and BTDA (29.4 mg, 0.1 mmol) were used instead of PMDA to synthesize CMP@2 and CMP@3, resulting in a CMP@2 of brown powder (39.4 mg, 85 %), CMP@3 of yellow powder (39.7 mg, 81 %).

Section C. Elemental analysis

Table S1. Elemental analysis data of the CMP@1, 2 and 3.

NO.	C	H	N
CMP@1	65.26	3.87	7.39
CMP@2	73.89	4.03	6.55
CMP@3	70.23	6.25	7.84

Section D. FT-IR spectra



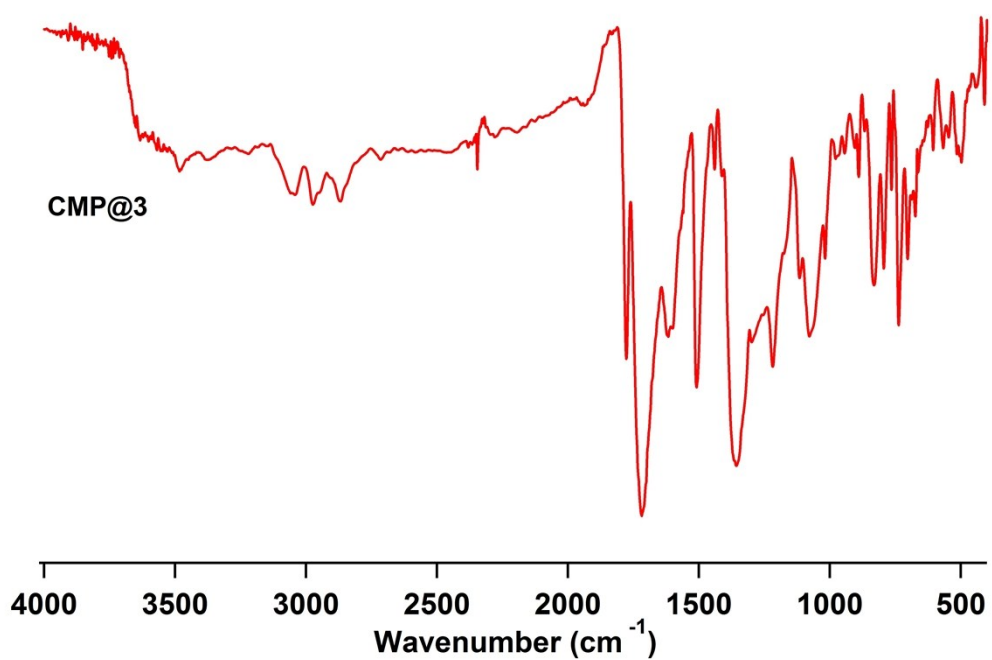
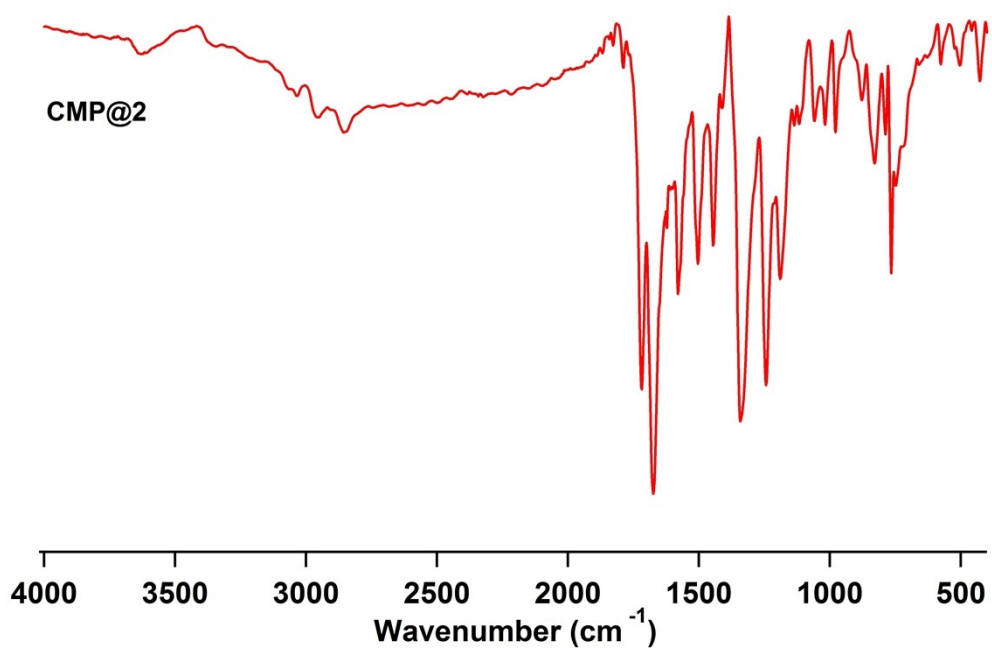


Fig. S1 FT-IR spectra of PMDA, NTDA, BTDA and CMP@1-3.

Section E. Powder X-ray diffraction patterns

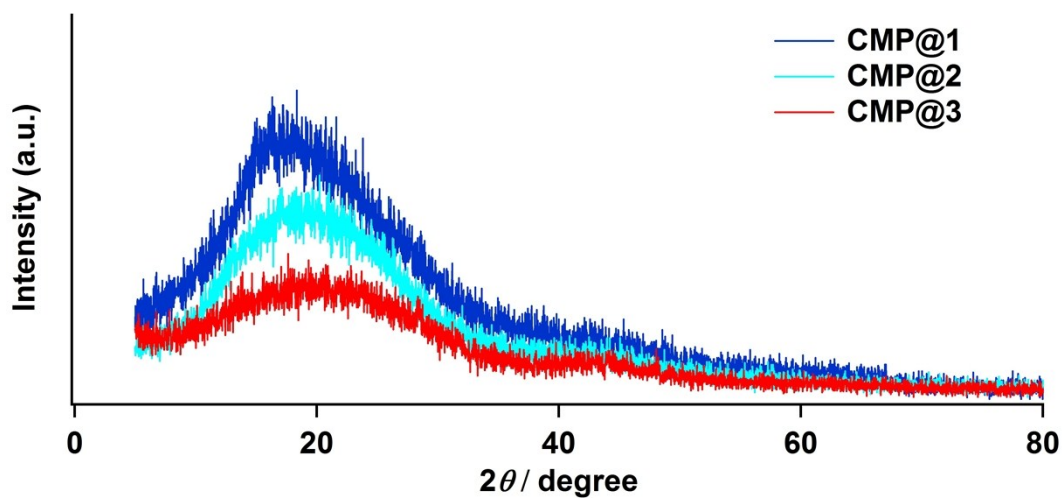


Fig. S2 Powder X-ray diffraction profiles of CMP@1-3.

Section F. TGA curves

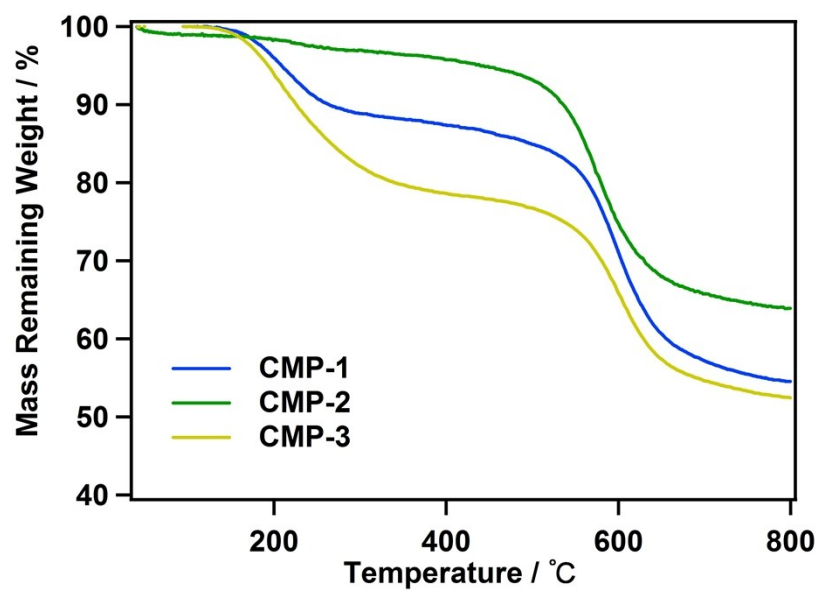


Fig. S3 TGA curves of CMP@1-3.

Section G. TEM images

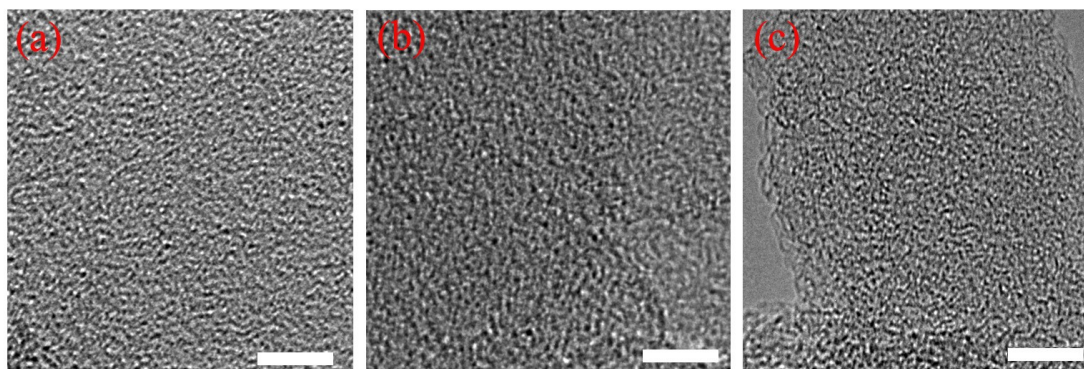


Fig. S4 TEM images of (a) CMP@1, (b) CMP@-2, and (c) CMP-3 (5 nm width).

Section H. The Solid-UV spectra

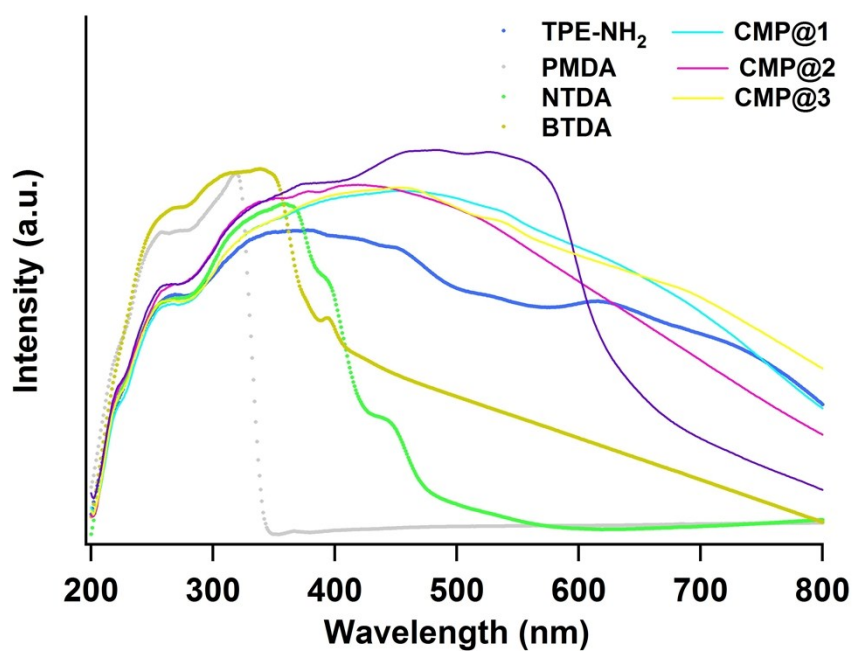


Fig. S5 The UV spectra of CMP@1-3 in solid state.

Section I. Summary of adsorption capacities of different porous adsorbents for CO₂.^{S2-S7}

Table S2. Comparison of CO₂ adsorption capacities of CMP@1, 2 and 3 and some reported adsorbents.

Polymers	S _{BET} (m ² g ⁻¹)	CO ₂ uptake (mmol/g)	Ref.
CMP@1	346	1.55 ^a	This work
CMP@2	325	1.44 ^a	This work
CMP@3	343	2.26 ^a	This work
PAF-1	5600	2.05 ^b	S2
PAF-3	2932	3.48 ^b	S2
PAF-4	2246	2.41 ^b	S2
PAF-19	250	0.90 ^a	S3
PAF-20	702	1.16 ^a	S3
CMP-1	837	2.05 ^a	S4
CMP-1-(OH) ₂	1043	1.80 ^a	S4
CMP-1-(CH ₃) ₂	899	1.64 ^a	S4
CMP-1-NH ₂	710	1.64 ^a	S4
CMP-1-COOH	522	1.60 ^a	S4
BPL carbon	1250	2.09 ^a	S5
HCP-1	1646	3.01 ^a	S6
HCP-2	1684	3.30 ^a	S6
HCP-3	1531	3.24 ^a	S6
HCP-4	1642	3.92 ^a	S6
MOP A	4077	2.65 ^a	S7
MOP B	1847	3.29 ^a	S7
MOP C	1237	3.86 ^a	S7
MOP D	1213	2.42 ^a	S7
MOP E	1470	2.95 ^a	S7
MOP F	653	1.80 ^a	S7
MOP G	1056	2.15 ^a	S7

^aAt 273 K and 1 bar. ^bAt 273 K and 1 atm.

Section J. Selectivity analyses

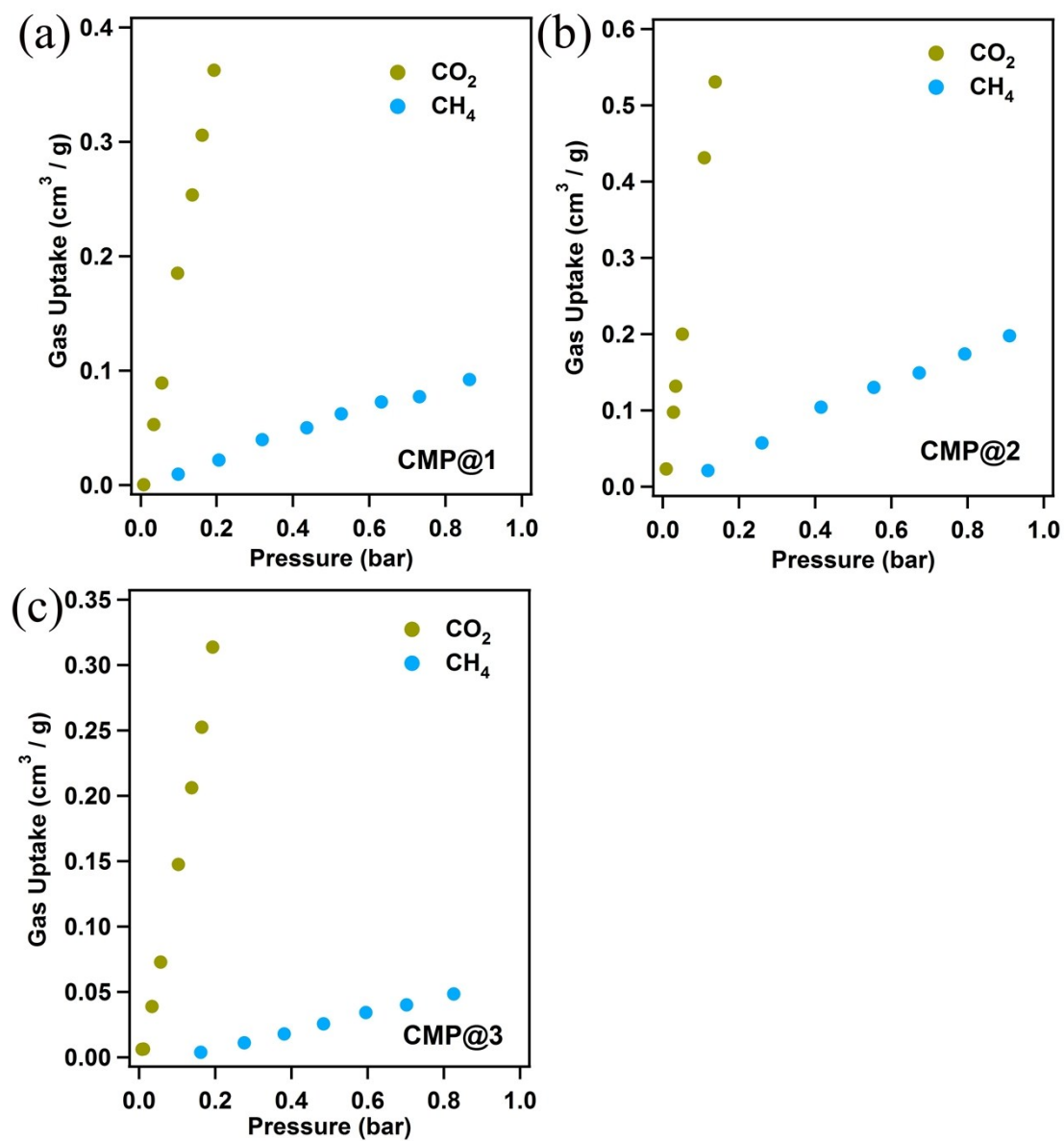


Fig. S6. CO₂/CH₄ initial slope selectivity studies for CMP@1-3 at 273 K and 1.05 bar.

Calculations of adsorption selectivity

Adsorption selectivities can be calculated by a virial fitting method based on the following equation:

$$\ln N / P = A_0 + A_1N + A_2N^2 + A_3N^3 + \dots \quad \text{eq. 1}$$

In eq. 1, P is pressure, N is amount adsorbed and A_0 , A_1 etc. present virial coefficients. A_0 is related to adsorbate–adsorbent interactions, and A_1 describes adsorbate–adsorbate interactions. The Henry’s Law constant (K_H) is equal to $\exp(A_0)$.

The Henry’s Law selectivity for gas component i over j is calculated based on eq. 2:^{S8}

$$S_{ij} = K_{Hi} / K_{Hj} \quad \text{eq. 2}$$

Section K. References

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