Electronic Supplementary Information (ESI)

Facile One-Pot Preparation of Porphyrin-based Microporous Organic Polymers for Adsorption of Carbon Dioxide, Ethane, and Methane

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Experimental Section

Materials

Pyrrole (98%), anhydrous dichloromethane (DCM), anhydrous tetrahydrofuran (THF), anhydrous N, N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), o-dichlorobenzen (o-DCB), propionic acid (99%), and all of the other chemicals were purchased from J&K Chemical Co., Ltd. Purification of the pyrrole was completed using reduced pressure distillation, and the other reagents were used exactly as received. The tri(4-formylphenyl)phosphine (TFPP)[43] and tetrakis(4-formylphenyl)silane (TFPSi)[21] were synthesized using the same method as previously reported.

Preparation of the PMOPs

PMOP-P was synthesized using the facile one-pot condensation method according to the following procedure: Under nitrogen flow, freshly distilled pyrrole (1.5 mmol, 0.10 g), tri(4-formylphenyl)phosphine (0.5 mmol, 0.17 g), and 27.0 ml propionic acid were added to a dry 100 ml Schlenk flask. The mixture was then refluxed and stirred for 24 hours. We collected the solid by vacuum filtration, then washed it with DMSO, DMF, and DCM. Eventually, the resulting solid was extracted with THF in a Soxhlet apparatus for 36 hours and dried at 120 °C for 48 hours to produce a black powder. The solid was 95%.

PMOP-Si was prepared under the same procedure described above for PMOP-P, using freshly distilled pyrrole (2.4 mmol, 0.16 g), tetrakis(4-formylphenyl)silane (0.6 mmol, 0.27 g), and 43.0 ml propionic acid. After drying, a black powder was collected and denoted as PMOP-Si. Yield: 98%.

Material characterization

The FTIR spectroscopy of the synthesized polymers using a Nicolet 20XB FTIR spectrophotometer in the wavenumber range 400−4000 cm^{-1}. The ^{1}H NMR spectra of the monomer were recorded on a 400 MHz Varian INOVA NMR spectrometer. In contrast, the solid-state ^{13}C NMR spectra of the resultant polymers were recorded on a Bruker AVANCE III HD 600 MHz Ascend Wide-Bore NMR spectrometer in conjunction with the cross-polarization (CP) and total suppression of spinning sidebands (TOSS) techniques. The morphology of the samples was conducted on a SUPRATM 55 field-emission scanning electron microscope (FE-SEM) at acceleration voltages of 1.0 kV. The samples were sputter-coated with gold. Transmission electron microscopy (TEM) images were obtained on a FEI TALOS F200X operated at 200 kV. Elemental analyses (EA) were recorded on the Elementar Vario EL III. The thermogravimetric analysis (TGA) curves were conducted on a NETZSCH TG 209 thermal analyzer by heating the samples (~3 mg) from room temperature to 800°C at a heating rate of 10°C/min under N_2 flow (60 mL/min). The physical adsorptions for CO_2, C_2H_6, CH_4, and N_2 were recorded on an Autosorb iQ2 gas sorption analyzer (Quantachrome Instruments). Before testing, the as-prepared polymers were degassed overnight under a high vacuum at 100°C.

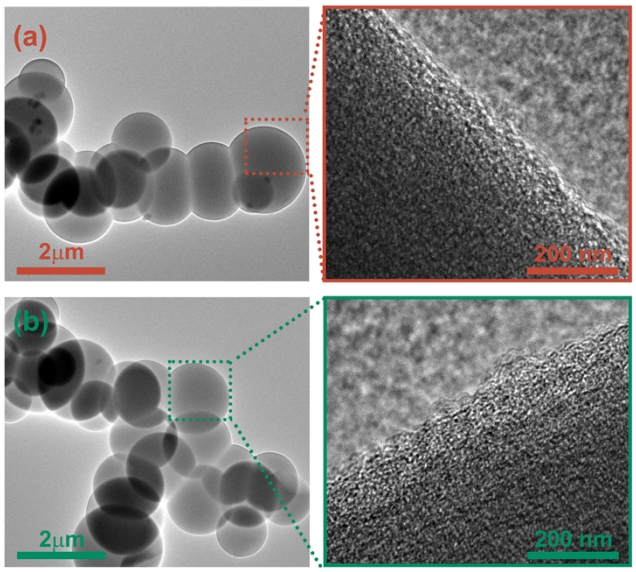

Fig S1. HR-TEM photos of PMOP-P (a) and PMOP-Si (b).

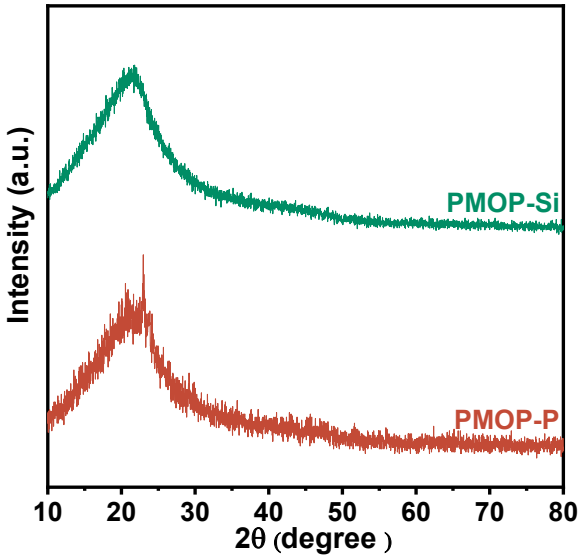

Fig S2. X-ray diffractions of PMOP-P and PMOP-Si.

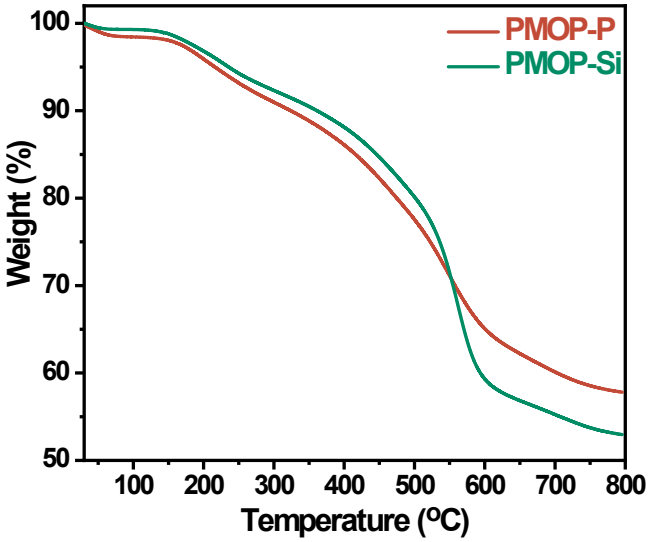

Fig S3. TGA curves of PMOPs.

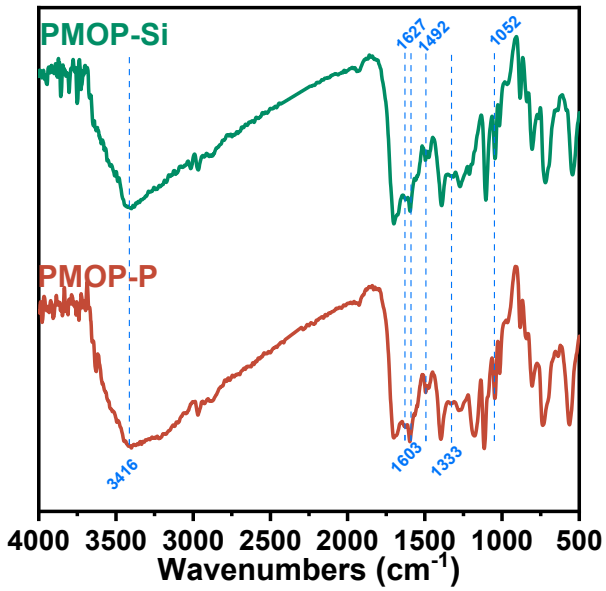

Fig S4. FTIR spectrum of PMOP-P and PMOP-Si.

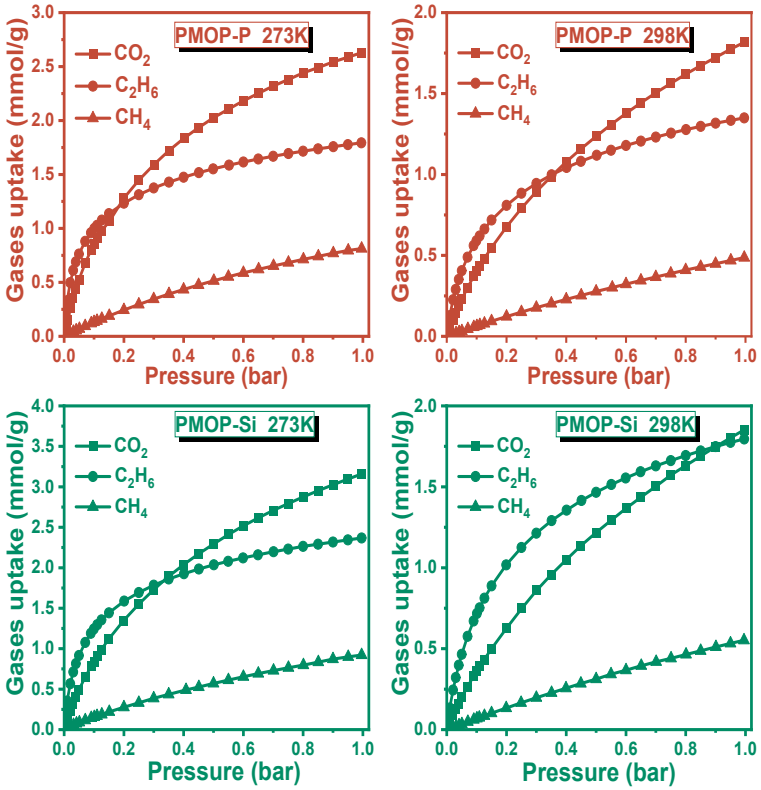

Fig S5. Adsorption isotherms obtained by the PMOP-P and PMOP-Si for CO_2, C_2H_6, and CH_4 at 273 K and 298 K.

Table S1. The chemical composition of porphyrin-based microporous organic polymers (PMOPs)

Sample	Measured value (wt%)			Theoretical value (wt%)		
	EA			C	H	N
	C	H	N			
PMOP-P	66.70	4.72	6.27	80.56	4.61	8.54
PMOP-Si	71.68	4.21	7.22	82.47	4.40	8.74

Table S2. K_H and A_0 value of CH_4, CO_2, and C_2H_6 Adsorption in the porphyrin-based microporous organic polymers

Sample	**Gases**	**T/K**	**Q_0/kJ/mol**	**K_H/mol/(g*Pa)**	**A_0/ln(mol/(g*Pa))**	**R^2**
PMOP-P	**CH_4**	273	23.8	1.565×10^{-8}	-17.973	0.997
		298		6.490×10^{-9}	-18.853	0.999
	CO_2	273	29.7	1.505×10^{-7}	-15.709	0.996
		298		5.021×10^{-8}	-16.807	0.998
	C_2H_6	273	34.2	5.907×10^{-7}	-14.342	0.999
		298		1.670×10^{-7}	-15.605	0.998
PMOP-Si	**CH_4**	273	23.3	1.688×10^{-8}	-17.897	0.994
		298		7.137×10^{-9}	-18.758	0.990
	CO_2	273	29.2	1.240×10^{-7}	-15.903	0.998
		298		4.215×10^{-8}	-16.982	0.998
	C_2H_6	273	33.6	5.286×10^{-7}	-14.453	0.999
		298		1.528×10^{-7}	-15.694	0.999