

Supporting Information

Facile synthesis of conjugated microporous polymer-based porphyrin units for adsorption of CO₂ and organic vapors

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Section A. Materials and methods

Pyrene, tetraphenylethylene, pyrrole, iron trichloride, 4-formylphenylboronic acid and tetrakis(triphenylphosphine)palladium(0) were purchased from Alfa. Potassium carbonate was purchased from Energy chemical. All solvents used were purchased from Aladdin.

^1H NMR spectra were recorded on Bruker AvanceIII models HD 400NMR spectrometers, where chemical shifts (δ 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 model FT-IR-frontier infrared spectrometer. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, and then compressed, and the pressed product can be directly tested. The solution UV-visible analyzer was used for shimadzuUV-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. 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. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xi electron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). 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. 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.

Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer, while benzene, toluene, cyclohexane, and water vapors sorption isotherms were collected at 25°C from an intelligent gravimetric analyzer (IGA) (HidenS-3Isochema, UK).

Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The non-local density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution.

Carbon dioxide, methane and nitrogen sorption isotherms were measured at 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.

Section B. Synthetic procedures

Synthesis of 1,3,6,8-Tetrabromopyrene (TBrPy)^{S1}

Bromine (3.50 g, 0.022 mol) was added dropwise, with vigorous stirring, to a solution of pyrene (1.0 g, 0.005 mol) in nitrobenzene (20 mL) at 120 °C. The mixture was kept at 120 °C for 4 h and then cooled to room temperature to yield a pale-green precipitate. This was filtered, washed with ethanol (15 mL), and dried under vacuum. The solid product (2.41 g, 94 %) was insoluble in all the common organic solvents.

Synthesis of 1,3,6,8-Tetrakis(p-formylphenyl)pyrene (TFPPy)^{S2}

1,3,6,8-tetrabromopyrene (1.00 g, 1.93 mmol), 4-formylphenylboronic acid (1.74 g, 11.6 mmol), palladium tetrakis(triphenylphosphine) (0.12 g, 0.10 mmol), and potassium carbonate (2.1 g, 15 mmol) were put into a 100 mL round-bottom flask; then the flask exchanged 3 cycles under vacuum/N₂, anhydrous tetrahydrofuran (30 mL) was added via a syringe under the N₂. The reaction mixture was brought to reflux at 80 °C for 3 days. After cooling to room temperature, the solid was collected by filtration, and washed with 3M HCl (20 mL), water and acetone three times. The obtained solid was dried to afford TFPPy as a bright yellow powder (1.05 g, 90%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 10.17 (s, 4H), 8.18 (s, 4H), 8.09 (d, 8H), 8.05 (s, 2H), 7.86 (d, 8H).

Synthesis of *p*-Tetrabromotetraphenylethene (TBTPE)^{S3}

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 SiO₂ (hexanes/CH₂Cl₂, 20:1 in vol.) gives TBTPE as a colorless solid (5.94 g) in 61% yield. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.26 (d, 8H), 6.85 (d, 8H).

Synthesis of 1,1,2,2-tetrakis(4-formyl-(1,1'-biphenyl))ethene(TFBPE)^{S4}

Tetrakis(4-bromophenyl)ethylene (684 mg, 1 mmol) and 4-formylphenylboronic acid (900 mg, 6 mmol) was dissolved in toluene (80 mL), and then an aqueous solution of K₂CO₃ (1.66 g, 12 mmol) in water (15 mL) and tetrabutyl ammonium chloride (1 mL) were added. Then Pd(PPh₃)₄ catalyst (10 mg) was added and the reaction mixture was stirred at 85 °C for 1 d. After cooling to room temperature, the reaction mixture was mixed with water and the organic layer was precipitated by CH₃OH to get crude product. Recrystallization with CHCl₃ and diethyl ether to obtain yellowish green solid (535 mg, 71%). ¹H NMR (DMSO-d₆ 400 Hz): δ (ppm) 10.03 (s, 4H), 7.96 (d, 8H), 7.90 (d, 8H), 7.69 (d, 8H), 7.24 (d, 8H).

Synthesis of Porp-Py-CMP

In a typical experimental procedure, a flame dried round bottom flask was charged with freshly distilled pyrrole (0.048 g, 0.72 mmol) and 1,3,6,8-Tetrakis(*p*-formylphenyl)pyrene (0.1 g, 0.16 mmol). Then 15 mL glacial acetic acid was taken in the flask with constant stirring along with ferric chloride (0.6 equivalent) under inert nitrogen atmosphere. The whole solution was stirred in a magnetic stirrer with stirring rate of 300 rpm to make the whole solution homogenized. After 6 h the mixture was transferred to a Teflon lined autoclave and kept under hydrothermal treatment for 72 h at 180 °C. The complete condensation takes

place after 3 days and the oven was slowly cooled to room temperature, resulting a dark brownish product which separates out from the mixture. The precipitated solid was filtered and thoroughly washed with distilled water methanol, acetone, THF, dichloromethane and then vacuum dried in an oven at 80 °C for another 48 h. The material was then rigorously washed by Soxhlet extractions for 24 h with water, dichloromethane, methanol, and tetrahydrofuran (THF), respectively, to give 0.13 g **Porp-Py-CMP** yield 88 % based on **TFPPy** and pyrrole. Found by EDX analysis (wt%) C, 91.65 %; N, 8.28 %; Fe, 0.06 %. Calcd. theoretical formula for an infinite **Porp-Py-CMP**: $\{C_{60}H_{32}N_4\}_n$ with C, 89.1 %; H, 4.0 %; N, 6.9 %.

Synthesis of Porp-TPE-CMP

Similar method was used for the preparation of **Porp-Py-CMP**, Pyrrole (0.04 g, 0.60 mmol), 1,1,2,2-tetrakis(4-formyl-(1,1'-biphenyl))ethene (0.1 g, 0.13 mmol) and 0.6 equivalent ferric chloride were hydrothermally reacted in 15 mL glac. acetic acid for 72 h at 180 °C to afford 0.11 g **Porp-TPE-CMP**, yield 79 % based on **TFBPE** and pyrrole. Found by EDX analysis (wt%) C, 90.85 %; N, 9.13 %; Fe, 0.02 %. Calcd. Theoretical formula for an infinite **Porp-TPE-CMP**: $\{C_{70}H_{42}N_4\}_n$ with C, 89.5 %; H, 4.5 %; N, 6.0 %.

Section C. FT-IR spectra

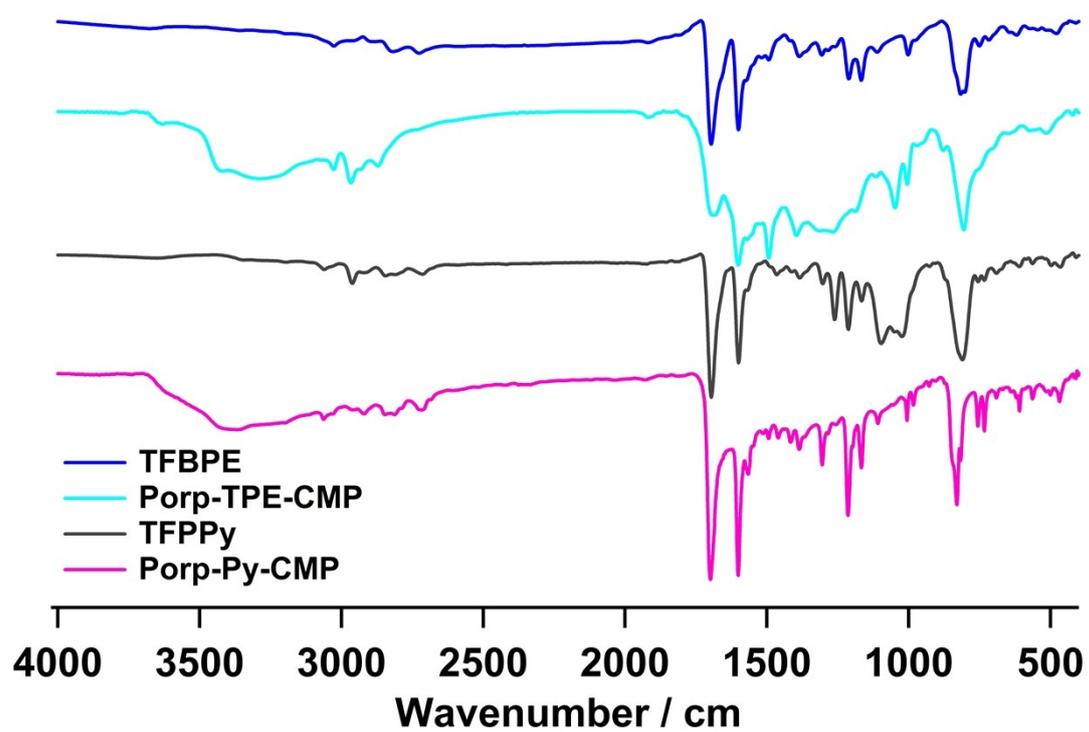


Fig. S1 FT-IR spectra of TFBPE, Porp-TPE-CMP, TFPPy and Porp-Py-CMP.

Section D. The solid-state ^{13}C NMR spectra

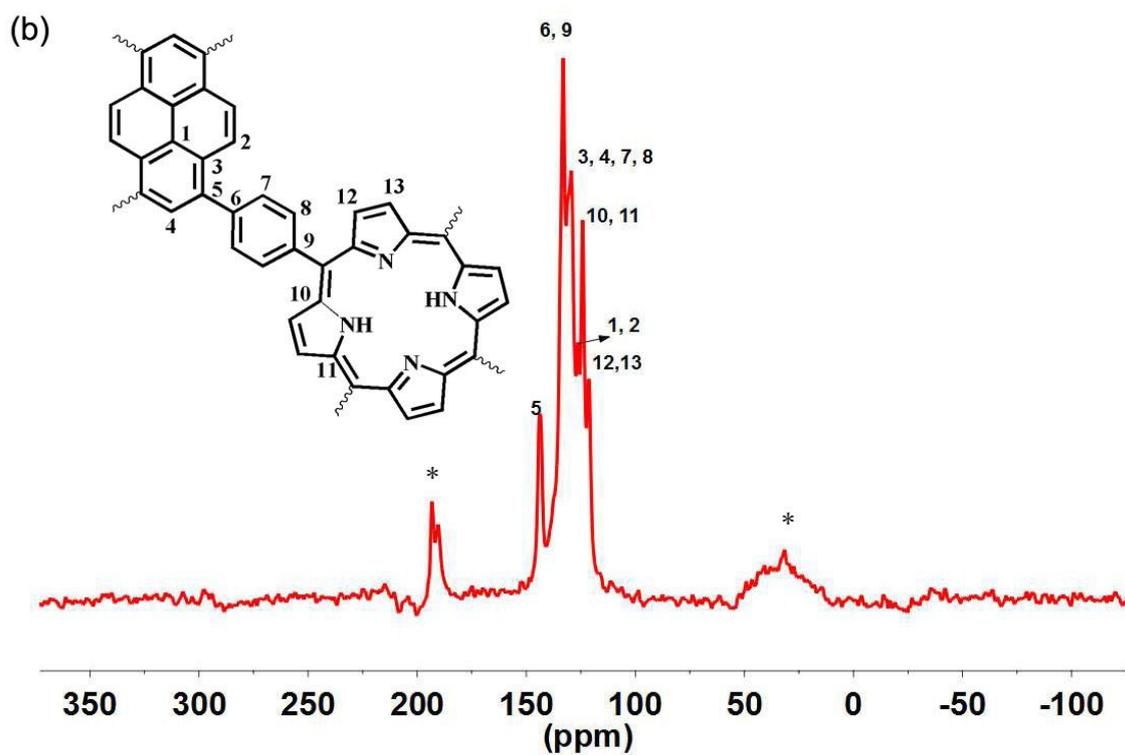
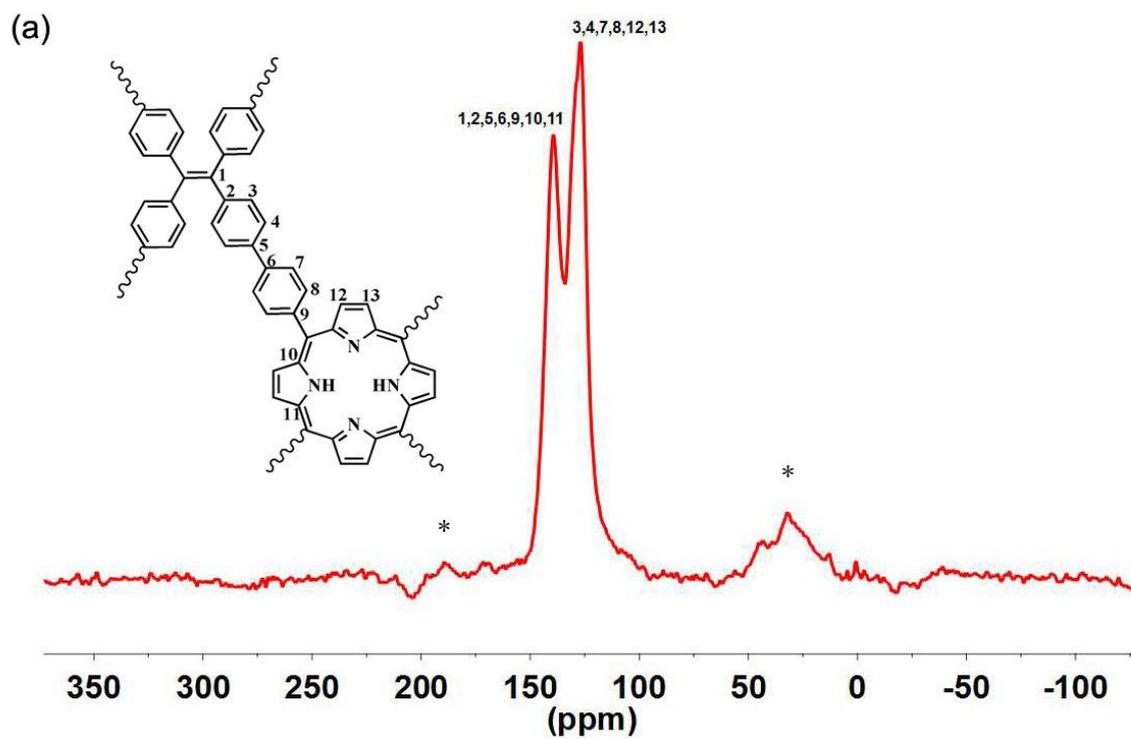


Fig. S2 The solid-state ^{13}C CP-MAS NMR of (a) Porp-TPE-CMP, (b) Porp-Py-CMP. Signals with * symbols are side peaks.

Section E. The Solid-UV spectra

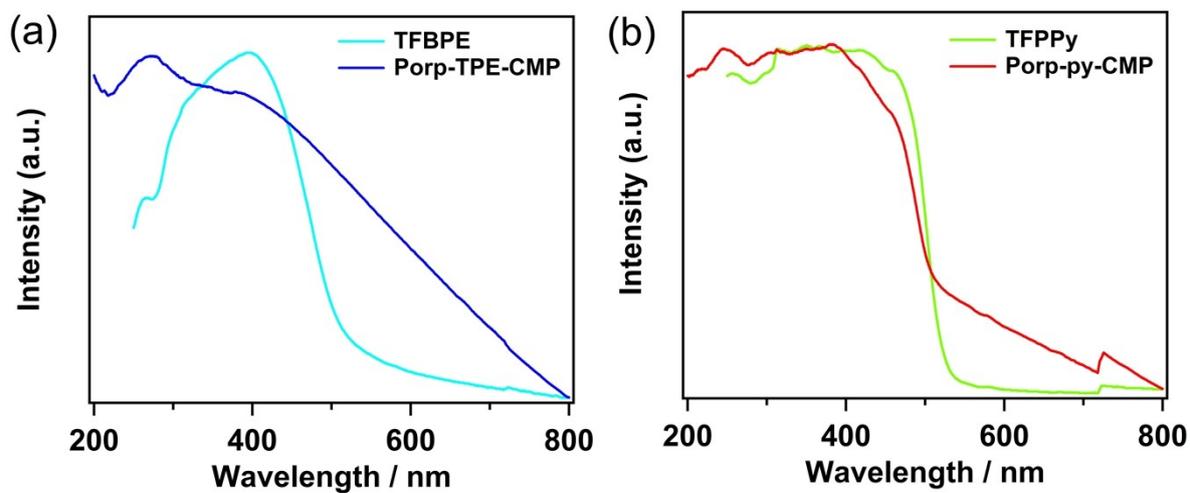


Fig.S3 Solid state UV spectra of (a) TFBPE and Porp-TPE-CMP; (b) TFPPy and Porp-Py-CMP.

Section F. TGA curves

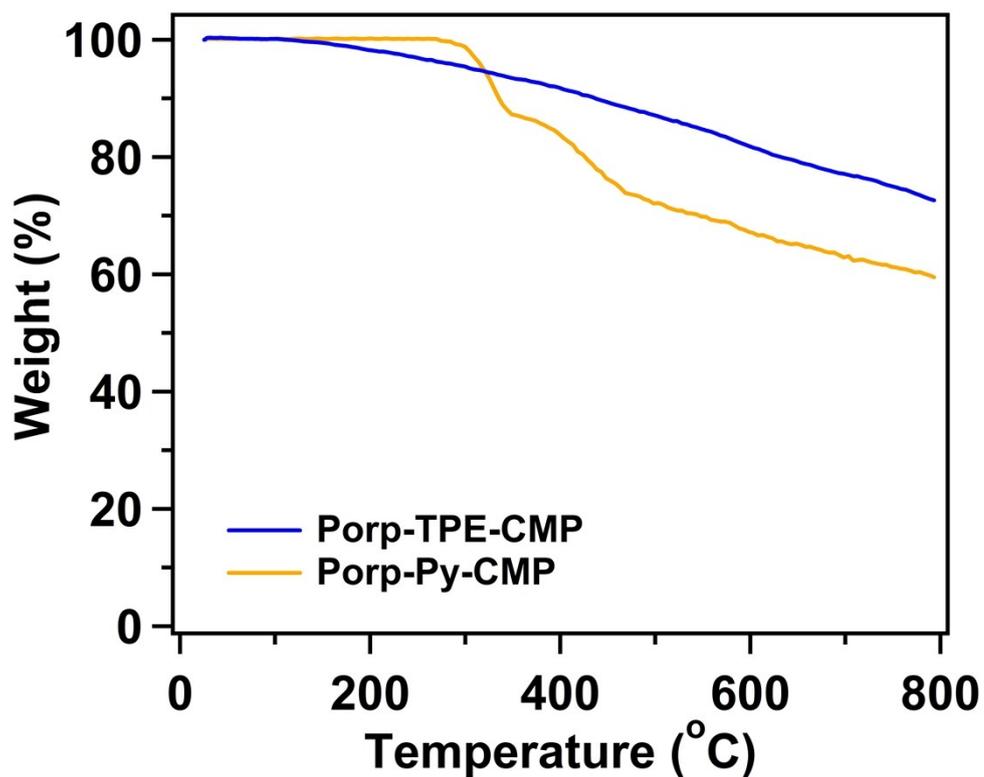


Fig. S4 TGA curves of Porp-TPE-CMP and Porp-Py-CMP.

Section G. Powder X-ray diffraction patterns

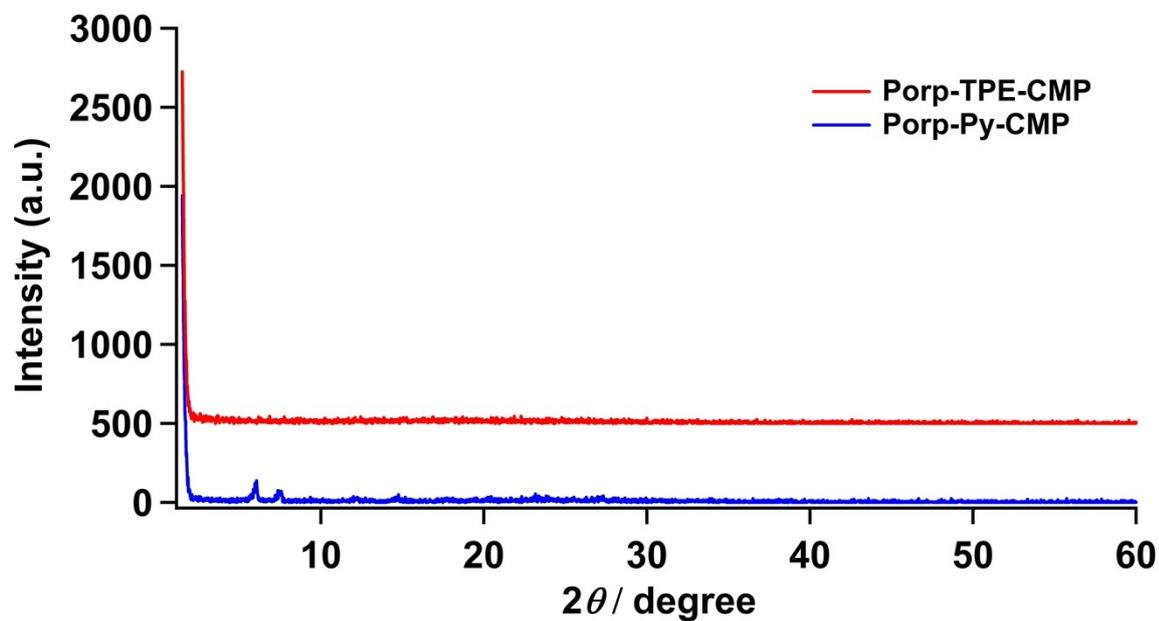


Fig. S5 Powder X-ray diffraction profiles of Porp-TPE-CMP and Porp-Py-CMP.

Section H. TEM images

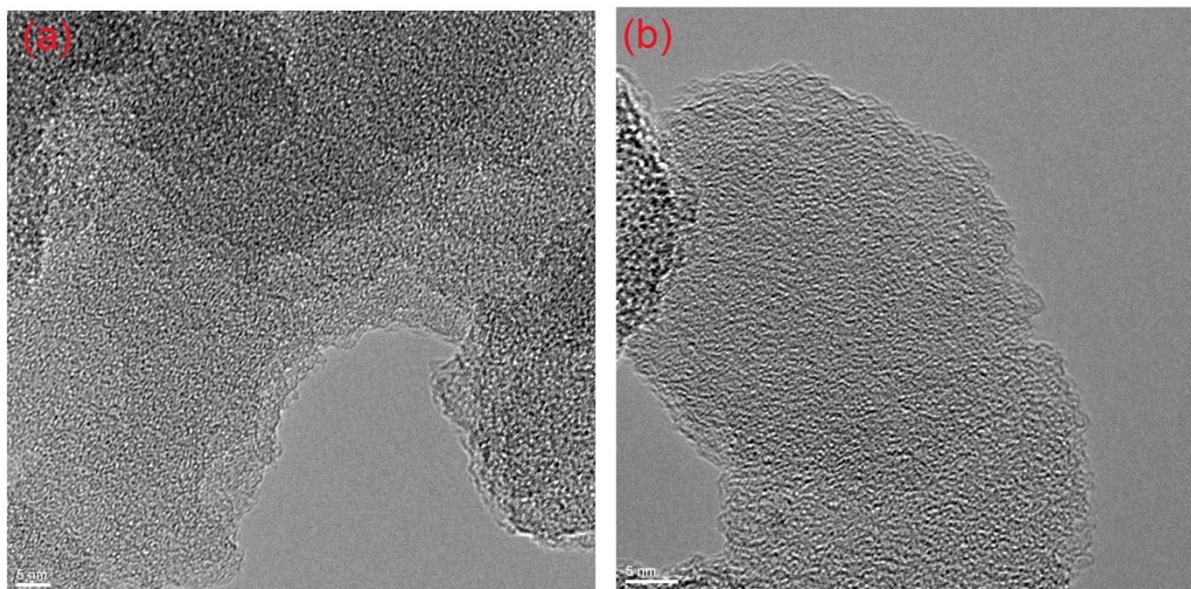


Fig. S6 TEM images of Porp-TPE-CMP and Porp-Py-CMP.

Section I. XPS spectrum

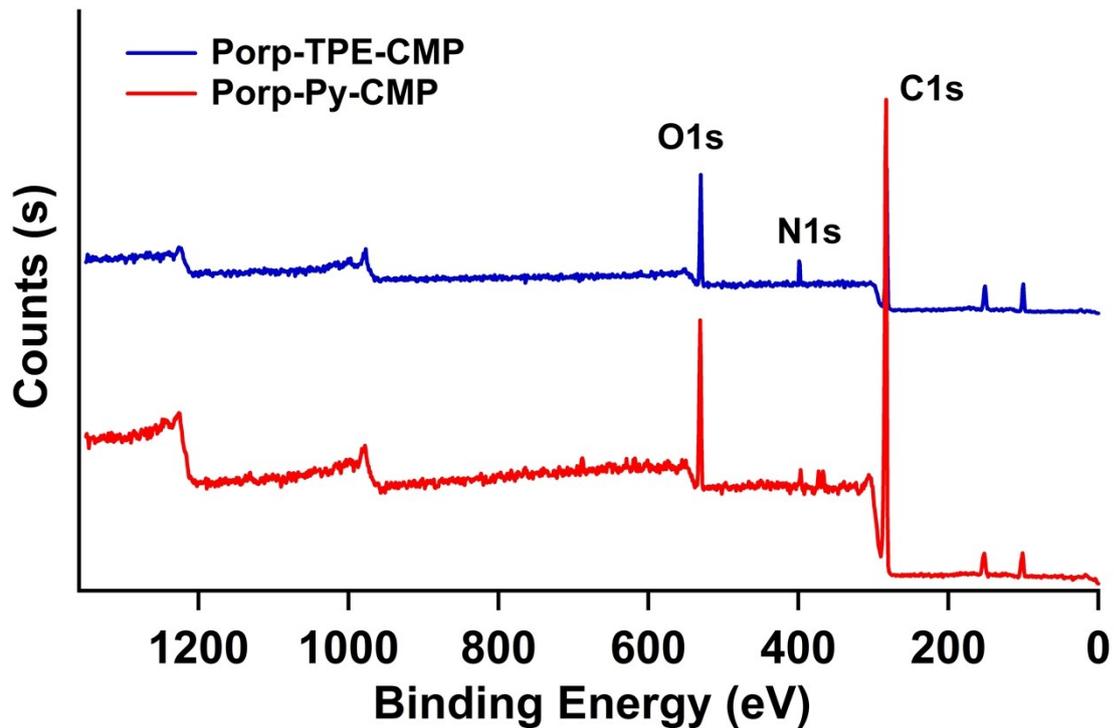


Fig. S7 XPS spectrum of Porp-TPE-CMP and Porp-Py-CMP.

Section J. CO₂, CH₄ and N₂ adsorption isotherms

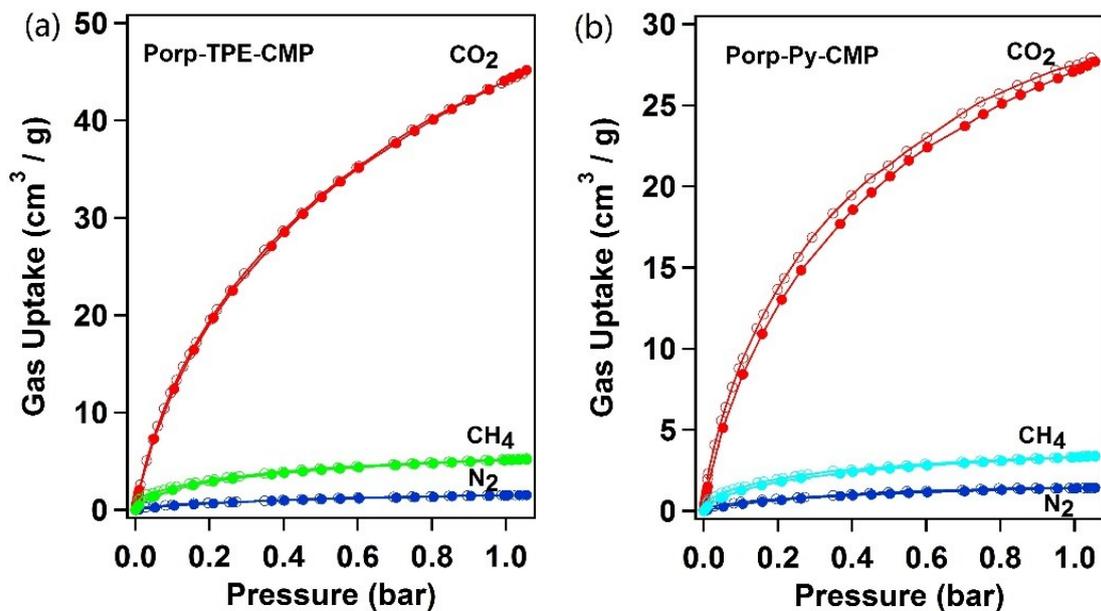


Fig. S8 CO₂, CH₄ and N₂ adsorption isotherms of (c) Porp-TPE-CMP and (d) Porp-Py-CMP

collected at 273 K and 1.05 bar.

Section K. Summary of Adsorption Capacities of Different Porous Adsorbents for Selected VOCs.^{S5-S12}

Table S1. Comparison of benzene, toluene, and cyclohexane capacities of Porp-TPE-CMP and Porp-Py-CMP and some reported adsorbents.

Polymers	P/P_0	Q_{benzene} mg g ⁻¹	Q_{toluene} mg g ⁻¹	$Q_{\text{cyclohexane}}$ mg g ⁻¹	S_{BET} m ² g ⁻¹	pore volume cm ³ g ⁻¹	Refs.
Porp-TPE-CMP	0.99	153	210	133	547	0.41	This work
Porp-Py-CMP	0.99	55	188	190	31	0.15	This work
PAN-1		726		527	925	0.77	S5
PAN-2		692		383	1242	1.15	S5
PAN-F	0.9	544		433	702	0.89	S6
PAN-T		570		518	795	0.73	S6
PSN-DA	0.9	861		779	1045	0.86	S7
PSN-TAPB		514		385	959	0.62	S7
PSN-TAPA		468		408	658	0.56	S7
PSN-TAPM		526		306	1312	0.88	S7
CE-1	0.9	585		357	960	0.97	S8
CE-2		351		298	588	0.47	S8
CE-3		344		249	540	0.43	S8
CMP-50	1.0	520			880	0.63	S9
AC	0.9		710			1.23	S9
Commercial AC	1.0	260			704	0.45	S10
AC	1.0	730				0.83	S11
F65C	0.9	310	530		1826		S12

S_{BET} is the specific surface area calculated using the BET method, Q is the reported adsorbed data of VOCs.

Section L. Selectivity analyses

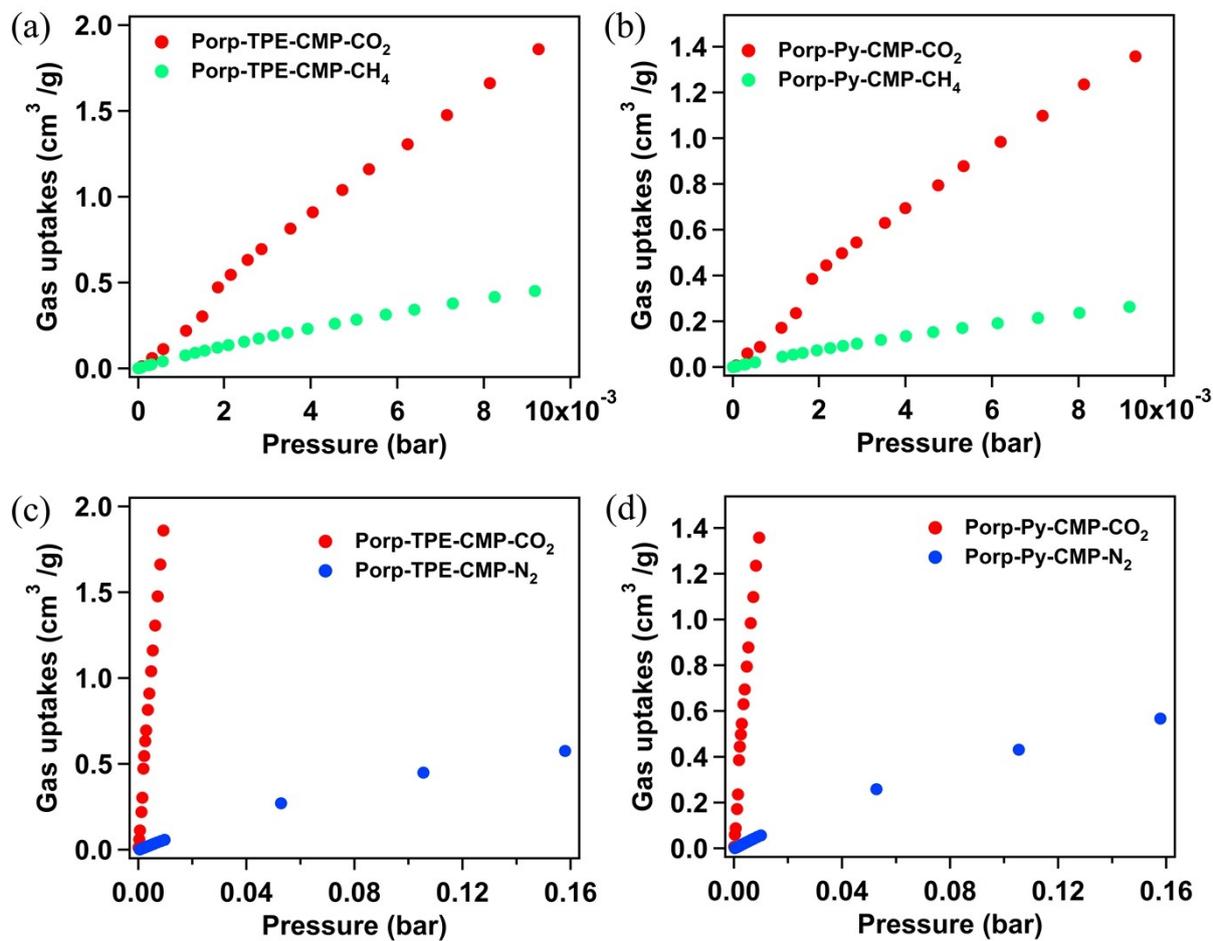


Fig. S9 (a) and (b) CO₂/CH₄ initial slope selectivity studies for Porp-TPE-CMP and Porp-Py-CMP at 273 K; (c) and (d) CO₂/N₂ initial slope selectivity studies for Porp-TPE-CMP and Porp-Py-CMP at 273 K. (Selectivity was calculated by Henry law at 273 K.)

Calculations of adsorption selectivity

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

$$\ln N / P = A_0 + A_1 N + A_2 N^2 + A_3 N^3 + \dots \quad \text{eq. 1}$$

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:^{S13}

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

Section M. Supporting references

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