Electronic Supplementary Information

The directing effect of linking unit on building microporous architecture in tetraphenyladmantane-based poly(Schiffbase) networks

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Experimental

Materials

Adamantane, *p*-phenylenediamine and *m*-phenylenediamine were purchased from J&K Chemical Co., Ltd. DMSO, DMF, THF and other reagents were purchased from Shanghai Chemical Reagent Co. DMSO was purified by distillation under reduced pressure and dehydrated with 4A molecular sieves, and other reagents were of reagent grade and used as received.

1,3,5,7-tetrakis(4-formylphenyl)adamantane (TFPA). 1,3,5,7-Tetraphenyladamantane (TPA) was prepared in reference to the procedure^{S1} with some modifications. TFPA was synthesized following the similar method as described in the literature^{S2}. TPA (3.80 g, 8.6 mmol, 1 eq.) and dichloromethane (DCM, 150 ml) was added to a 250 mL three-necked roundbottomed flask with a magnetic stir-bar. Under a dried argon-flowing, the mixture was stirred rapidly and cooled to -10 °C with an ice/salt bath. Titanium tetrachloride (19.0 mL, 172.4 mmol, 20 eq.) was then added slowly to the mixture and stirred at -10 °C for 30 min. α, α -Dichloromethyl methylether (12.5 mL, 137.9 mmol, 16 eq.) was subsequently added dropwise to the mixture, which turned pale yellow during the addition. The reaction was held at -10 °C for 3 h and then allowed to warm to room temperature with stirring overnight. The mixture was poured into 300mL ice-water, and 100 mL of 1M HCl was added. Then, the resulting mixture was stirred for 30 min. During this time, the red/black organic phase turned bright yellow and some white precipitate was observed. The two-phase mixture was separated and the aqueous phase was washed twice with 100 mL DCM. The combined organic phases were washed once with 100 mL of 1M HCl, twice with deionized water, once with saturated aqueous NaHCO₃, once with saturated aqueous NaCl, and dried with MgSO4. The solution was filtered and removed solvent by rotary evaporation. The resulted yellow solid was purified by column chromatography and then recrystallized from dioxane to give white to very pale yellow crystals of TFPA. M. p. >280 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.02 (s, 1H), 7.91 (d, 2H), 7.67

(d, 2H), 2.27 (s, 3H). FTIR (KBr, cm⁻¹): 2928, 2852, 1700, 1600, 1162, 845, 756.

Poly(Schiff base) Microporous Networks. PSN-1 was prepared in a dry Schlenk flask equipped with a stirrer and a condenser was degassed using two evacuation-argon-backfill cycles. Under argon flow, TFPA (0.66 g, 1.2 mmol), *m*-phenylenediamine (0.26 g, 2.4 mmol) and 12 mL DMSO were added and heated for 3d. Finally, the system was cooled down and the solid was isolated, washed successively with DMF, methanol and THF. The resultant product was extracted with THF in a Soxhlet apparatus for 24 h, and dried at 120 °C under vacuum to constant weight in a good yield (90–95%). Elemental analysis: Calculated (%): C, 85.93; H, 6.06; N, 8.02. Found (%): C, 83.21; H, 6.18; N, 7.54.

The polymerization of **PSN-2** was carried out under the same condition as **PSN-1** with the similar yield. Elemental analysis: Calculated (%): C, 85.93; H, 6.06; N, 8.02. Found (%): C, 80.96; H, 6.23; N, 7.37.

Instruments

Fourier transform infrared spectra (FTIR) of synthesized products were recorded using a Nicolet 20XB FT-IR spectrophotometer in 400-4000 cm⁻¹. Samples were prepared by dispersing the complexes in KBr to form disks. ¹H NMR spectra were recorded on a 400 MHz Varian INOVA NMR spectrometer, using tetramethylsilane as an internal standard. Solid-state ¹³C CP/MAS (cross-polarization with magic angle spinning) spectra were measured on a Varian Infinity-Plus 400 spectrometer at 100.61 MHz at an MAS rate of 10.0 kHz using zirconia rotors 4 mm in diameter using a contact time of 4.0 ms and a relaxation delay of 2.0 s. Wide-angle X-ray diffractions (WAXD) from 5° to 60° were performed on Rigku D/max-2400 X-ray diffractometer (40 kV, 200 mA) with a copper target at a scanning rate of 2° min⁻¹. Elemental analyses were determined with an Elementar Vario EL III elemental analyzer. TG 209 thermal analyzer by heating the samples (~8 mg) up to 800 °C with ramping rate of 10 °C min⁻¹ under nitrogen flow. Adsorption and desorption measurements for all the gases and vapors were conducted on an Autosorb iQ (Quantachrome) analyzer. Prior to measurements, the samples

were degassed at 150 °C under high vacuum overnight. Adsorption and desorption isotherms of nitrogen were measured at 77 K. The surface areas were calculated according to the Brunauer-Emmett-Teller (BET) model in the relative pressure (P/P₀) range from 0.07 to 0.15 for **PSN-1** and from 0.20 to 0.30 for **PSN-2**. CO₂ adsorption isotherms were measured at 273 K and 298 K up to 1.0 bar. H₂ adsorption isotherms were measured at 77 K and 87 K up to 1.0 bar. The isosteric enthalpies of adsorption (Q_{st}) were calculated from the gas isotherms at different temperatures according to Clausius-Clapeyron equation.^{S3} From the virial plots of gases, the first virial coefficients (A₀) could be calculated. Subsequently, Henry's law constant (K_H) were obtained using the equation $K_H = \exp(A_0)$, whereas the limiting enthalpies of adsorption (Q₀), i.e., Q_{st} at zero surface gas coverage, were derived from the plot slope of lnK_H vs. 1/T.

References

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Fig. S1 TGA curves of the two poly(Schiff base)s.



Fig. S2 FTIR spectra of the two poly(Schiff base)s.



Fig. S3 Solid-state ¹³C CP/MAS NMR spectra the two poly(Schiff base)s.

(Asterisks (*) indicate peaks arising from spinning side bands)

	\mathbf{S}_{BET}	$\mathbf{S}_{\text{Langmuir}}$	S _{micro}	V _{total}	V _{micro}	Pore size
Samples	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$	(nm)
PSN-1	1045	1499	589	0.86	0.27	0.7
PSN-2	376	611	74	0.39	0.05	1.1 / 2.2

Table 1 Porous parameters of the two poly(Schiff base)s obtained by N_2 adsorption



Fig. S4 Wide angle X-ray diffractions of the two poly(Schiff base)s.

		CO ₂ uptake ^a	L		H ₂ uptake	b
Sample	273K	298K	$Q_{ m o}$	77K	87K	$Q_{ m o}$
	(wt%)	(wt%)	(kJ/mol)	(wt%)	(wt%)	(kJ/mol)
PSN-1	15.0	9.8	31.4	1.26	0.75	7.4
PSN-2	6.7	4.6	30.0	0.90	0.63	7.0

Table 2 Uptakes of CO_2 , H_2 and Q_0 values for the two porous poly(Schiff base)s

^a Uptakes for CO_2 were determined at 273/298 K and 1 bar. ^b Uptakes for H_2 were determined at

77/87 K and 1 bar.



Fig. S5 Variations of CO₂ isosteric enthalpies with the adsorbed

amount for PSN-1 and PSN-2.



Fig. S6 FTIR spectrum of the 1,3,5,7-tetrakis(4-formylphenyl)adamantane.



Fig. S7 ¹H NMR spectrum of the 1,3,5,7-tetrakis(4-formylphenyl)adamantane.