Electronic Supplementary Information (ESI)

Nanoporous Semi-cycloaliphatic Polyaminal Networks for Capture of SO_2, NH_3, and I_2

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Experimental Section

Materials

Piperazine, anhydrous dimethyl sulfoxide (DMSO 99.7%, Superdry), N, N-dimethylformamide (DMF, 99.8%, SuperDry), N, N-dimethylacetamide (DMAc), adamantane, tetraphenylmethane, and all other reagents were purchased from J&K Chemical Co., Ltd. THF was purified by refluxing over sodium with a benzophenone complex indicator. The two tetraaldehyde monomers 1,3,5,7-tetrakis(4'-aldehydephenyl)adamantane (TFPAd)[1] and tetrakis(4-aldehydephenyl)methane (TFPM)[2] were prepared using the same synthetic process described previously without modification.

sPAN synthesis

The sPAN-1 was synthesized using the following procedure: In a Schlenk flask of 50 mL, TFPAd (0.5527 g, 0.1 mmol), piperazine (0.3446 g, 0.4 mmol), and DMSO (18.0 mL) were charged under argon. The mixture was heated to 180 °C and stirred for 48 h. The solid was isolated by filtration and subsequently washed with DMSO, DMF, and THF. As a final step, the isolated solid was extracted with THF in a Soxhlet apparatus for three days and dried at 120°C under vacuum to produce sPAN-1 (Yield: 97%).

The sPAN-2 was similarity prepared except that the tetraaldehyde monomer was TFPM instead of TFPAd.

Material characterization

Field-emission scanning electron microscopy (FE-SEM), fourier transform infrared (FTIR) spectroscopy, solid-state ^{13}C cross-polarization (CP)/total suppression of spinning side bands (TOSS) NMR spectrometer, elemental analyses (EA), powder wide-angle X-ray diffraction

(WAXD), and thermogravimetric analysis (TGA) were performed involving similar methodology and device as in our prior works.[3-6] Raman spectra were collected on a HORIBA HR Evolution equipped with a 532 nm laser. Adsorption measurements for SO_2, NH_3, and CO_2 were conducted on a gas adsorption analyzer (BSD-PMC, BeiShiDe Instrument Co. Ltd., China). A Quantachrome Instruments Autosorb iQ gas sorption analyzer was used to analyze the N_2 sorption isotherms (77 K) of the as-synthesized polymers. Before all the testing, the polymers were degassed overnight at 120 °C under vacuum. In a sealed sPANs container, a sample of sPANs powder (40 mg) and an excess of crystalline iodine was heated at 348 K under ambient pressure. The container was swiftly cooled to room temperature after a set time, and the sPANs sample was weighed. The I_2 uptake of sPANs was obtained using weight gain: = $(m_2–m_1)/m_1$, where the I_2 uptake and m_1 and m_2 are the masses of the sPANs sample before and after I_2 vapor exposure, respectively.

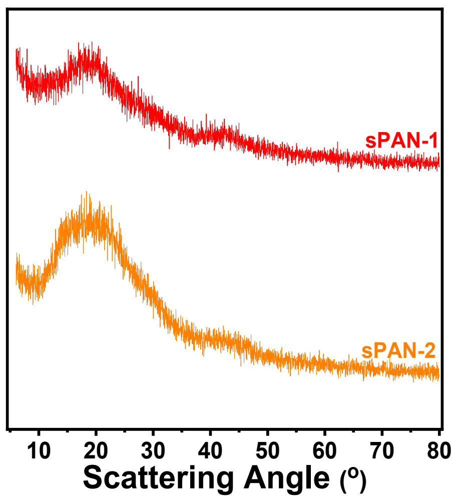

Fig. **S1** X-ray diffractions of the two sPANs.

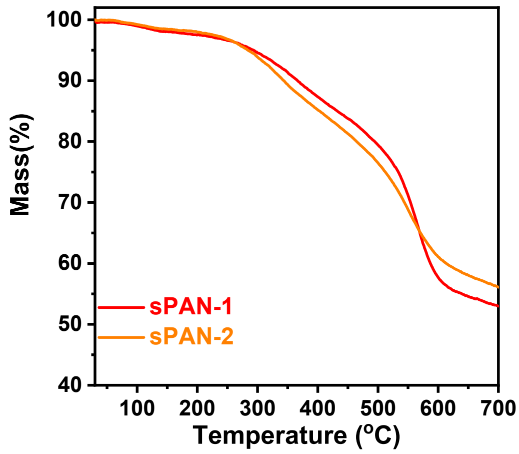

Fig. **S2** TGA curves of sPANs.

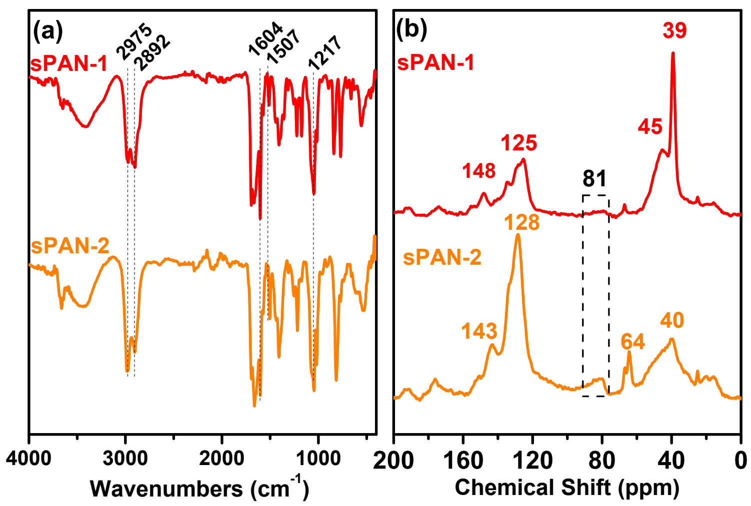

Fig. **S3** FT-IR spectrum (a) and Solid-state ^{13}C CP/TOSS NMR spectra (b) of sPAN-1 and sPAN-2.

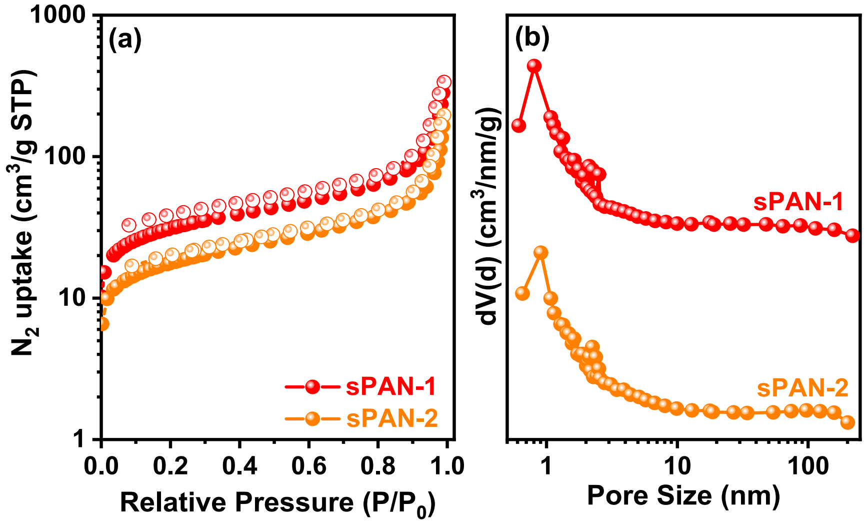

Fig. S4 Specific surface area testing of the sPANs: (a) N_2 adsorption (filled symbol) and desorption (empty symbol) isotherms obtained at 77 K; (b) pore size distribution curves calculated based on NLDFT.

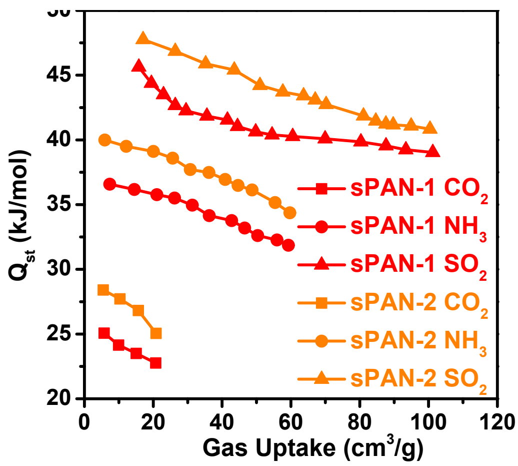

Fig. S5 Variation of the adsorption enthalpies for SO_2, NH_3, and CO_2 with the adsorbed amount in the sPANs.

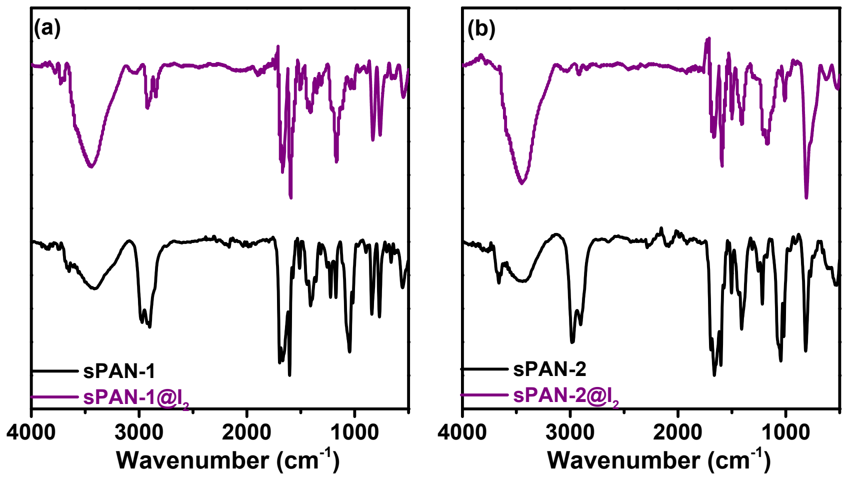

Fig. S6 FT-IR spectra of sPAN-1 (a) and sPAN-2 (b) before (black line) and after (purple line) adsorption of iodine vapor.

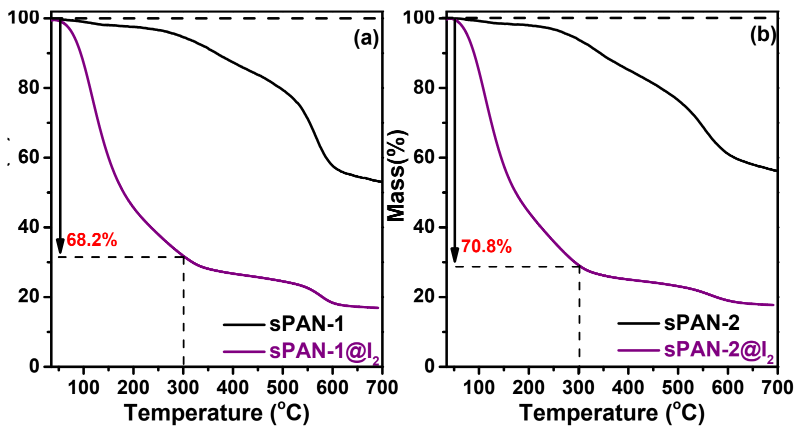

Fig. S7 TGA curves of sPAN-1 (a) and sPAN-2 (b) before (black line) and after (purple line) adsorption of iodine vapor.

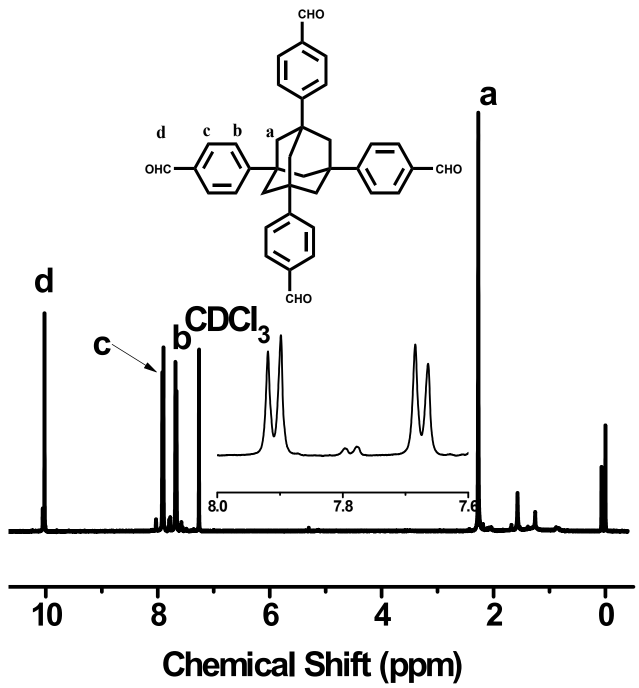

Fig. S8 ^{1}H NMR spectrum of 1,3,5,7-tetrakis(4'-aldehydephenyl)adamantane (TFPAd).

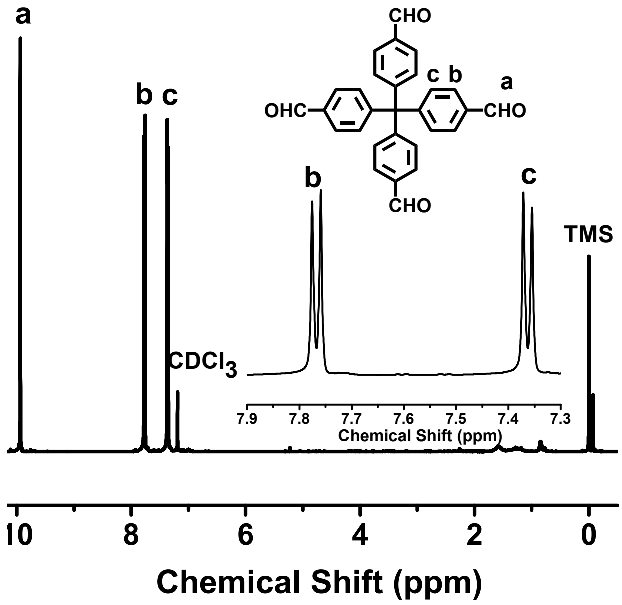

Fig. S9 ^{1}H NMR spectrum of tetrakis(4-aldehydephenyl)methane(TFPM).

Table S1. The chemical composition of sPANs

Samples	Measured value (wt%)			Theoretical value (wt%)		
	C	H	N	C	H	N
sPAN-1	66.05	5.180	6.65	78.60	7.82	13.58
sPAN-2	68.11	5.603	8.43	76.67	7.44	15.90

Table S2. SO_2, NH_3, and CO_2 uptakes in sPANs and some reported porous materials

Samples	S_{BET}	SO_2 (mmol/g)		NH_3 (mmol/g)		CO_2 (mmol/g)		Ref
	m²/g	273 K	298 K	273 K	298 K	273 K	298 K	
sPAN-1	113	8.45	5.56	5.35	3.55	1.55	1.09	This Work
sPAN-2	65	9.36	5.64	6.62	3.60	1.35	0.94	This Work
IRA-900 (Cl)	16.9	-	3.69	-	-	-	0.01	7
SIFSIX-3-Zn	-	about 2.34	2.10	-	-	-	-	8
SIFSIX-3-Ni	223	about 3.00	2.74	-	-	-	2.80	8
ELM-12	706	3.0	2.73	-	-	2.23	1.30	9
CC3	402	-	2.78	-	-	-	-	10
RCC3	-	-	12.34	-	-	-	-	10
6FT-RCC3	396	-	13.78	-	-	-	-	10
SU-101	350	-	2.20	-	-	2.50	-	11
NOT-300	-	8.1	-	-	-	7.0	-	12
NPC-1	3186.5	-	2.45	-	-	-	-	13
NPC-2	2426.2	-	1.76	-	-	-	-	13
NPC-3	2252.1	-	2.44	-	-	-	-	13
PIM-1	800	-	5.53	-	3.92	-	-	14
PIM1-AX	550	-	5.89	-	6.82	-	-	14
PIM-1-COOH	500		7.32	-	12.2	-	-	14
POP-BPh	965	-	6.5	-	-	1.92	1.07	15
PDVB	639	-	3.8	-	-	0.7	0.39	15
PI-COF-m	1003	-	6.5	-	-	-	-	16
PI-COF-m10	831	-	6.3	-	-	-	-	16
PI-COF-m20	548	-	5.6	-	-	-	-	16
$[HOOC]_0$-COF	713	-	-	-	-	-	7.00	17
$[HOOC]_{17}$-COF	652	-	-	-	-	-	9.34	17
$[HOOC]_{33}$-COF	458	-	-	-	-	-	8.21	17
$[HOOC]_{50}$-COF	279	-	-	-	-	-	6.67	17
$[HOOC]_{100}$-COF	150	-	-	-	-	-	4.14	17
PAF-1	4240	-	-	-	-	-	about 2.8	18
1T	915	-	-	-	-	-	3.8	19
1TC	552	-	-	-	-	-	6.41	19
1TCS	72.5	-	-	-	-	-	8.52	19

HCP-PN-1	420	-	-	-	-	1.63	1.32	[20]
HCP-PN-2	210	-	-	-	-	1.11	0.86	[20]
MPI	1001	-	-	-	-	2.76	1.71	[21]
MPI-S	448	-	-	-	-	1.58	1.07	[21]
MPI-Ag	103	-	-	-	-	1.46	0.97	[21]
PAN-5F	502	-	-	-	-	1.14	0.88	[22]
3AM2CL	196	-	-	-	-	1.21	0.60	[23]
2AM3CL	105	-	-	-	-	1.10	0.56	[23]
2AM2CL	47	-	-	-	-	0.99	0.52	[23]
TAM-POF	974	13.0	9.45	-	-	3.0	1.40	[24]
PCN-H	2000	-				-	2.28	[25]
ANOP-1	149	-	-	-	-	1.45	0.95	[26]
ANOP-2	638	-	-	-	-	2.31	1.38	[26]

Table S3. Single-site Langmuir−Freundlich simulated parameters for the two polymers.

Samples	**Gas**	**T (K)**	***a*** **(×10^2 mmol/g)**	***b*** **(×10^{-4} kPa^{-1})**	***c***	**R^2**
sPAN-1	**SO_2**	298	6.9667	9.3843	0.4524	0.9953
	NH_3	298	3.8517	8.3475	0.5197	0.9991
	CO_2	298	1.2736	1.2862	0.8996	0.9912
sPAN-2	**SO_2**	298	6.6838	9.7857	0.4604	0.9958
	NH_3	298	4.2162	8.8968	0.4895	0.9996
	CO_2	298	1.1304	0.9517	0.9348	0.9722

Table S4. SO_2/CO_2 selectivity of sPANs and some reported porous materials at 298 K and 100 kPa

Samples	$V(SO_2)/V(CO_2)$	SO_2/CO_2 selectivity	**Ref**
sPAN-1	10:90	37.6	This Work
sPAN-2	10:90	50.3	This Work
ELM-12	10:90	30	[9]
MFM-170	10:90	30	[27]
MFM-601	10:90	32	[28]
POP-Py	10:90	31	[15]
POP-BPy	10:90	29.8	[15]
POP-PyI	10:90	19.5	[15]
POP-PyA	10:90	25.0	[15]
POP-BPh	10:90	17.8	[15]
PDVB	10:90	19.5	[15]
AC from Petcoke	10:90	30	[29]
HNIP-TBMB-1	10:90	91	[30]
HNIP-TBMB-2	10:90	50	[30]
HNIP-DCX-1	10:90	23	[30]
GU-0.2	10:90	13.5[a]	[31]
GU-0.5	10:90	15.8 [a]	[31]
GU-1	10:90	16 [a]	[31]
Gu-2	10:90	13.3 [a]	[31]
ECUT-100	1:99	26.9-27.5	[32]

[a]296.2 K and 100 kPa.

Table S5. I_2 uptakes in sPANs and some reported porous materials

Samples	S_{BET} (m^2/g)	T(K)	I_2 (mg/g)	Ref
sPAN-1	113	348	2505	This Work
sPAN-2	65	348	2656	This Work
NRPP-1	1579	353	1920	33
NRPP-2	1028	353	2220	33
MALP-1	1179	350	2086	34
MALP-2	1126	350	2185	34
MALP-3	1141	350	1867	34
MALP-4	1093	350	2038	34
PAN-FPP5	788.0	345	2225	35
PAN-TPDA	752.0	345	1453	35
HCP-PN-1	420	353	1560	20
HCP-PN-2	210	353	1900	20
CSU-CPOPs-1	1032.4	353	4940	36
CSU-CPOPs-2	554.8	353	4240	36
CSU-CPOPs-3	268.8	353	3470	36
NOP-53	744	348	1770	37
NOP-54	1178	348	2020	37
NOP-55	526	348	1390	37
OM-COF-300	1410	348	3150	38
NM-COF-300	1374	348	1480	38
FcTz-POP	410	348	3960	39
BpTz-POP	414	348	2160	39
HCPs-B	717	348	1070	40
HCPs-N	579	348	2100	40
HCPs-S	167	348	1790	40
CMP-LS4	462	353	3320	41
CMP-LS5	1185	353	4400	41
CMP-LS6	679	353	2440	41
TTPT	315.5	350	1770	42
BDP-CPP-1	635	348	2830	43
BDP-CPP-2	235	348	2230	43
NBDP-CPP	658	348	1500	43
Azo-Trip	510.4	350	2380	44
ANOP-1	149	348	3111	26
ANOP-2	638	348	3209	26

Table S6. Results from Linear Regression of Adsorption Rate Experiments of sPAN-1 and sPAN-2

Samples	**Pseudo-first order kinetics (PFO)**			**Pseudo-second order kinetics (PSO)**		
	a (mg/g)	**K_1 (h^{-1})**	**R^2**	**a (mg/g)**	**K_2 ($\times 10^{-5}$ g/(mg×h))**	**R^2**
sPAN-1	2516	0.2012	0.9992	2897	8.509	0.9867
sPAN-2	2723	0.1386	0.9969	3298	4.497	0.9851

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