

Supporting Information

A Facile Approach to Prepare Microporous Polycarbazole Network P-Tetra(4-(N-carbazolyl)phenyl)silane with High CO₂ Storage and Separation Properties

Fei Jiang,^{‡a} Jianling Sun,^{‡b} Renqiang Yang^{*c}, Shanlin Qiao,^c Zengjian An,^a Jianqing Huang,^a Haifang Mao,^a Guie Chen^a and Yujie Ren^{*a}

^a School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China.

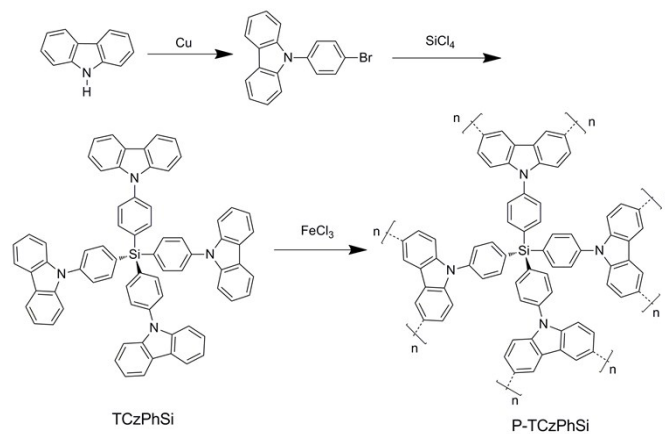
E-mail: clab@sit.edu.cn; Fax: +86 21 60877220; Tel: +86 21 60877223

^b Beijing Municipal Research Institute of Environmental Protection, Beijing 100037, China.

^c CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China.

E-mail: yangrq@qibebt.ac.cn; Fax: +86 532 80662778; Tel: +86 532 80662700

[‡] These authors contributed equally to this work.



Scheme S1. Synthetic route of network **P-TCzPhSi**.

Materials

All chemicals were commercial grade and used as received unless otherwise specified. Toluene and tetrahydrofuran (THF) were freshly distilled from sodium and benzophenone under nitrogen prior to use. P-TCzPhSi was synthesized shown in **Scheme 1**.

1-Bromo-4-(N-carbazolyl)benzene

A mixture of CuSO₄ (6.38 g, 40.0 mmol), K₂CO₃ (13.82 g, 100.0 mmol), dibromobenzene (23.59 g, 100.0 mmol) and carbazole (8.36 g, 50.0 mmol) was heated to 210 °C for 12 h under argon atmosphere. After cooling to room temperature, the mixture was dissolved in CH₂Cl₂ (200 mL) and washed with H₂O. The organic layer was extracted with CH₂Cl₂ and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane as the eluent to give a white solid (8.38 g, 52%). ¹H NMR (CDCl₃): 8.05 (d, 2 H, J = 7.6 Hz), 7.58 (d, 2 H, J = 8.4 Hz), 7.39-7.27 (m, 4 H), 7.22 (t, 3 H, J = 7.2 Hz). ¹³C NMR (CDCl₃): δ140.8, 137.0, 133.4, 128.9, 126.4, 123.8, 121.1, 120.8, 120.6, 109.9.

Tetra (4-(N-carbazolyl)phenyl)silane (TCzPhSi)

n-BuLi in 2.5 M hexane (2.64 mL, 6.6 mmol) was added dropwise to a solution of 1-Bromo-4-(N-carbazolyl)benzene (1.93 g, 6.0 mmol) in dry THF (30 mL) at -78 °C. After stirring for 30 min., tetrachlorosilane (0.76 ml, 6.0 mmol) was added slowly to the mixture. The mixture was then allowed to warm to ambient temperature and stirred overnight. After the reaction, the precipitate in the mother liquid was filtered and washed with H₂O and CH₂Cl₂ to afford pure monomer as a white solid in 70% yield. ¹H NMR (CDCl₃): δ 8.18 (d, 8 H, J = 7.6 Hz), 8.06 (d, 8 H, J = 8.4 Hz), 7.80 (d, 8 H, J = 8 Hz), 7.61 (d, 8 H, J = 8.4 Hz), 7.45 (t, 8 H, J = 7.2 Hz, J = 7.2 Hz), 7.32 (t, 8 H, J = 8 Hz, J = 6.8 Hz). ¹³C NMR (CDCl₃): δ 140.6, 139.8, 138.1, 132.5, 126.7, 126.2, 123.8, 120.6, 120.4, 110.1.

P-Tetra (4-(N-carbazolyl)phenyl)silane (P-TCzPhSi)

The monomer (TCzPhSi) (100 mg, 0.48 mmol) and ferric chloride (FeCl₃) (324 mg, 1.92 mmol) were dissolved in 6 mL anhydrous chloroform within a Pyrex tube (o.d × i.d = 10 mm × 8 mm) under sonication for 10 min. After freezing the solution

with liquid N₂, which was then took three times of freeze-pump-thaw cycles, the frozen tube was vacuumed and then quickly sealed with a torch reducing the length of the tube into about 25 cm. After heating at 60 °C for 72 h, yellow solid was isolated by hot filtration and washed with anhydrous tetrahydrofuran (THF). The obtained powder was immersed in anhydrous THF, and the solvent was exchanged with fresh THF and methanol for several times and concentrated hydrochloric acid solution for three times. After extracted in a Soxhlet extractor with methanol for 24 h, then with THF for another 24 h extraction, the desired polymer was collected and dried in vacuum oven at 80 °C overnight, afford as a yellow solid in 91% yield. ¹³C NMR (CDCl₃): δ 140.6, 139.8, 138.1, 132.5, 126.7, 126.2, 123.8, 120.6, 120.4, 110.1. Calcd: C, 86.71%; N, 5.62%; H, 4.85%. Found: C, 85%; N, 4.85%; H, 4.22%.

Characterization

The structure of P-TCzPhSi was confirmed by ¹³C NMR and FT-IR spectroscopy. P-TCzPhSi was measured by the Bruker Avance III model 600 MHz using CDCl₃ as solvent. ¹³C CP/MAS solid-state NMR measurement was carried out on a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 kHz to confirm the structure of P-TCzPhSi. FT-IR spectra were collected in attenuated total reflection (ATR) mode on a Thermo Nicolet 6700 FT-IR Spectrometer. Scanning electron microscopy (SEM) was recorded using a Hitachi S-4800 with acceleration voltage 5.0 kV and working distance 9.6 mm. Samples were coated on a thin layer of Au before investigation. The polymer was degassed at 120 °C for 10 hours under vacuum to remove residual moisture and other trapped gases before analysis. All the samples were tested on a Autosorb-iQ-MP-VP volumetric adsorption analyzer with the same degassing procedure. BET surface areas and pore size distributions of P-TCzPhSi were measured by nitrogen adsorption-desorption at 77 K in a liquid nitrogen bath. CO₂, and CH₄ isotherms were measured at 273 K and 298 K up to 1.1 bar, respectively. H₂ isotherms were measured at 77 K up to 1.1 bar.

Clausius-Clapeyron equation

To determine the binding affinity of polymer for CO₂, the isosteric heat of adsorption (Q_{st}) is calculated using the following Clausius–Clapeyron equation.

$$\ln P = - Q^0(n^m) / RT + C(n^m) \text{ (at constant } n^m) \quad (1)$$

Here P and T are the pressure and temperature at the equilibrium state, R is the universal gas constant. C is an integration constant which is a function of n^m only.

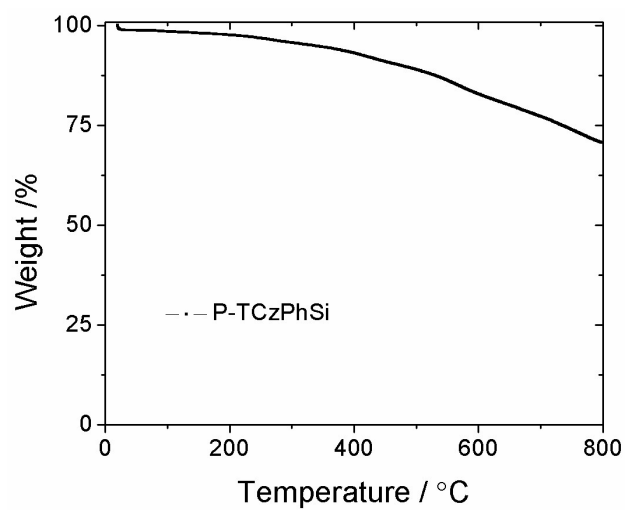
Thermogravimetric analysis

Figure S1. TGA of network **P-TCzPhSi**.