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Supporting Information

Porous Organic Materials with Ultra-small Pores and Sulfonic Functionality for Xenon Capture with Exceptional Selectivity

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Experimental Section

Chemicals: Biphenyl (99%, Aladdin), anhydrous $AlCl_3$ (99%, Aladdin), chlorosulfonic acid (HSO_3Cl) (99%, Alfa) were purchased from the corresponding chemical companies, and the solvents of tetrahydrofuran (THF), chloroform ($CHCl_3$), methanol (CH_3OH), acetone (CH_3COCH_3), ethanol (C_2H_5OH), hydrochloric acid (HCl), and dichloromethane (CH_2Cl_2) were commercially supplied.

Syntheses of PAF-45 and PAF-45S:

PAF-45: 1000 mg anhydrous $AlCl_3$ was added into a 250 ml round-shaped flask, and this flask was first evacuated and then inflated with N_2 for 3 times. 60 ml dried $CHCl_3$ was injected into the flask *via* a syringe and the mixture was heated to 60 °C for 3 h. Another solution containing 400 mg biphenyl in 40 ml dried $CHCl_3$ was added into the above solution and the mixture was kept under stirring at 60 °C for 24 h. After reaction, the raw powder was collected by filtration and washing with 1.0 M HCl, CH_3OH, and acetone. The brown powdered sample was further purified by Soxhlet extraction with C_2H_5OH, THF, and $CHCl_3$ for 48 h. The final product was obtained after drying at 120 °C for 8 h in vacuum.

PAF-45S (PAF-45-SO_3H): 500 mg PAF-45 in dichloromethane (20 ml) was added into a round-shaped flask (100 ml) which was protected by N_2 gas and cooled in an ice bath. Then, the chlorosulfonic acid (5.0 ml) was added into the round-shaped flask by dropwise. The resulting mixture was stirred at room temperature for three days. The raw product was poured into an ice water for quenching the smoke from the chlorosulfonic acid. The collected solid was subsequently washed with water substantially and dried to yield the final product of PAF-45S (PAF-45-SO_3H).

Characterizations: The porosities of PAF-45 and PAF-45S samples were identified by using N_2 physical adsorption measurements, which were performed at 77 K on Autosorb-iQ2 adsorptometer (Quantachrome Instruments). The adsorption isotherms for Xe and Kr at 273 K and 298 K were also recorded on the same apparatus. Prior to the tests, the samples were degassed at 150 ºC for 12 h under vacuum. X-ray diffraction (XRD) tests were carried out on a Rigaku SmartLab X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å) at 40 kV and 30 mA. Fourier-Transform infrared (FT-IR) spectra were acquired using a Nicolet iS50 Fourier transform infrared spectrometer. The element analysis was conducted on a EuroEA 3000 Series-CHNS/O analyzer.

Details of GCMC Simulation and DFT Calculations: The structures of PAF-45 and PAF-45S materials (Fig. S5) were built by using the Amorphous Cell module as implemented in Materials Studio 7.0. The pore properties of PAF-45 and PAF-45S were calculated by Zeo++ software,[1-2] and the adsorption isotherms were obtained by the grand canonical Monte Carlo (GCMC) method using the RASPA software,[3] total 1×10^6 steps were used in this simulation, the first 5×10^5 steps were used to equilibrate the system, and the last 5×10^5 steps were used for sampling and statistics. The Dreiding force field [4] was used to describe the framework atoms of PAF-45 and PAF-45S; and Kr and Xe were modeled using the single-site potential parameters taken from Pellenq.[5] The adsorption energy between the benzenesulfonic group (or benzene ring) and noble gas was calculated by using the density functional theory (DFT) method, in which wB97XD/def2-TZVPP method with BSSE correction as implemented in Gaussian 09 is employed.[6]

Breakthrough Measurement: Xe and Kr column breakthrough measuments were perfomed on home-made equipment with plug-flow dynamics. Approximately 1.0 g sample was packed into a 6.5 mm diameter and 15 cm long U-shaped stainless steel tube and then pretreated with N_2 at 100 °C for 6 h to remove the impurities. The pretreated sample was exposed to gas streams (supplied by gas cylinders) containing 0.5% Xe, 0.05% Kr and N_2 as a balance (total flow rate of 10 ml min^{-1}) at room temperature (~25 °C) and ambient pressure (~1.0 bar). Gas concentrations in the feed (by-pass mode) and effluent streams (sorption mode) were measured using an ultrasensitive gas chromatography (SCION 456GC) by direct transfer through transfer lines equipped with BR-Q PLOT (15m × 0.53mm × 20μm) and BR-Molsieve 5A columns (30m × 0.53mm × 50μm) connected to a thermal conductivity detector (TCD). Adsorption amounts were reported as gas moles adsorbed per sample weight (g or kg). For repeated uses, the sample was fully regenerated at 100 ºC in dry N_2 (10 ml min^{-1}) for 6 h.

Supplementary Tables

Table S1 Textural data for PAF-45 and PAF-45S samples

Sample	S_{BET} (m^2 g^{-1})[a]	Pore Size (Å)[b]	V_{total} (cm^3 g^{-1})[c]	V_{micro} (cm^3 g^{-1})[d]
PAF-45	785.9	5.2	0.362	0.248
PAF-45S	455	5.2	0.260	0.179

[a] BET surface areas were calculated at P/P_0 = 0.005-0.05, [b] pore sizes in diameter were determined by QS-DFT method, [c] total pore volumes were calculated at P/P_0 = 0.98, [d] cumulative pore volumes were calculated at pore width ≤ 2.0 nm (micropore volumes).

Table S2 Simulated pore properties of PAF-45 and PAF-45S samples

Sample	Surface Area [a] (m^2 g^{-1})	Pore Volume [b] (cm^3 g^{-1})	Void [c] (%)	Pore Size [d] (Å)
PAF-45	2453	0.263	51.8	6.6
PAF-45S	2129	0.183	49.1	6.4

[a] the accessible surface area, [b] free pore volume, [c] ratio of free volume to total pore volume, [d] the maximal pore diameter.

Table S3 Adsorption energies ΔE and distances *d* between the noble gas and the centroid of benzene ring in PAF-45 and PAF-45S samples

	C_6H_6-SO_3H		C_6H_6	
	ΔE, kJ mol^{-1}	*d*, Å	ΔE, kJ mol^{-1}	*d*, Å
Kr	-6.98	3.688	-5.69	3.700
Xe	-9.54	3.863	-7.95	3.869

Table S4 A summary of the Xe/Kr selectivity for PAF-45 and PAF-45S samples

Sample	Henry's constant of Xe	Henry's constant of Kr	Xe/Kr

	adsorption (cm^3 g^{-1} bar^{-1})	adsorption (cm^3 g^{-1} bar^{-1})	selectivity
PAF-45	243.23	30.02	8.1
PAF-45S	250.24	14.96	16.7

Table S5 Breakthrough results of the Xe uptake and the Xe/Kr selectivity at 1.0 bar for selected adsorbent materials

Material	Breakthrough Xe uptake (mmol g^{-1})	Breakthrough Selectivity (Xe/Kr)
CC3	0.011	20.4[a]
Ni-DOBDC	0.048	7.3[a]
CROFOUR-1-Ni	-	19.8[a]
CROFOUR-2-Ni	-	14.3[a]
SBMOF-1	0.0132	~16[a]
$Co_3(HCOO)_6$	-	6[b]
HKUST-1	0.0085	2.6[c]
Activated Carbon	-	2.8[c]
MOF-505	-	9[c]
MOF-74-Co	-	6.4[d]
UiO-66(Zr)	-	3.8[d]
PAF-45	0.0924	12.3[a]
PAF-45S	0.053	24.1[a]

[a] From breakthrough experiment (Xe 500 ppm, Kr 50 ppm), [b] From breakthrough experiment (Xe/Kr: 10/90), [c] From breakthrough experiment (Xe/Kr: 20/80), [d] From breakthrough experiment (Xe/Kr: 20/80, at 303 K).

Supplementary Figures

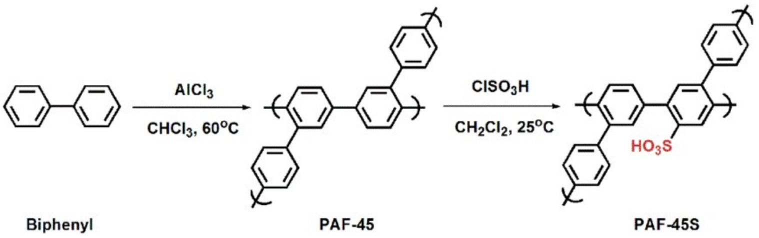

Fig. S1 Schematic representation for the synthesis of PAF-45S.

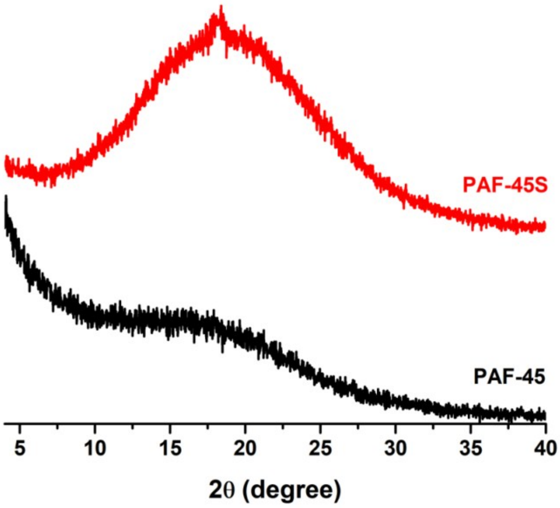

Fig. S2 XRD patterns of PAF-45 and PAF-45S samples.

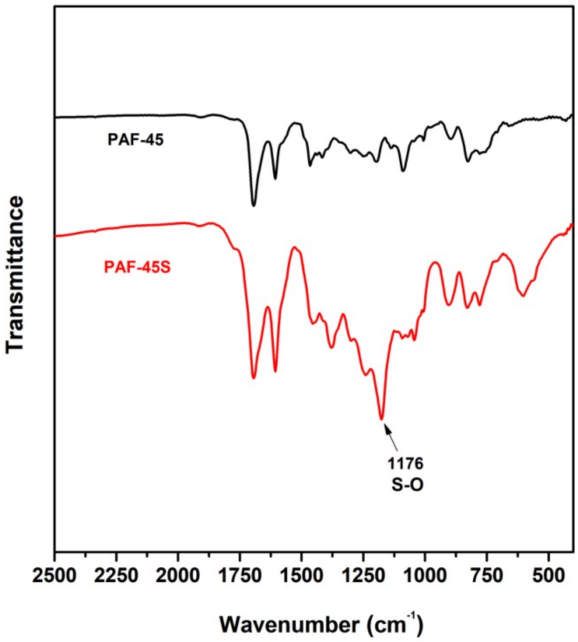

Fig. S3 IR spectra of PAF-45 and PAF-45S samples.

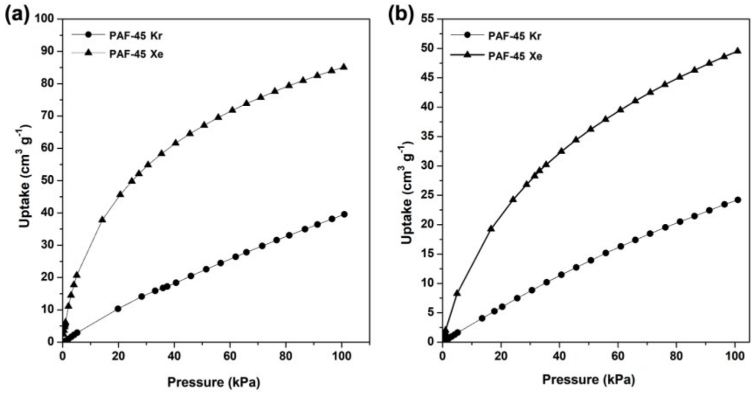

Fig. S4 Xe and Kr adsorption isotherms for the PAF-45 sample at 273 K (a), and 298 K (b).

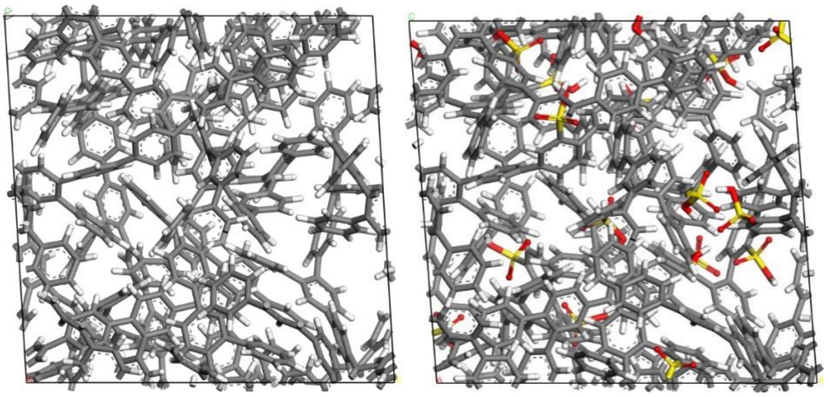

Fig. S5 Optimized structures of PAF-45 and PAF-45S materials derived from DMol3.

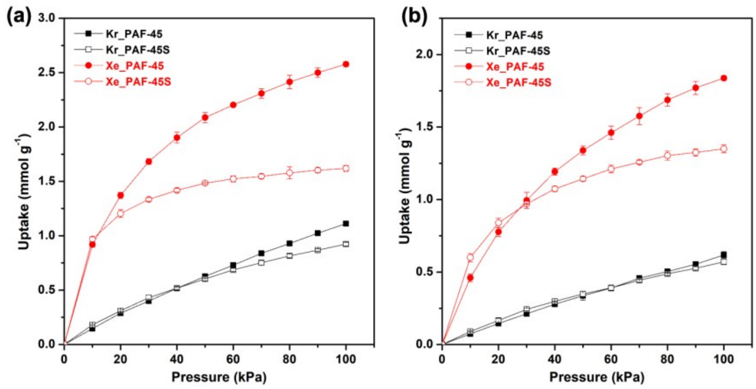

Fig. S6 Simulated adsorption isotherms of Kr and Xe on PAF-45 and PAF-45S samples at 273 K (a) and 298 K (b).

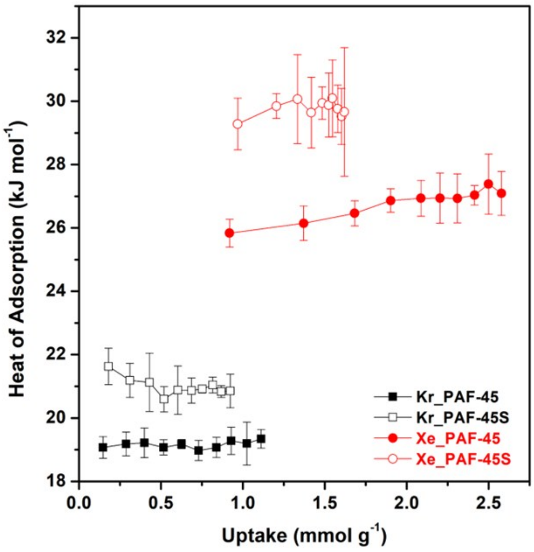

Fig. S7 Simulated adsorption heats for Kr and Xe on PAF-45 and PAF-45S samples at 298 K.

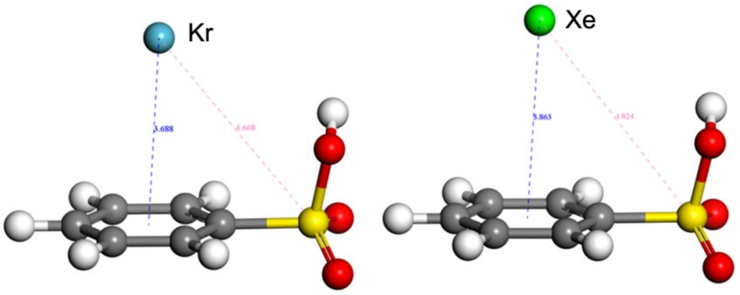

Fig. S8 The adsorption configurations between benzenesulfonic group and noble gas, which is calculated by using wB97XD/def2-TZVPP method with BSSE correction.

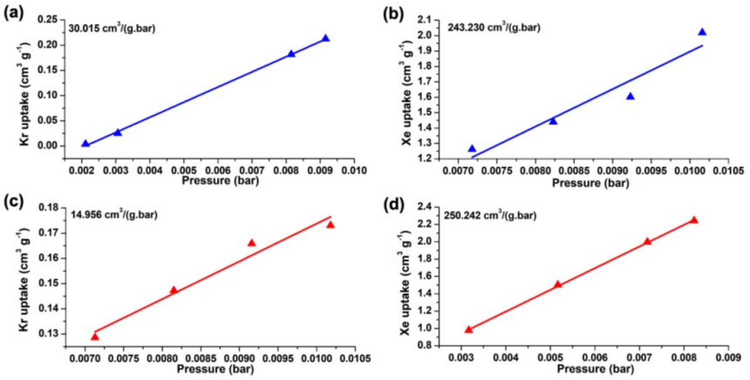

Fig. S9 Respective fittings of Henry's constants in PAF-45 (a-b) and in PAF-45S (c-d) using Kr and Xe adsorption isotherms at 298 K.

Supplementary References

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