Supporting Information

A series of thiophene- and nitrogen-rich conjugated microporous polymers for efficientiodine and carbon dioxide capture

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Contents

Section A. Experimental

Materials

N,N′,N″,N‴-Terta(*p*-phenylene)paraphenylenediamine, sodium tert-butoxide, 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl were purchased from san bang chemical. 3,3',5,5'-Tetrabromo-2,2'-benzothiophene, 4-formylphenylboronic acid, bis(dibenzylideneacetone)palladium were purchased from Aladdin. All solvents used were purchased from Aladdin.

Synthetic procedures

Synthesis of SNCMP-1 : 3,3',5,5'-Tetrabromo-2,2'-benzothiophene (36 mg, 0.075 mmol), *N,N′,N″,N‴*-terta(*p*-phenylene)paraphenylenediamine (35.4 mg, 0.113 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (28.6 mg, 0.06 mmol), bis(dibenzylideneacetone)palladium (23 mg, 0.03 mmol) and sodium tert-butoxide (255.6 mg, 2.66 mmol) were added to a 50 mL two-necked flask. Next, add 5.33 mL of anhydrous toluene and 2.67 mL of anhydrous n-butanol to the flask, and then circulate the flask 3 times under vacuum/N_2. After evacuating 3 times, it was refilled with nitrogen, and then the reaction was heated to 150 °C for 72 h. After the completion of the reaction, the obtained product was cooled to room temperature and washed with water, acetone and chloroform three times, respectively, to obtain SNCMP-1 (67% yield) as a black powder. Elemental Analysis (%) Calcd: C 77.94, H 3.93, N 7.18, S 10.95. Found by EDX analysis (%): C 75.95, H 3.31, N 6.72, S 10.02.

Synthesis of SNCMP-2 : 3,3',5,5'-Tetrabromo-2,2'-benzothiophene (36 mg, 0.075 mmol), *N,N′,N″,N‴*-terta(*p*-phenylene)paraphenylenediamine (35.4 mg, 0.113 mmol), 4-formylphenylboronic acid (11.8 mg, 0.078mmol) 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (28.6 mg, 0.06 mmol), bis(dibenzylideneacetone)palladium (23 mg, 0.03 mmol), sodium tert-butoxide (255.6 mg, 2.66 mmol), and copper(I) iodide (5 mg, 0.039 mmol) were added to a 50 mL two-necked flask. Next, add 6 mL of anhydrous toluene and 2 mL of anhydrous n-butanol to the flask, and then circulate the flask 3 times under vacuum/N_2. After evacuating 3 times, it was refilled with

nitrogen, and then the reaction was heated to 150 °C for 72 h. After the completion of the reaction, the obtained product was cooled to room temperature and washed with water, acetone and chloroform three times, respectively, to obtain SNCMP-2 (60% yield) as a black powder. Elemental Analysis (%) Calcd: C 78.22, H 4, N 8.3, S 9.48. Found by EDX analysis (%): C 76.47, H 3.39, N 7.87, S 8.27.

Materials characterization

The main paragraph text follows directly on here. Fourier transform Infrared (FT-IR) spectra were recorded on a Perkin-elmer model FT-IR-frontier infrared spectrometer. 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). 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. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from 2θ = 1.5° up to 60° with 0.02° increment. 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. TGA analysis was carried out using a Q5000 IR 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. 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 Barrett-Joyner-Halenda. (BJH) method was applied for the estimation of pore size and pore size distribution. The adsorption isotherms of carbon dioxide and methane were measured at 323 K and 70 bar with the iSorbHP2 analyzer. Before the measurement, the sample was also degassed in a vacuum at 120 °C for more than 10 hours.

Table S1. Summary of iodine capacity of porous materials.

Polymers	S_{BET} ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	Iodine Uptake (wt.%)	Ref.
SNCMP-1	16.1	0.22	570	This work
SNCMP-2	41.7	0.54	698	
TDTPAPz	561.3	1.9	441	S1
TTDPz	13.5	0.216	312	
CMP-LS4	462	0.31	332	S2
CMP-LS5	1185	1.36	440	
CMP-LS6	679	1.26	244	
CMPH	222.4	0.213	195	S3
$CMPNH_2$	6.44	0.01	283	
CMPN	86.2	0.218	502	
TDP	261.9	0.30	61	S4
PCPP	43	0.3036	307	
TTPAP	187.5	0.0999	349	
TDTPAP	695.2	0.4913	419	

Section B. FT-IR spectra

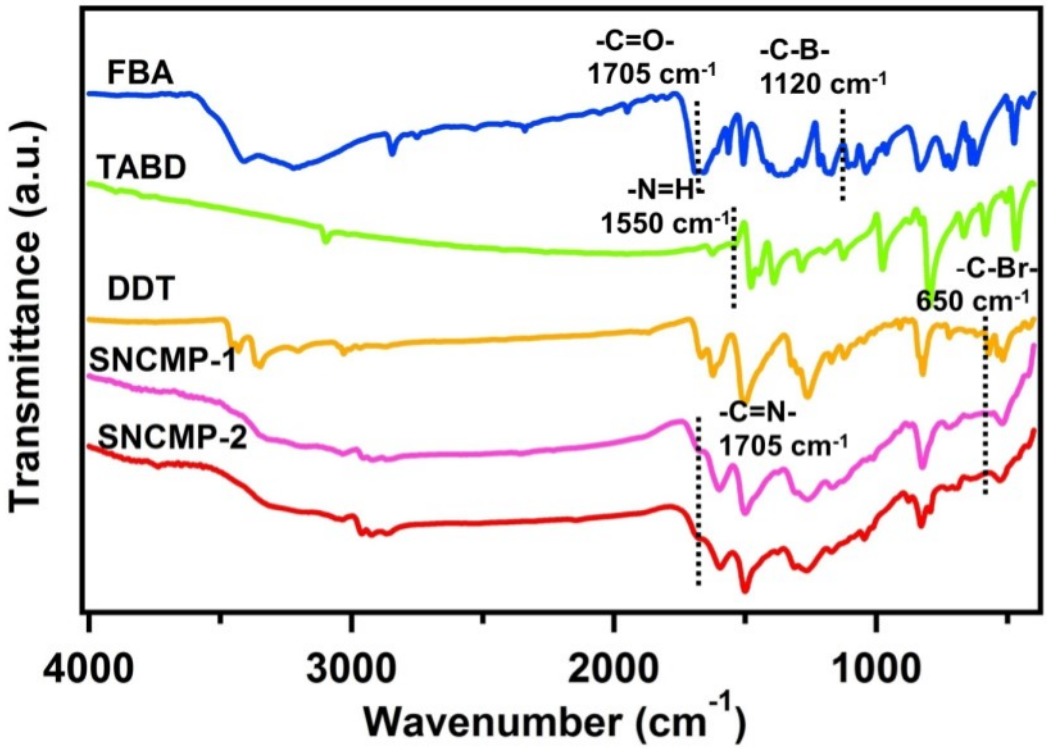

Figure S1. FT-IR spectra of SNCMP-1 and SNCMP-2.

Section C. ^{13}C NMR spectra

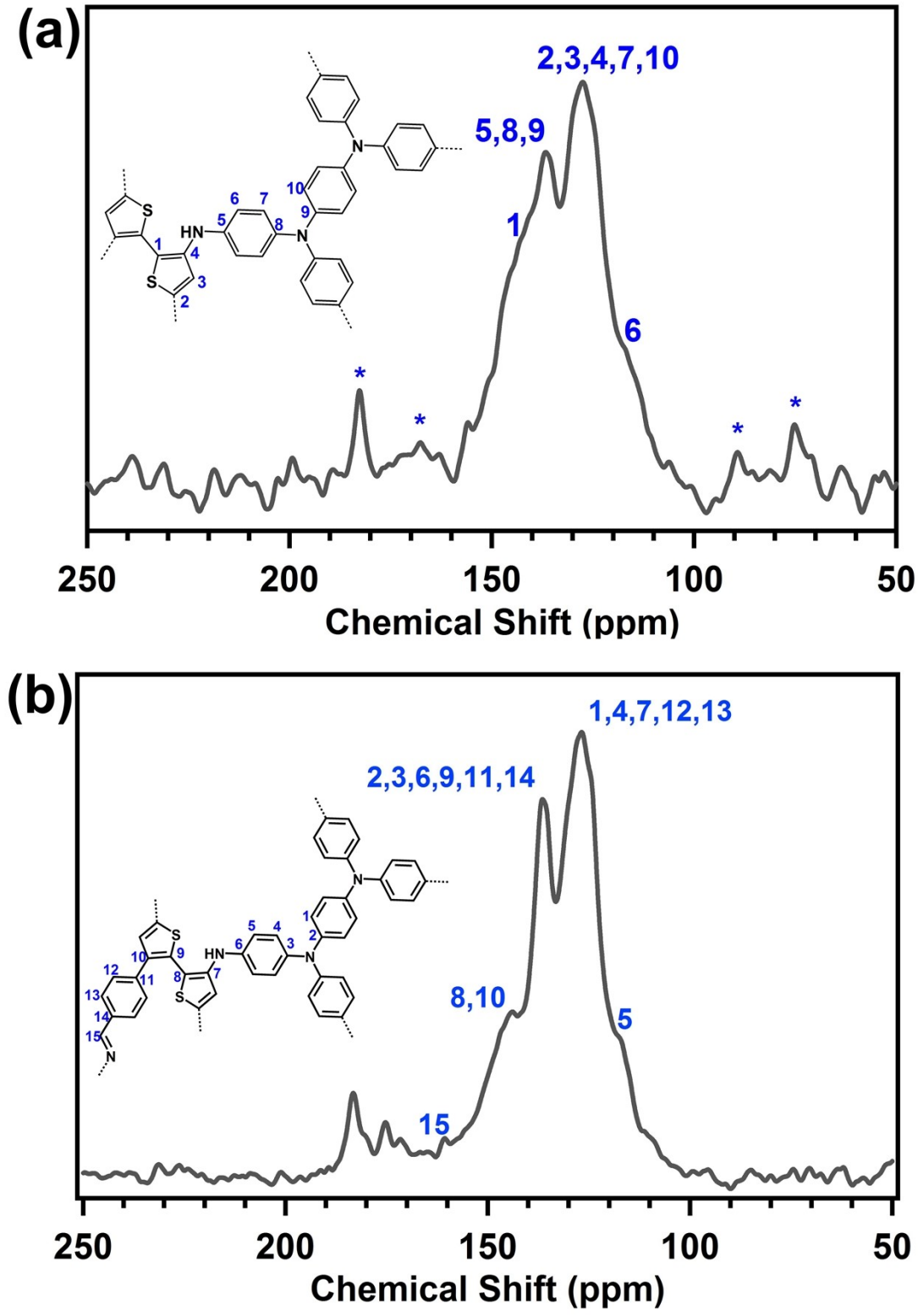

Figure S2. The solid-state ^{13}C CP-MAS NMR of (a) SNCMP-1 and (b) SNCMP-2.

Section D. XPS spectrum

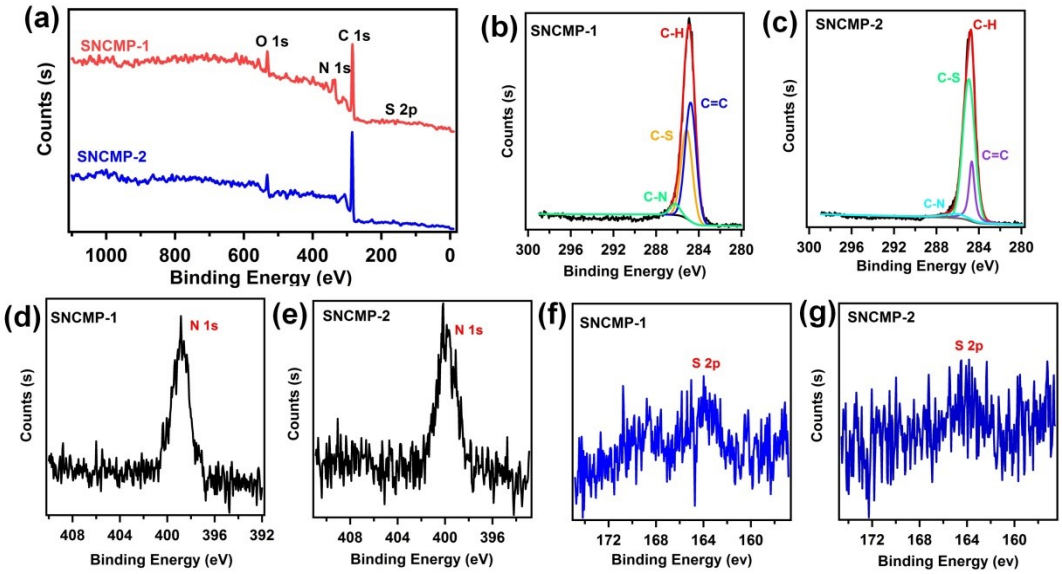

Figure S3. (a) X-ray photoelectron spectroscopy of SNCMP-1 and SNCMP-2, (b) C 1s spectrum of SNCMP-1. (c) C 1s spectrum of SNCMP-2. (d) N 1s spectrum of SNCMP-1. (e) N 1s spectrum of SNCMP-2. (f) S 2p spectrum of SNCMP-1. (g) S 2p spectrum of SNCMP-2.

Section E. The Solid-UV spectra

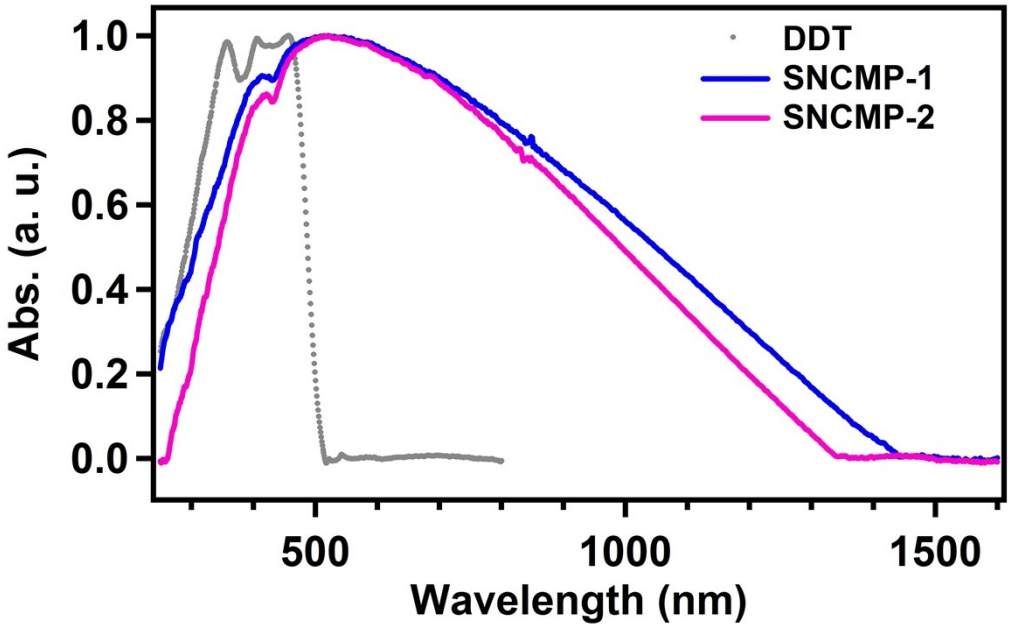

Figure S4. The normalized solid state UV-Vis spectra of SNCMP-1 and SNCMP-2.

Section F. Powder X-ray diffraction patterns

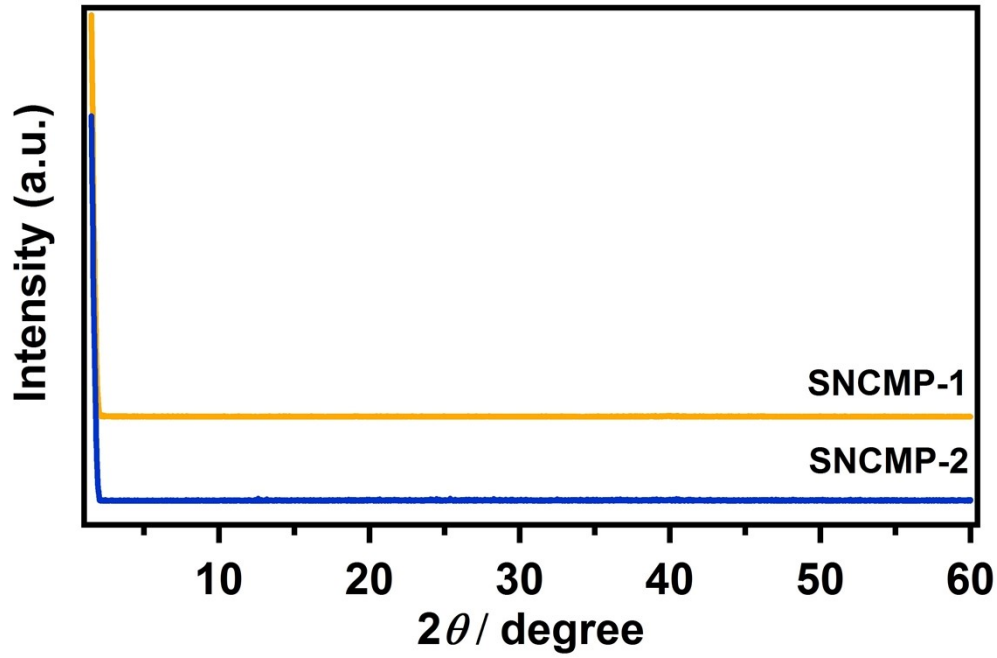

Figure S5. Powder X-ray diffraction profiles of SNCMP-1 and SNCMP-2.

Section G. TGA curves

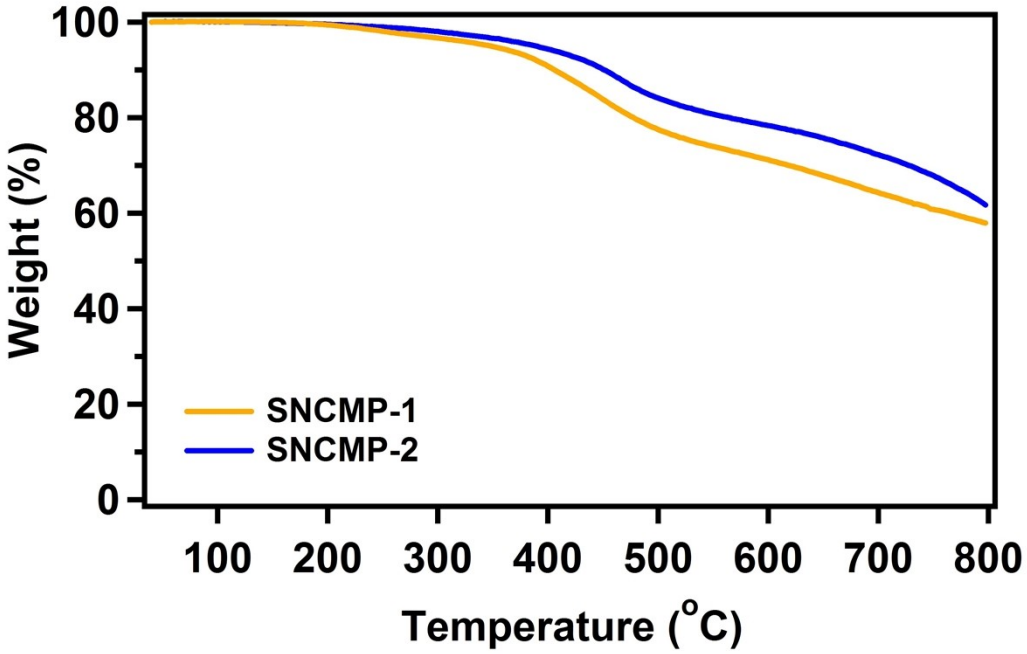

Figure S6. TGA curves of SNCMP-1and SNCMP-2.

Section H. Pore property

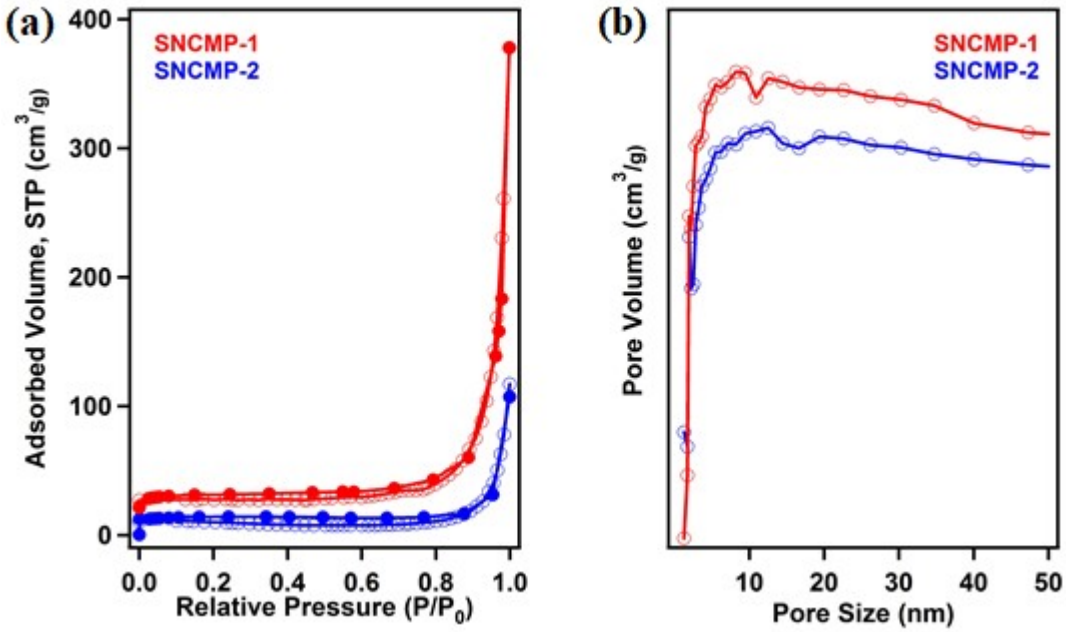

Figure S7. (a) Nitrogen sorption curves and (b) pore size distribution curves of SNCMP-1 and SNCMP-2.

Section I. Iodine capture analyses

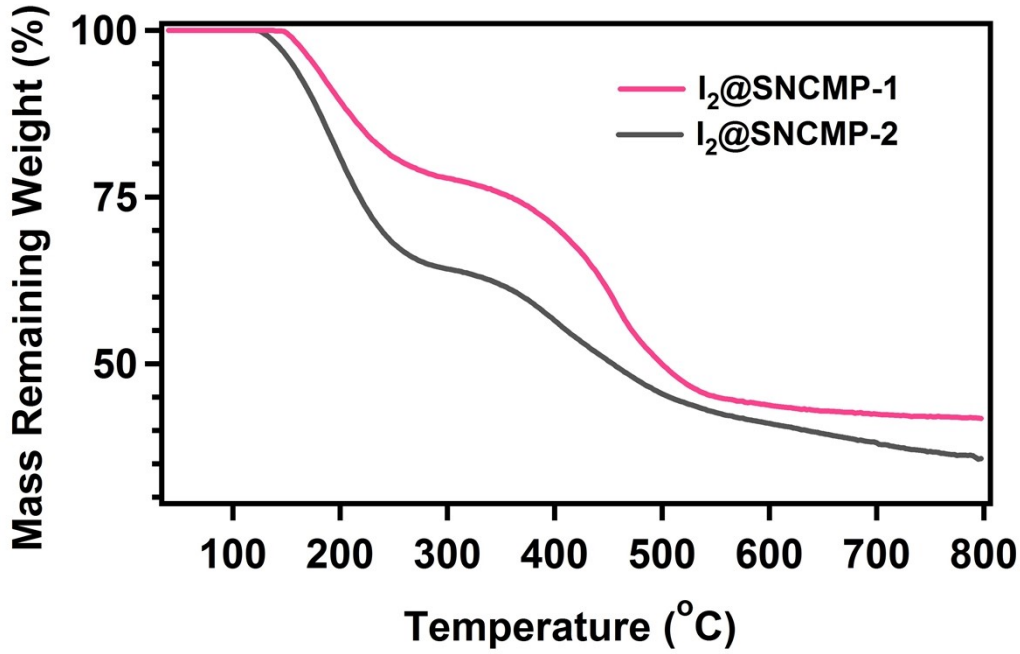

Figure S8. TGA curves of I_2@SNCMP-1 and I_2@SNCMP-2.

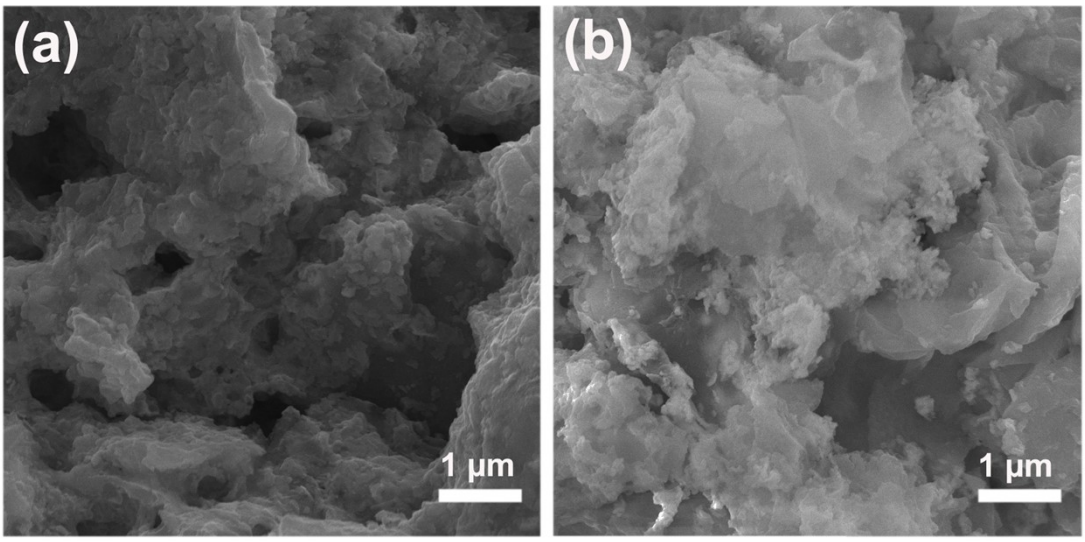

Figure S9. FE-SEM images (a) I_2@SNCMP-1 and (b) I_2@SNCMP-2.

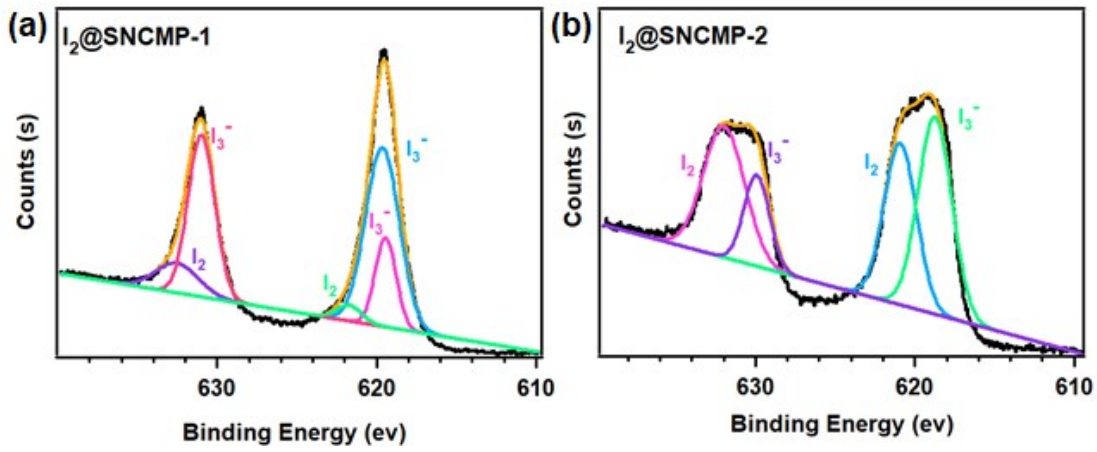

Figure S10. XPS spectra for I3d3 and I5d5 in the (a) I_2@SNCMP-1 and (b) I_2@SNCMP-2.

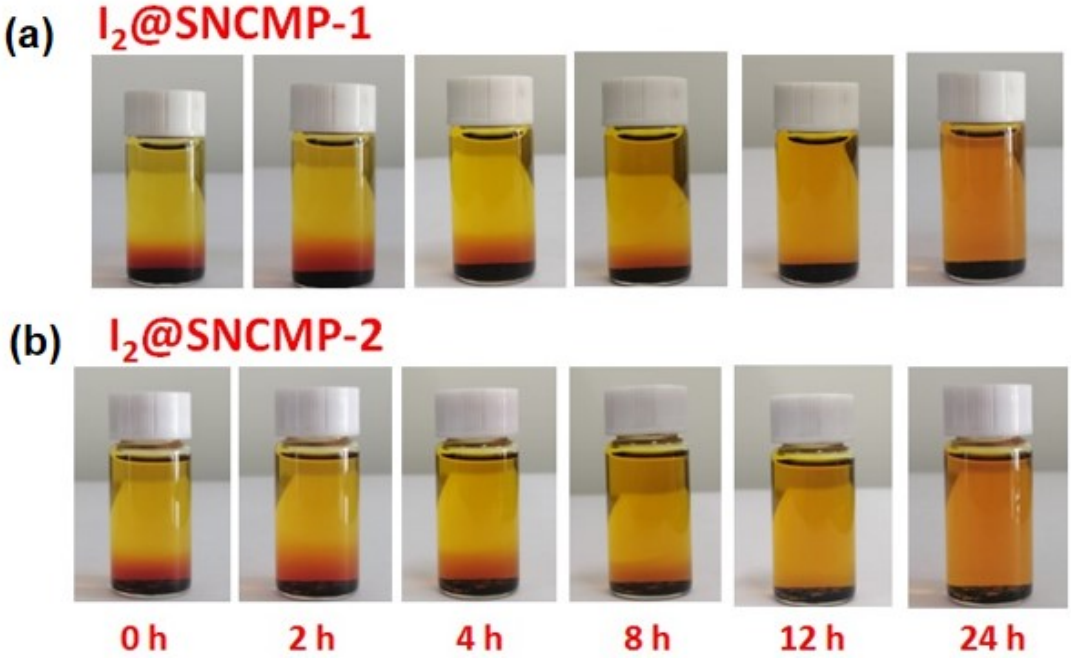

Figure S11. Photographs showing progress of the iodine release from (a) I_2@SNCMP@1 and (b) I_2@SNCMP@2, when the containing iodine polymer networks were immersed in ethanol.

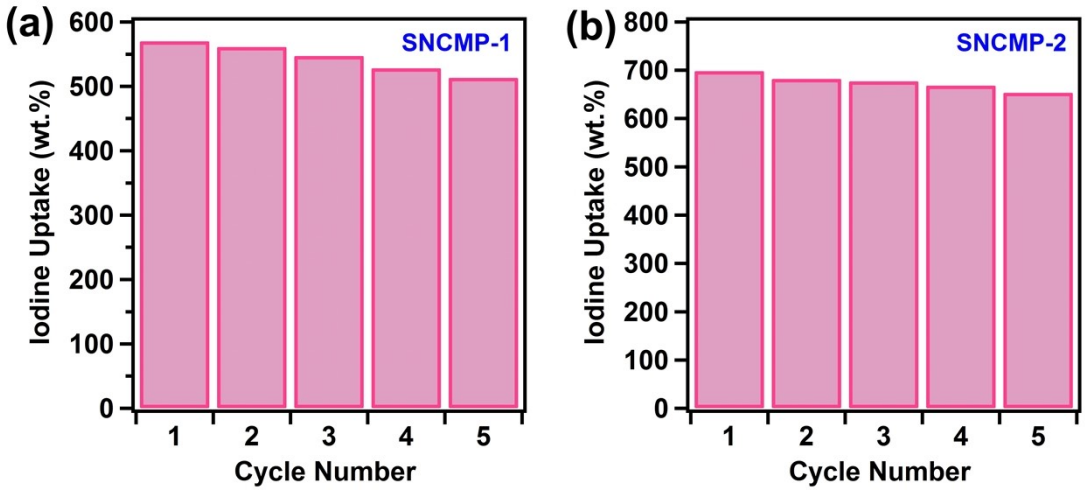

Figure S12. Reusabilities of the (a) SNCMP-1 and (b) SNCMP-2 polymers for iodine adsorption by vapor sublimation.

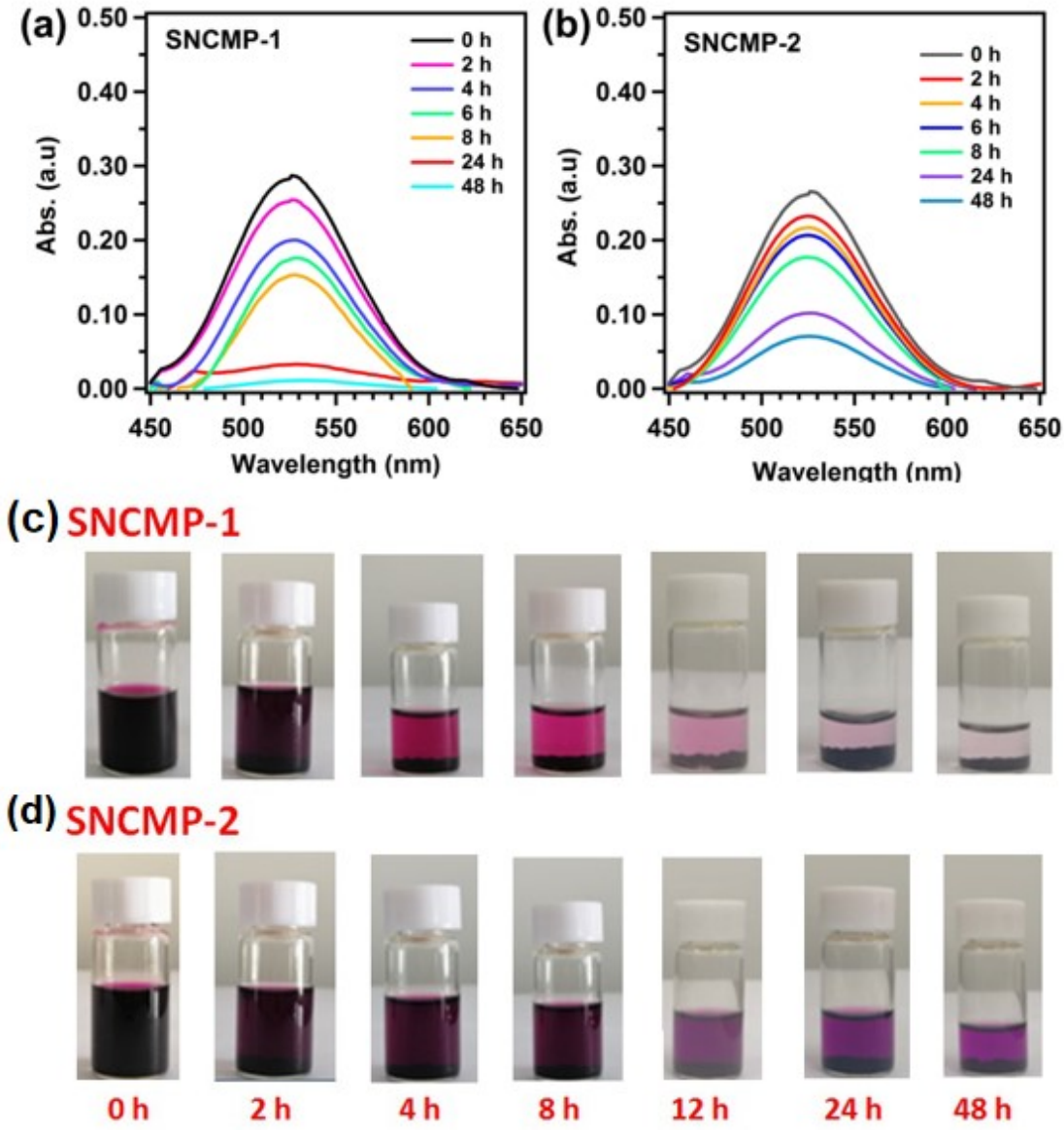

Figure S13. (a-b) the UV-Vis spectra upon immersion of 30 mg SNCMPs in cyclohexane solution of I_2 (6 mg ml^{-1}). All experiments were performed at ambient temperature and pressure. (c-d) Photographs show the adsorption rates of SNCMPs at various time intervals. The weight of the adsorbent (30 mg) immersed in a cyclohexane solution of I_2 (6 mg mL^{-1}, 5 mL) at room temperature.

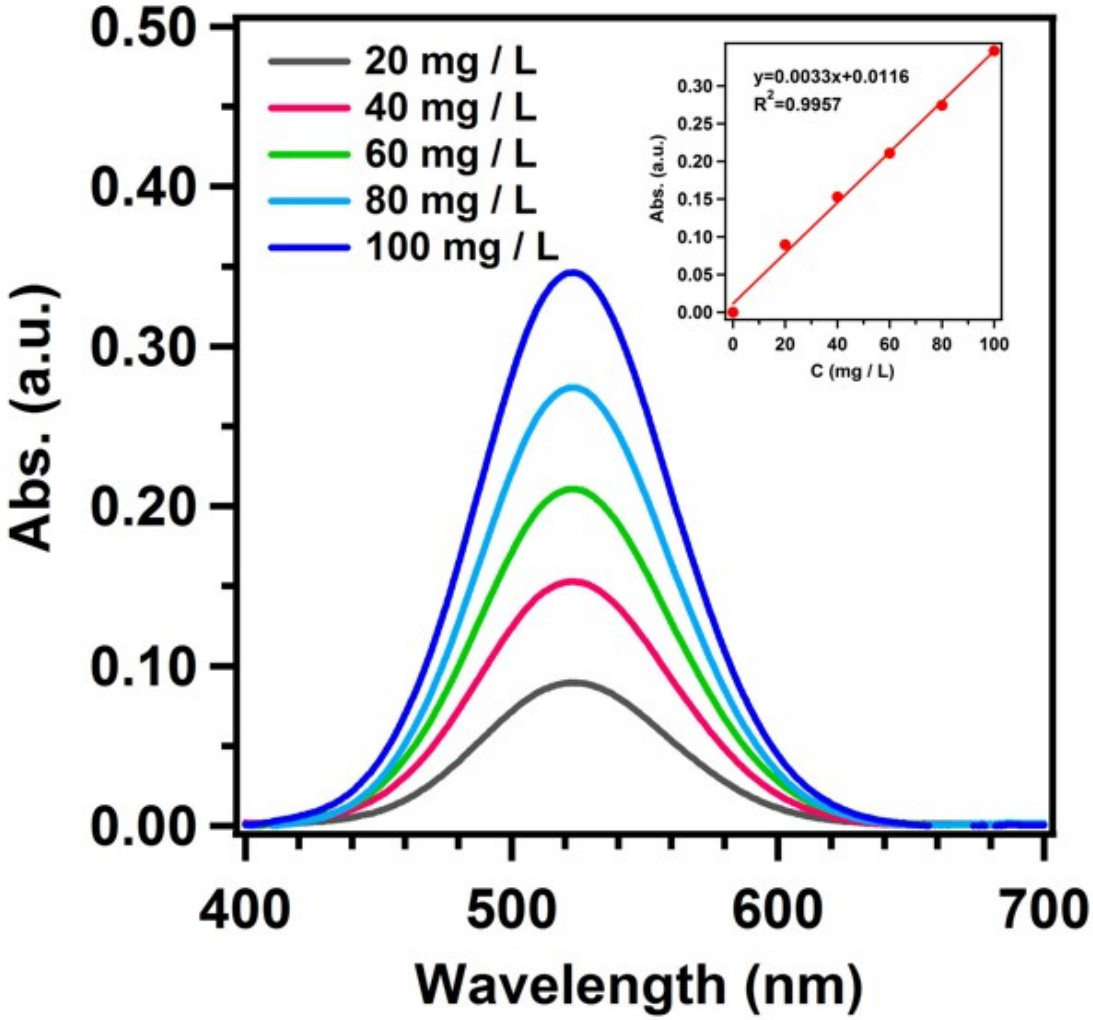

Figure S14. The standard curve of iodine in cyclohexane solution (Inset is the fitting curve of Abs value vs concentration of iodine in cyclohexane solution, the value of R^2 indicated that the curve with the relatively good linearity satisfies Lambert-Beer Law. The iodine adsorption capacity of SNCMPs was calculated according to the standard curve).

Section J. CO_2 capture analyses

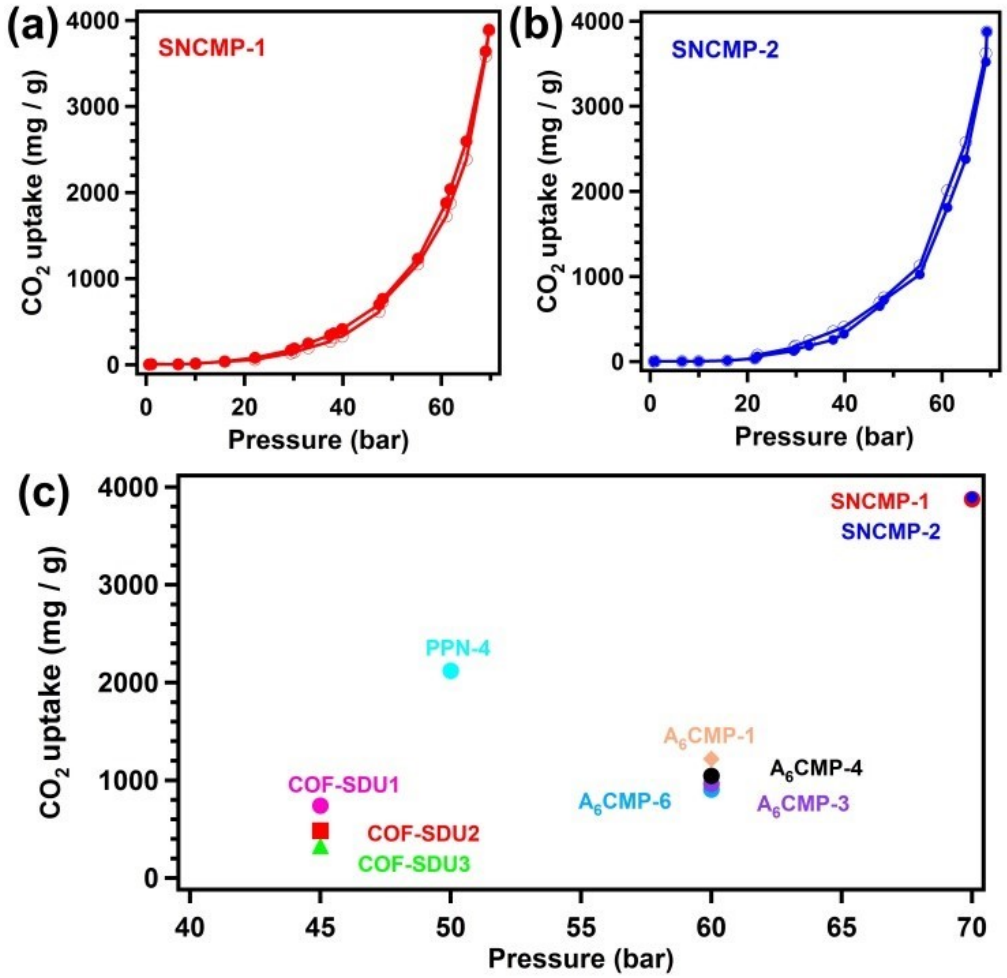

Figure S15. CO_2 adsorption isotherms of (a) SNCMP-1 and (b) SNCMP-2 collected at 70 bar and 323 K, (c) the summary of CO_2 capture of polymers at high pressure.

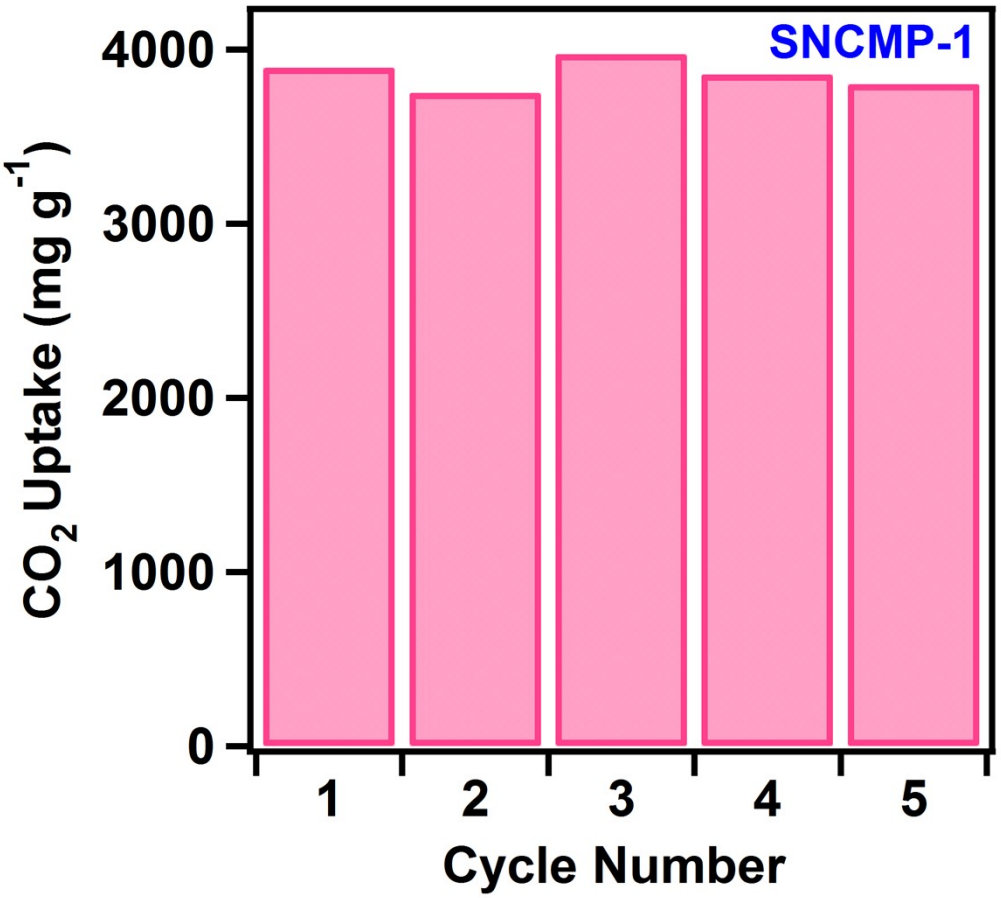

Figure S16 Carbon dioxide adsorption cycle of SNCMP-1.

Section K. References

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