

## ELECTRONIC SUPPLEMENTARY INFORMATION

# Building Ultramicropores within Organic Polymers Based on a Thermosetting Cyanate Ester Resin

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## Experimental Section

**Instrumentation.** Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-20DXB IR spectrophotometer. 64 scans were signal averaged with a resolution of  $2\text{ cm}^{-1}$  at room temperature. Samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on 400-MHz Varian INOVA NMR spectrometer, with the tetramethylsilane as an internal reference. Elemental analyses were determined with an Elementar Vario EL III elemental analyzer. TGA was performed on a NETZSCH TG 209 thermal analyzer both in purified nitrogen and air atmosphere, and all samples (around 10mg) were heated from 25 to 700 °C at a rate of 10 °C /min, under the gas flow rates of 60 ml/min. Differential scanning calorimetry (DSC) measurements were conducted with a NETZSCH DSC 204 instrument. The calorimeter was calibrated with indium metal as a standard. About 10-14 mg samples were used at a heating rate of 10 °C /min under a flow of nitrogen (20 ml/min). A wide angle X-ray diffraction (WAXD) study of the sample was performed using Rigku D/max-2400 X-ray diffractometer (40 kV, 200 mA) with a copper target at a scanning rate of 2 deg/min, scanned from 5 to 60 deg. Nitrogen adsorption-desorption experiments were conducted using an automated micropore gas analyzer Autosorb-1-MP (Quantachrome Instruments). Before sorption analysis, all samples were degassed at 150 °C under a high vacuum overnight.

**Materials.** Tetrachlorosilane, cyanogen bromide, *n*-butyllithium, and 1,4-dibromobenzene were purchased from J&K-Chemical Co., Ltd. Triisopropyl

borate and diphenylsulfone was purchased from Shanghai Chemical Reagent Co. Diethyl ether and tetrahydrofuran(THF) were purified by refluxing over sodium with the indicator benzophenone complex. Triethylamine were purified by distillation under reduced pressure over calcium hydride. The other solvents were of reagent grade and were used as received.

#### **Synthesis of Tetrakis (4-bromophenyl)silane (TBS).**

Tetrakis(4- bromophenyl)silane was prepared according to a modified procedure of the literature.<sup>1</sup> A solution of 1,4-dibromobenzene (25.0 g, 105.2 mmol) in ether (300 mL) was stirred at  $-50^{\circ}\text{C}$  under dry  $\text{N}_2$  and treated dropwise with a solution of *n*-butyllithium (42.1 mL, 2.5 M in hexane, 105.2 mmol). The resulting mixture was kept at  $-10^{\circ}\text{C}$  for 30 min, and then  $\text{SiCl}_4$  (3.0 mL, 26.3 mmol) was added dropwise. The mixture was stirred at  $-10^{\circ}\text{C}$  for 30 min and at  $25^{\circ}\text{C}$  for 2 h. Then 1 M aqueous HCl was added, and the resulting mixture was extracted with ether. The combined extracts were washed with  $\text{H}_2\text{O}$  and brine, dried over  $\text{MgSO}_4$ , and filtered. Volatiles were removed by evaporation under reduced pressure, and the residue was recrystallized twice from  $\text{CH}_2\text{Cl}_2$  to afford tetrakis(4- bromophenyl)silane as a colorless solid (16g, 93.0%). IR (KBr,  $\text{cm}^{-1}$ ):1377, 1066, 1010.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.53 (d, 8H), 7.38 (d, 8H). Melting point: 242-243  $^{\circ}\text{C}$ .

#### **Synthesis of Tetrakis (4-hydroxyphenyl)silane (THS).**

Tetrakis(4-hydroxyphenyl)silane was prepared according to a modified procedure of the literature.<sup>2</sup> A solution of tetrakis(4-bromophenyl)silane (TBS; 1.30 g, 1.99 mmol) in THF (125 mL) was stirred at  $-78^{\circ}\text{C}$  under dry  $\text{N}_2$  and treated dropwise with

a solution of *n*-butyllithium (6.40 mL, 2.5 M in hexane, 16.00 mmol). The resulting mixture was kept at  $-78^{\circ}\text{C}$  for 30 min, and then  $\text{B}(\text{O-}i\text{-Pr})_3$  (5.50 mL, 24.00 mmol) was added dropwise. The mixture was stirred  $-78^{\circ}\text{C}$  for 20 min and then at  $25^{\circ}\text{C}$  for 12 h. To the solution was added 3 M aqueous NaOH (6 mL), followed by 30% aqueous  $\text{H}_2\text{O}_2$  (4 mL), and then the mixture was heated at reflux for 1 h. The resulting mixture was acidified with 1 M aqueous HCl and concentrated by partial evaporation of volatiles under reduced pressure. The aqueous concentrate was extracted with ethyl acetate, and the combined extracts were washed with water and brine, dried over  $\text{MgSO}_4$ , and filtered. Volatiles were removed by evaporation under reduced pressure, and the residue was dried in air to afford tetrakis(4-hydroxyphenyl)silane as a colorless solid (THS; 0.51 g, 63.2%). IR (KBr,  $\text{cm}^{-1}$ ): 3330.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 8.49 (s, 4H), 7.35 (d, 8H), 6.87 (d, 8H). Melting point:  $276\text{--}280^{\circ}\text{C}$ .

#### **Synthesis of Tetrakis(4-cyanatophenyl)silane (TCS)**

To a 100 ml three-necked flask was charged 20 ml of dried acetone, and the system was cooled to  $-30^{\circ}\text{C}$ . Then BrCN (0.867 g, 8.18 mmol) and tetrakis(4-hydroxyphenyl)silane (THS; 0.712 g, 1.78 mmol) was dissolved in acetone. Under the nitrogen atmosphere, to the above solution, triethylamine (1 ml, 7.20 mmol) in acetone (10 ml) was added slowly over a period of 1 h. After addition was completed, the reaction temperature was increased to  $-20^{\circ}\text{C}$ , and the reaction was allowed to proceed at this temperature for another 2 h. Then, the mixture was filtered to remove the  $\text{Et}_3\text{N} \cdot \text{HBr}$  salt. The filtrate was evaporated to dryness. The solid residue was

dissolved in 20 ml of dichloromethane and washed with deionized water three times ( $3 \times 50$  ml). The organic layer was dried over  $\text{MgSO}_4$ , filtered and concentrated by rotary evaporation under reduced pressure. The resulting solution was poured into diethyl ether, and the mixture was placed in a refrigerator overnight to afford tetrakis(4-cyanatophenyl)silane as an off-white crystalline solid (TCS; 0.71g, 80%). IR (KBr,  $\text{cm}^{-1}$ ): 2271, 2235.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 7.76 (s, 8H), 7.55 (d, 8H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 155.5, 139.8, 132.2, 116.6, 108.9. Anal. Calcd for  $\text{C}_{28}\text{H}_{16}\text{N}_4\text{O}_4\text{Si}$ : C, 67.19; H, 3.22. Found: C, 67.21; H, 3.20. Melting point: 165–168 °C.

### **Preparations of Microporous Polycyanurate Networks**

A typical procedure was as follows. TCS was polymerized in diphenylsulfone under nitrogen. A cure schedule of 170 °C for 4 h, 190 °C for 4 h, 230 °C for 8 h, and lastly 270 °C for 20 h was employed. The gel obtained was crushed, and extracted with THF in a Soxhlet apparatus for 48h. The solid was then dried *in vacuo* at 180 °C.

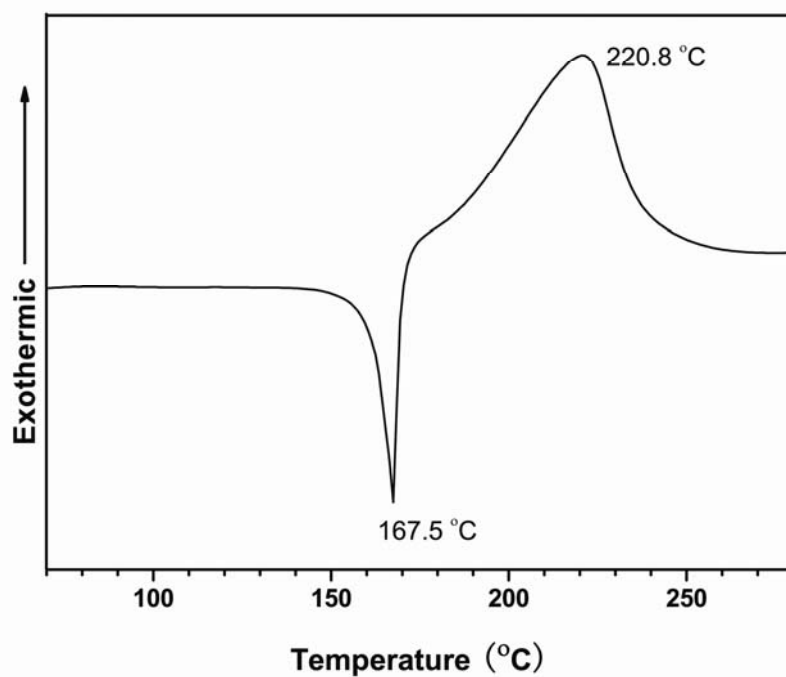


Fig. S1 DSC thermograms of TCS at a heating rate of 10 °C/min.

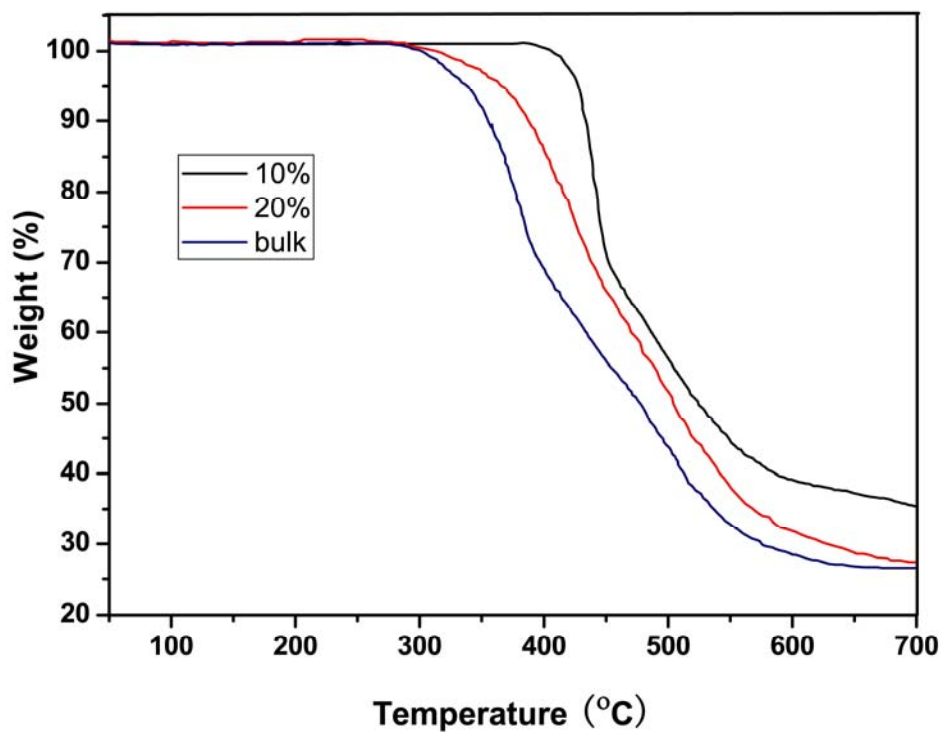
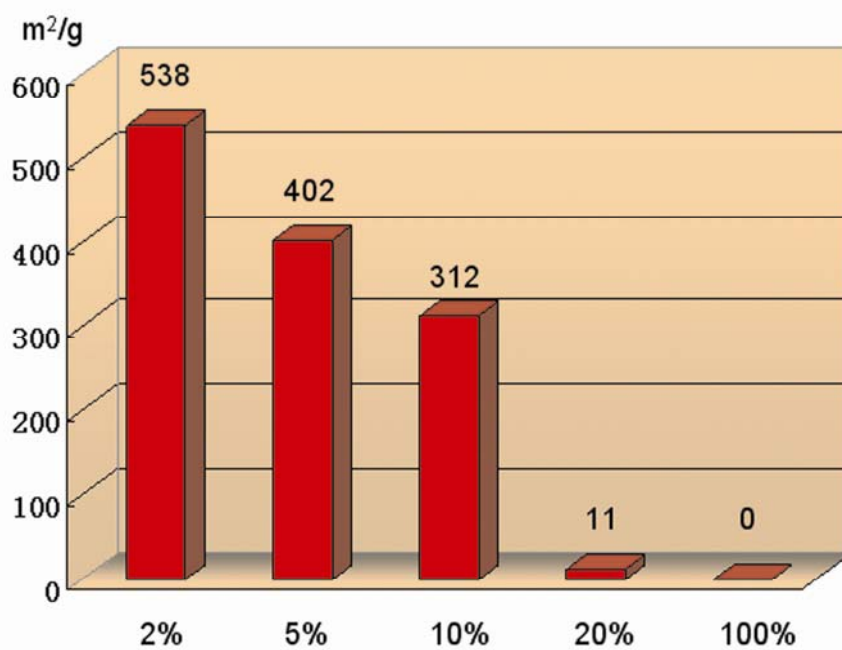
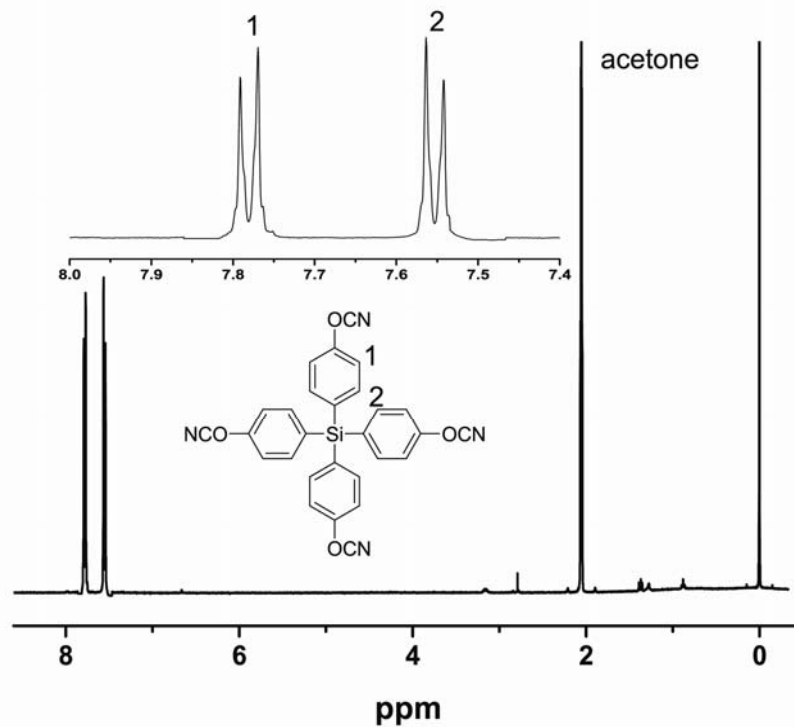


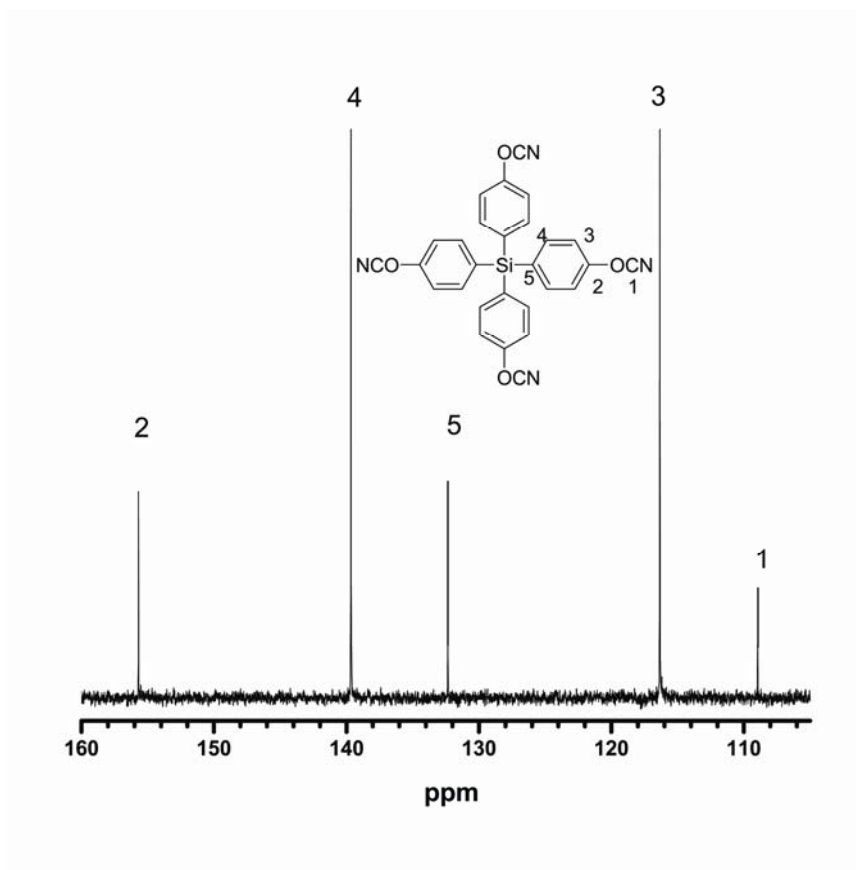
Fig. S2 Thermogravimetric analysis of networks cured in different media concentration (10 wt%, 20 wt%, bulk ).



**Fig. S3** Effect of media concentration on the surface area of the final cured network.

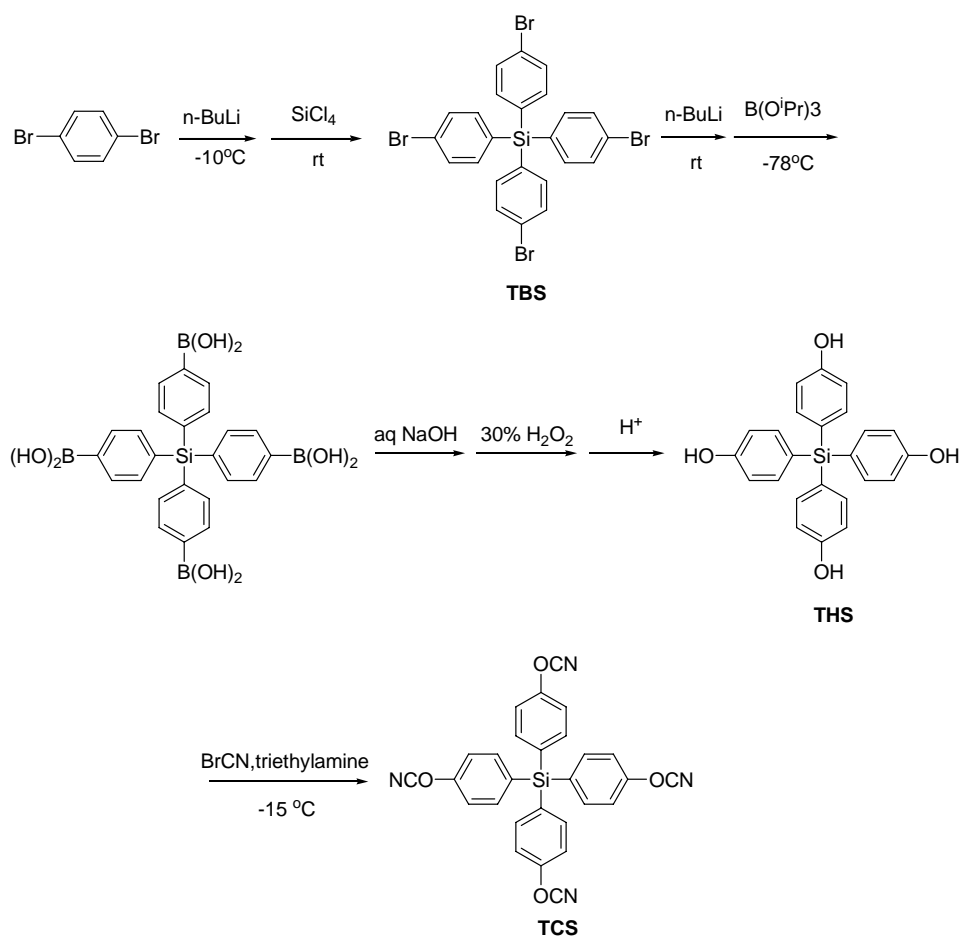


**Fig. S4** The <sup>1</sup>H NMR spectrum of TCS.



**Fig. S5** The  $^{13}\text{C}$  NMR spectrum of TCS.





**Scheme S1** Preparation of cyanate ester monomer TCS.

## References

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