

**Pyridine-based conjugated microporous polymers as adsorbents for CO₂ uptake
via weak supramolecular interaction**

Yuwei Zhang,^{ab} Chunyu Zhang,^a Wei Shi,^{c*} Zhenwei Zhang,^b Yanning Zhao,^a Xiaolong
Luo,^{d*} and Xiaoming Liu^{b*}

^aLaboratory of Preparation and Applications of Environmental Friendly Materials (Jilin Normal University), Ministry of Education, Changchun, 130103, China.

^bCollege of Chemistry, Jilin University, Changchun, 130012, China.

^cState Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

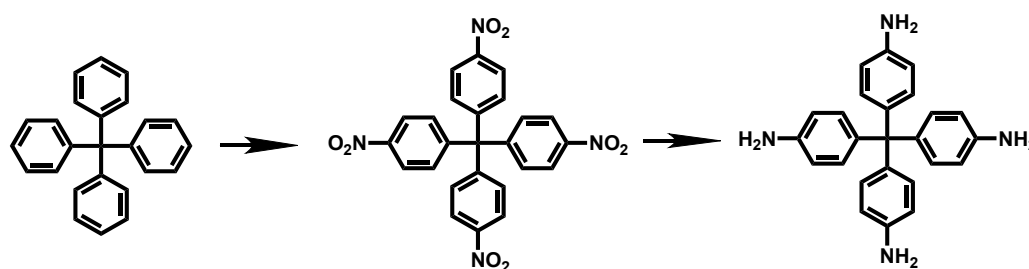
^dAdvanced Institute of Materials Science, School of Chemistry and Biology, Changchun University of Technology, Changchun 130012, China.

Materials and Methods

Methods: The infrared spectra were recorded from 500 to 3500 cm^{-1} on an Avatar FT-IR 360 spectrometer by using KBr pellets. Elemental analyses were measured by an Elementar model vario EL cube analyzer. Field emission scanning electron microscopy was recorded on a SU8020 model HITACHI microscope. Powder X-ray diffraction data were performed on a PANalytical BV Empyrean diffractometer by depositing powder on glass substrate, from $2\theta = 2.0^\circ$ to 35° with 0.02° . Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter with the heating at a rate of $10^\circ\text{C min}^{-1}$ from 35°C to 800°C under nitrogen. Nitrogen sorption and carbon dioxide isotherms were measured at 77 K with a JW-BK 132F analyzer.

Materials: The 1,3,5-tris(4-aminophenyl)benzene, mesitylene, 1,4-dioxane, acetic acid, tetrahydrofuran, and other chemicals were obtained from Energy Chemistry, J&K Scientific, TCI, Wako, and Aldrich.

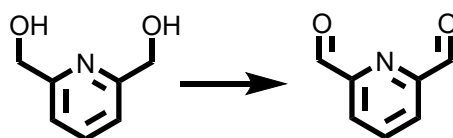
Synthesis of 4,4',4'',4'''-methanetetrayltetraaniline^{S1}



Tetraphenylmethane (3.0 g, 9.3 mmol) was added into fuming nitric acid (15 mL) at 40 °C under vigorous stirring. Then acetic anhydride (5 mL) and acetic acid (18 mL) were slowly added and stirred for 10 h. After filtration, the precipitate was washed with H₂O and dried at 60 °C under vacuum for 10 h. The resultant yellow solid was used directly for the next step without further purification.

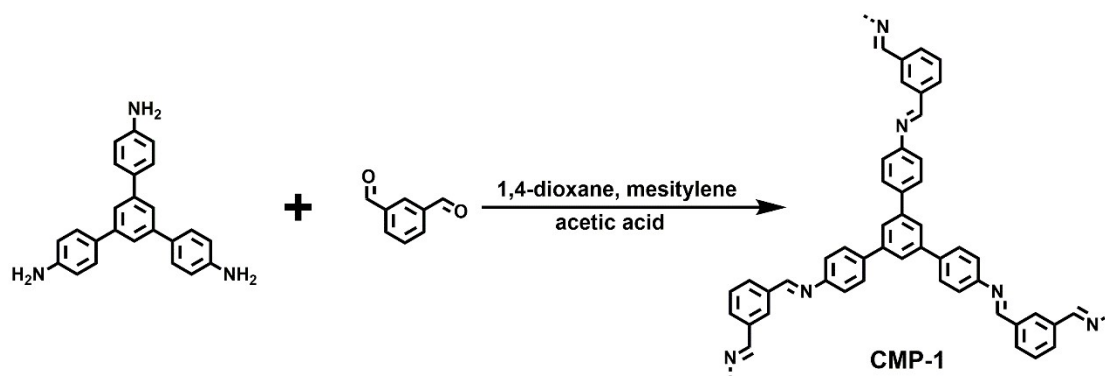
Tetrakis-(4-nitrophenyl)-methane (1.0 g, 2.0 mmol) was placed in a 100 mL schlenk tube, and anhydrous ethanol (60 mL) was added as the solvent, followed by Pd/C (30 mg, 9 %). A hydrazine hydrate solution (1 mL of 80 %) was then added dropwise with vigorous stirring. The resulting mixture was heated to reflux for 16 hours. After the solution was cooled to room temperature, the crude product was collected by vacuum filtration. After purification by running a flash column chromatography (with 9 % ethanol in dichloromethane as the eluent), the pure product was collected as a white solid (0.71 g, 96 %). ¹H NMR (d₆-DMSO, 400 MHz) δ 4.87 (s, 8H), 6.38-6.40 (m, 8H), 6.67-6.69 (m, 8H).

Synthesis of pyridine-2,6-dicarbaldehyde^{S2}

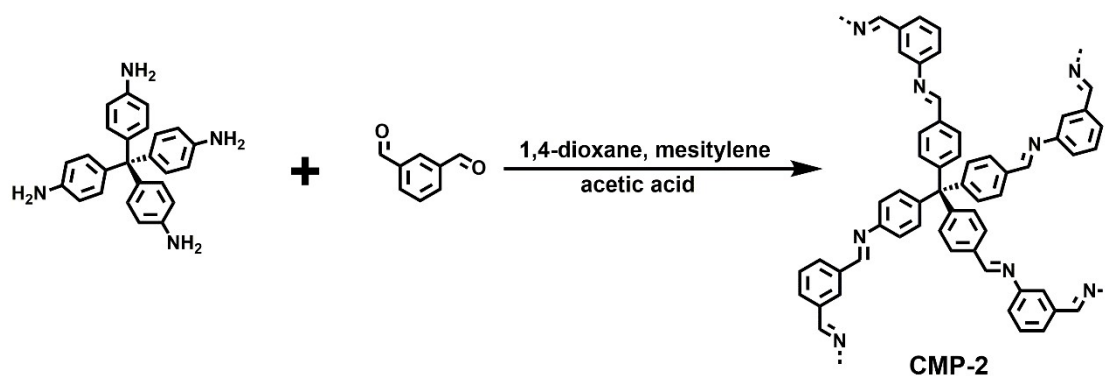


SeO₂ (6.4 g, 57.68 mmol) was suspended into a solution of 2,6-di(hydroxymethyl)pyridine (4 g, 28.76 mmol) in dioxane (30 mL). The oxidation reaction was completed within 6 h under reflux. Insoluble solid was filtered off and the solvent was removed on a rotary evaporator to give a yellow solid. The crude filtered through a silica funnel with CH₂Cl₂ as eluent and the pink product (3.40 g, 85%). ¹H NMR (CDCl₃, 300 MHz): δ=10.17 (s, 2 H), 8.20 (m, 2 H; J=3.0), 8.06 (m, 1 H; J=15.0).

Synthesis of CMP-1



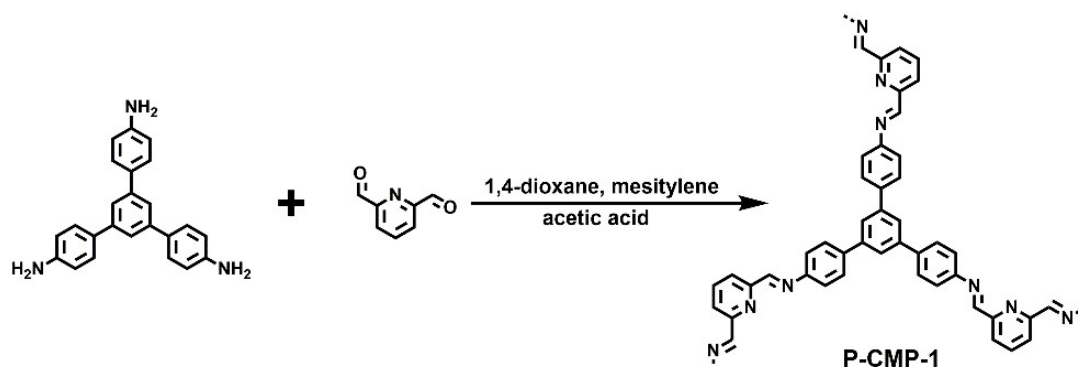
A pyrex tube is charged with 1,3,5-tris(4-aminophenyl)benzene (35.1 mg, 0.10 mmol), 1,3-benzenedicarboxaldehyde (20.2 mg, 0.15 mmol), mesitylene (0.8 mL), 1,4-dioxane (0.8 mL), and aqueous acetic acid (0.2 mL 6 M). The reaction mixture was heated at 120 °C for 3 d. After the reaction, the solid at the bottom of the tube was isolated by filtration, soxhleted by tetrahydrofuran for 24 h, and then dried at 120 °C under vacuum for 24 h to give a yellow powder in 89% (P-CMP-1).



Synthesis of CMP-2

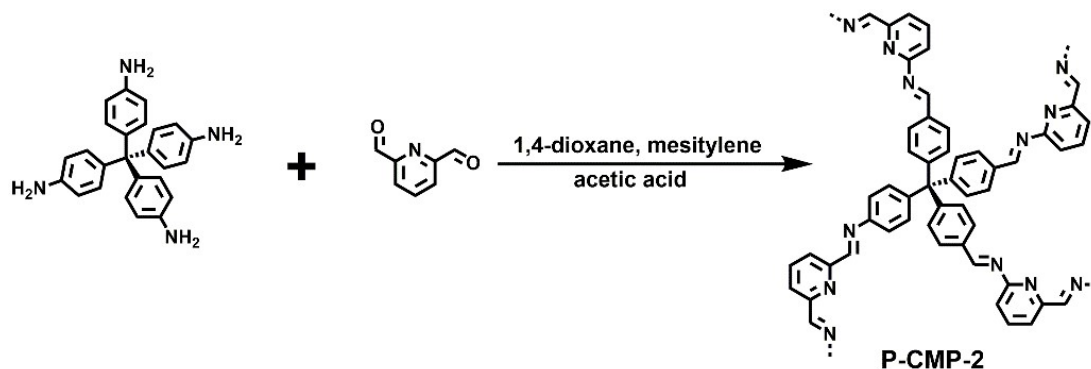
A pyrex tube is charged with 4,4',4'',4'''-methanetetrayltetraaniline (38 mg, 0.10 mmol), 1,3-benzenedicarboxaldehyde (26.8 mg, 0.20 mmol), mesitylene (0.8 mL), 1,4-dioxane (0.8 mL), and aqueous acetic acid (0.2 mL 6 M). The reaction mixture was heated at 120 °C for 3 d. After the reaction, the solid at the bottom of the tube was isolated by filtration, soxhleted by tetrahydrofuran for 24 h, and then dried at 120 °C under vacuum for 24 h to give a yellow powder in 90% (P-CMP-2).

Synthesis of P-CMP-1



A pyrex tube is charged with 1,3,5-tris(4-aminophenyl)benzene (35.1 mg, 0.10 mmol), pyridine-2,6-dicarbaldehyde (23 mg, 0.17 mmol), mesitylene (0.8 mL), 1,4-dioxane (0.8 mL), and aqueous acetic acid (0.2 mL 6 M). The reaction mixture was heated at 120 °C for 3 d. After the reaction, the solid at the bottom of the tube was isolated by filtration, soxhleted by tetrahydrofuran for 24 h, and then dried at 120 °C under vacuum for 24 h to give a yellow powder in 85% (P-CMP-1).

Synthesis of P-CMP-2



A pyrex tube is charged with 4,4',4'',4'''-methanetetrayltetraaniline (38 mg, 0.10 mmol), pyridine-2,6-dicarbaldehyde (27 mg, 0.20 mmol), mesitylene (0.8 mL), 1,4-dioxane (0.8 mL), and aqueous acetic acid (0.2 mL 6 M). The reaction mixture was heated at 120 °C for 3 d. After the reaction, the solid at the bottom of the tube was isolated by filtration, soxhleted by tetrahydrofuran for 24 h, and then dried at 120 °C under vacuum for 24 h to give a light-yellow powder in 87% (P-CMP-2).

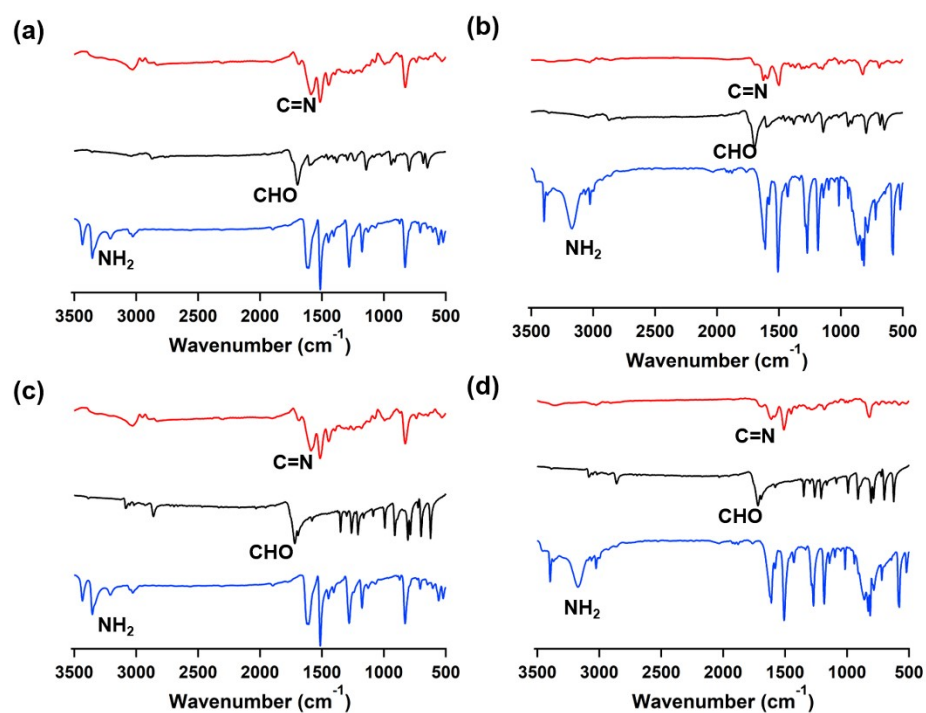


Fig. S1. FT-IR spectra of (a) CMP-1 (red), 1,3-benzenedicarboxaldehyde (black), and 1,3,5-tris(4-aminophenyl) benzene (blue); (b) CMP-2 (red), 1,3-benzenedicarboxaldehyde (black), and 4,4',4'',4'''-methanetetrayltetraaniline (blue); (c) P-CMP-1 (red), pyridine-2,6-dicarbaldehyde (black), and 1,3,5-tris(4-aminophenyl) benzene (blue); (d) P-CMP-2 (red), pyridine-2,6-dicarbaldehyde (black), and 4,4',4'',4'''-methanetetrayltetraaniline (blue).

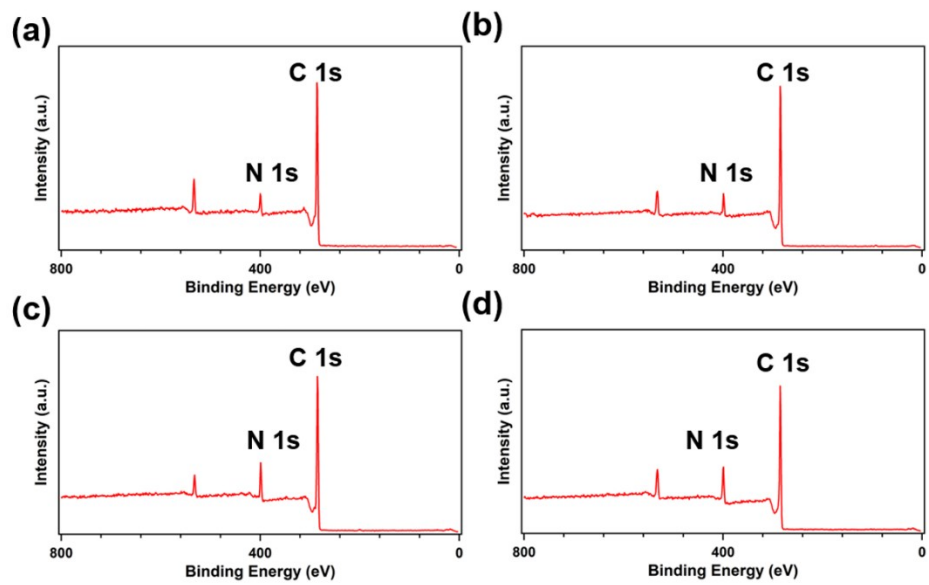


Fig. S2. XPS spectra of (a) CMP-1, (b) CMP-2, (c) P-CMP-1, and (d) P-CMP-2.

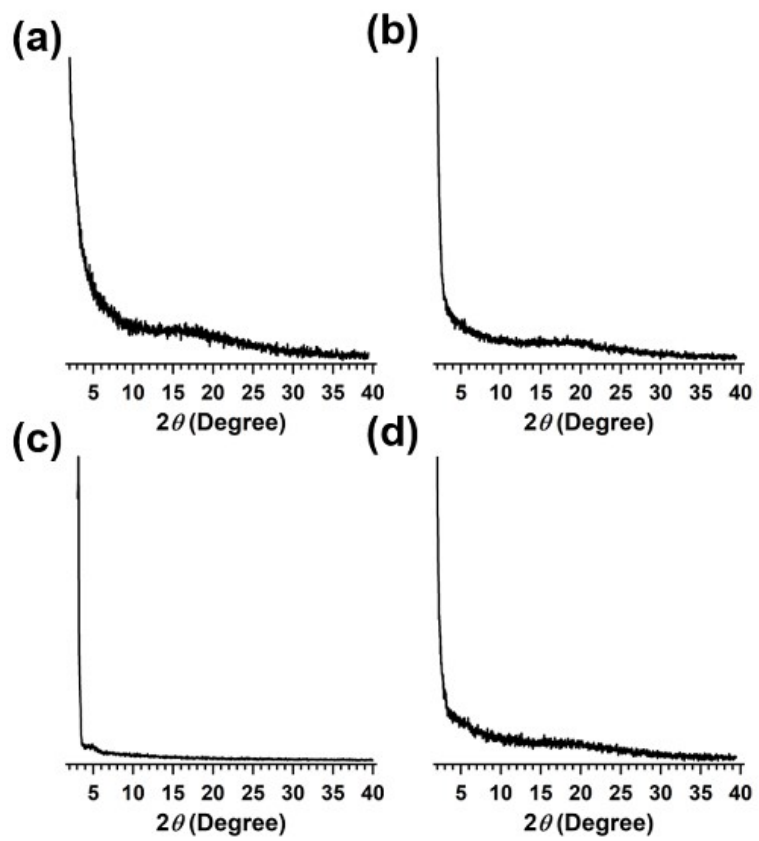


Fig. S3. PXRD patterns of (a) CMP-1, (b) CMP-2, (c) P-CMP-1, and (d) P-CMP-2.

Table S1. Elemental analysis of CMPs

		C (%)	H (%)	N (%)
CMP-1	Observed	85.89	5.16	7.97
	Calculated	86.72	4.85	8.43
CMP-2	Observed	84.92	5.05	9.11
	Calculated	85.39	4.89	9.72
P-CMP-1	Observed	82.23	4.37	12.25
	Calculated	82.86	4.54	12.60
P-CMP-2	Observed	80.56	4.21	13.84
	Calculated	81.34	4.44	14.23

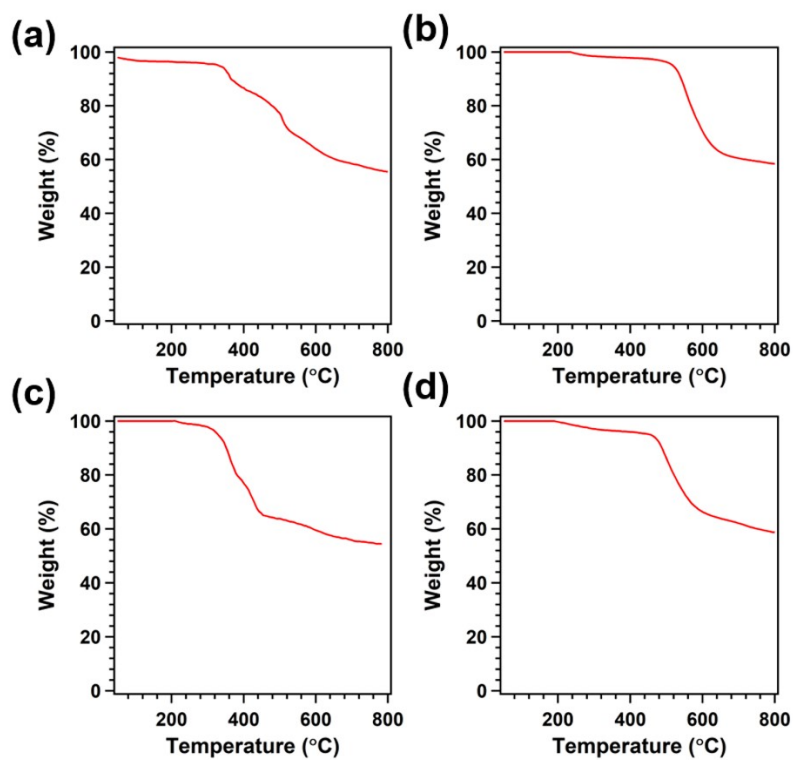


Fig. S4. TGA curves of (a) CMP-1, (b) CMP-2, (c) P-CMP-1, and (d) P-CMP-2.

Table S2. The thermogravimetric temperature and percentage of polymers

	1st Step (°C)	2nd Step (°C)	Percentage
CMP-1	322	499	55%
CMP-2	459	592	64%
P-CMP-1	340	478	54%
P-CMP-2	458	590	58%

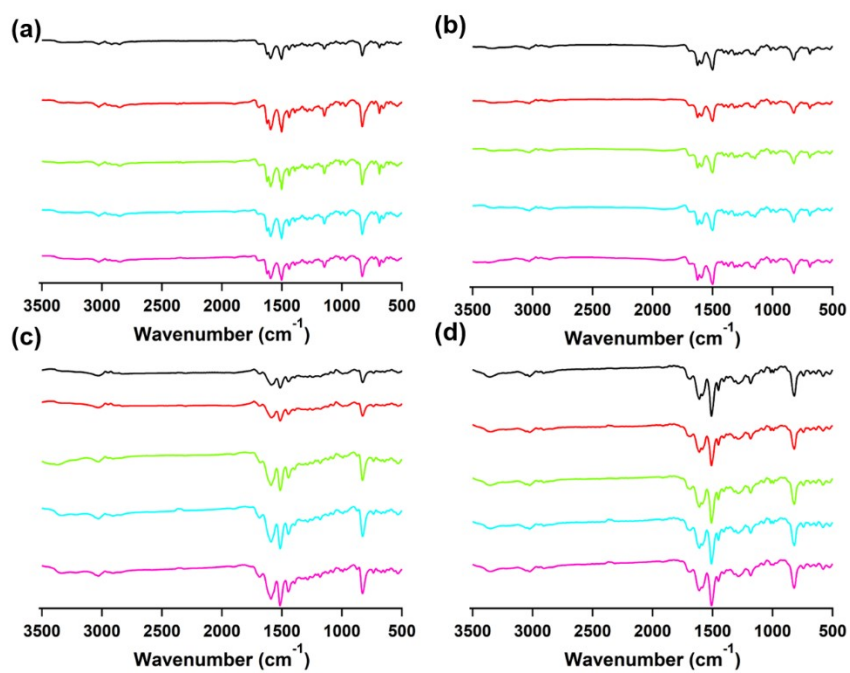


Fig. S5. FT-IR spectra of (a) CMP-1, (b) CMP-2, (c) P-CMP-1, and (d) P-CMP-2 under different conditions (as-synthesized: black; THF: red; Water: green; 1 M HCl: sky-blue; 1 M NaOH: purple).

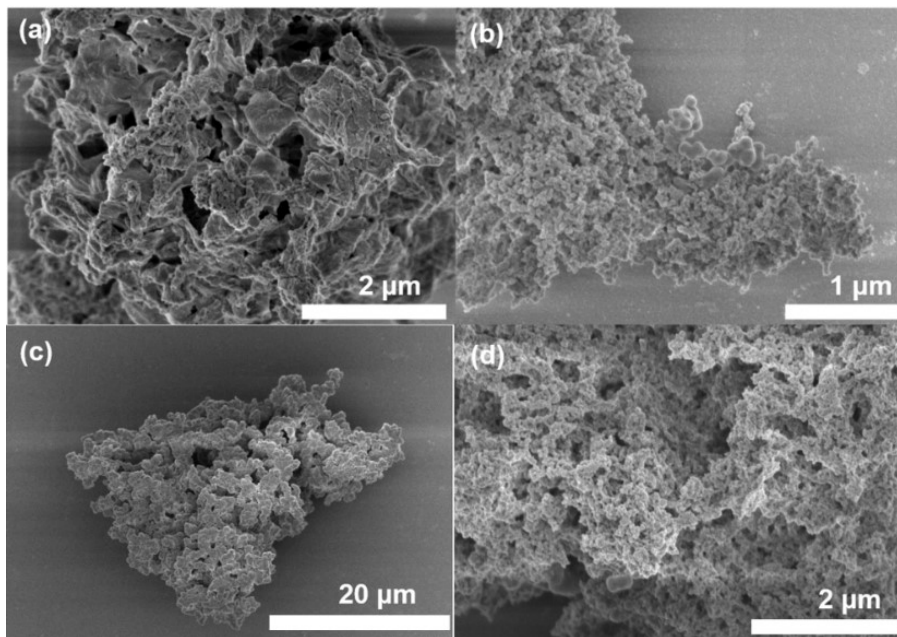


Fig. S6. FE SEM images of (a) CMP-1, (b) CMP-2, (c) P-CMP-1, and (d) P-CMP-2.

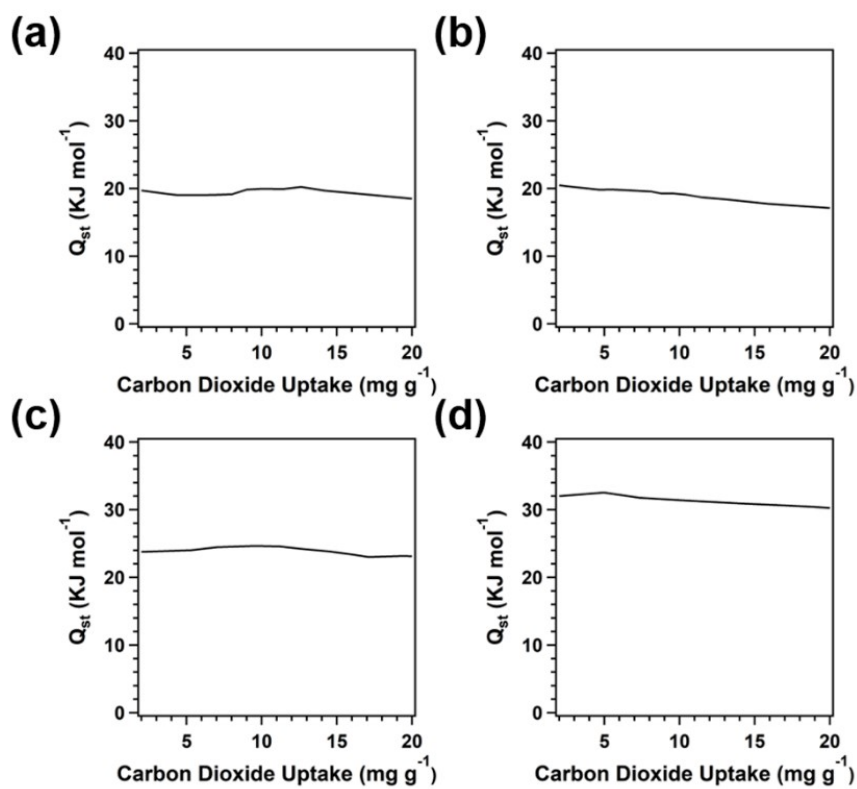


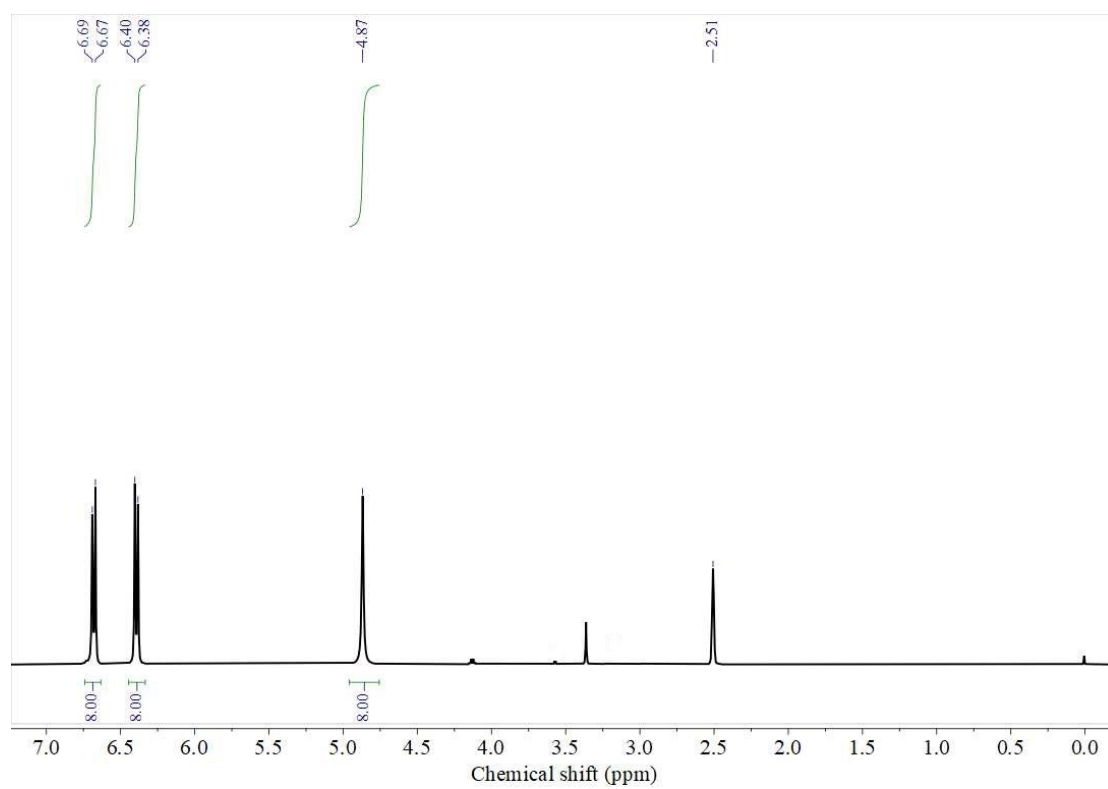
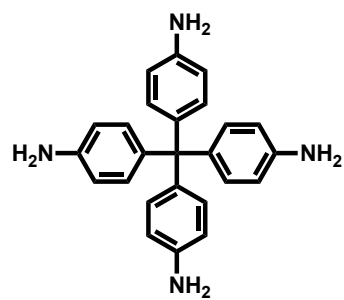
Fig. S7. CO_2 isosteric heat of (a) CMP-1, (b) CMP-2, (c) P-CMP-1, and (d) P-CMP-2.

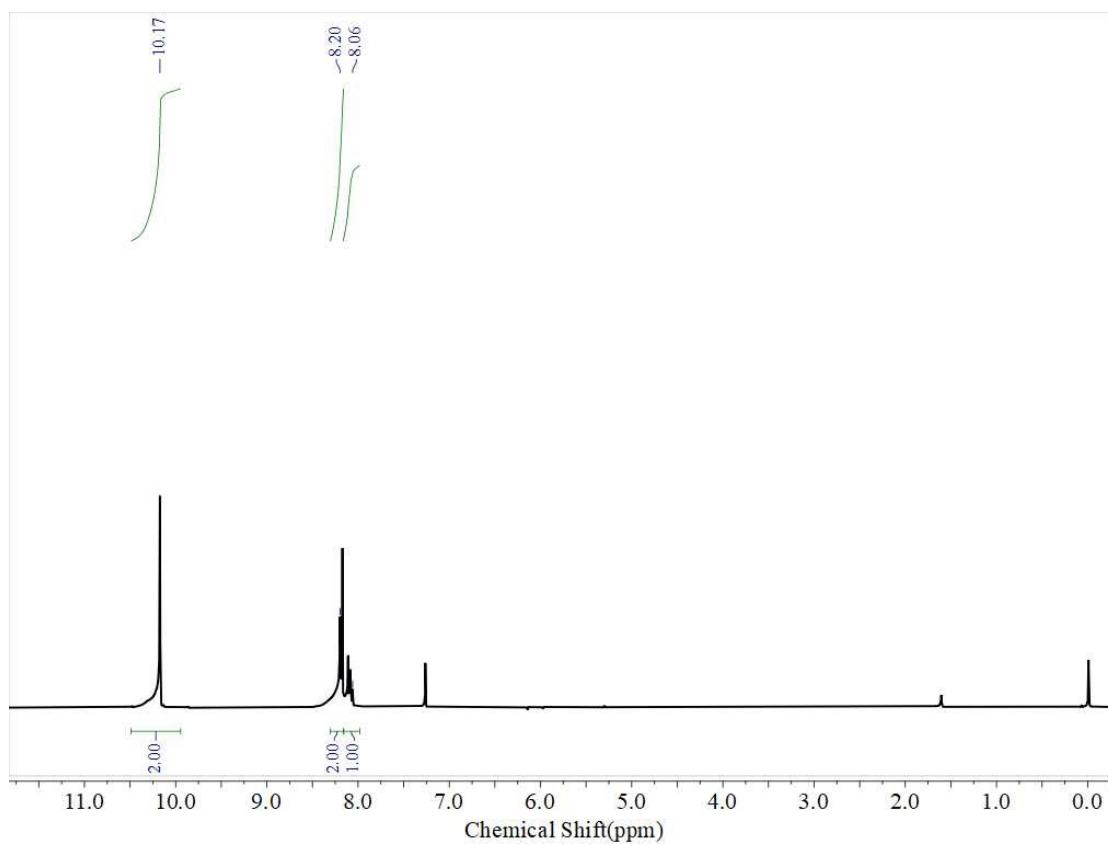
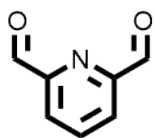
Table S3. Gas adsorption isosteric heats of the reported porous organic polymers

	Qst kJ mol⁻¹	Ref.
CMP-1	20	This work
CMP-2	21	
P-CMP-1	24	
P-CMP-2	32	
PDCPF	26.03	<i>Polymer</i> , 2021, 233 , 124192
HCTPM	17	<i>New J. Chem.</i> , 2017, 41 , 3915-3919.
PCZN-1	25.6	<i>Polym. Chem.</i> , 2017, 8 , 7240–7247.
SC-TPB	26.5	<i>J. Mater. Chem. A</i> , 2019, 7 , 549-557.
Sbf-TMP@4:0	27.9	<i>Macromolecules</i> 2017, 50 , 8512–8520
PCTF-7	25	<i>J. Mater. Chem.</i> , 2013, 1 , 14990–14999.

Table S4. Gas adsorption capacities of the reported porous organic polymers.

	CO₂ Uptake (273 K) mg g⁻¹	CO₂ Uptake (298 K) mg g⁻¹	Ref.
CMP-1	62	36	This work
CMP-2	88	56	
P-CMP-1	106	65	
P-CMP-2	136	88	
TAP-1	95	62	<i>ACS Appl. Polym. Mater.</i> , 2019, 1 , 959–968.
Co-CMP2	-	64.6	<i>ChemCatChem</i> , 2017, 9 , 2584–2587
PCTF-1	73.0	44.9	<i>J. Mater. Chem.</i> , 2013, 1 , 14990–14999.
Sbf-TMP@4:0	92	61	<i>Macromolecules</i> 2017, 50 , 8512–8520.
ZnP-50%N3-CMPs	87	49	<i>Chem. Commun.</i> , 2017, 53 , 11422–11425.





Reference

- S1. G. Li, Z. Wang, *Macromolecules* 2013, **46**, 3058–3066.
- S2. (a) A. Abeyayehu, R. Dutta, C.-H. Lee, *Chem. Eur. J.*, 2016, **22**, 13850–13856. (b) A. MD. Mahbubul, *J. Anal. Sci. Technol.*, 2011, **35**, 61–65.