100% thiol-functionalized ethylene PMOs prepared by "thiol acid-ene" chemistry

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Supporting information

Experimental

Materials

1,2-(*E*)-bis(triethoxysilyl)ethene was obtained according to a previously described procedure.¹ 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Aldrich) and thioacetic acid (96%, Aldrich) were used as supplied. Propylamine, purchased from Aldrich, was distilled from sodium hydroxide (NaOH, 99%, Aldrich) under inert atmosphere. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$), Bu^tOH and HCl were obtained from Aldrich for the synthesis of the 1-thiol-ethylene-bridged PMO.

Characterization

¹H and ¹³C NMR spectra of the liquid solutions were recorded on a Bruker spectrometer at 300 MHz with CDCl₃ as NMR solvent. XRD measurements were performed on an ARL X'TRA Diffractometer from Thermo using radiation CuKa (45 kV and 44 mA). N₂ adsorption-desorption measurements at the temperature of liquid nitrogen (77K) were measured using a Belsorp-mini II gas analyzer. Prior to measurement, the samples were dried overnight under vacuum at 120 °C. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method and pore size distribution was calculated by analysis of the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method. The diffuse reflectance infrared Fourier transform (DRIFT) and Raman spectra of the samples were collected on a Thermo FTIR spectrometer. For DRIFT measurements, the powder sample was placed in a diffuse reflectance environmental chamber connected to a temperature controller. The sample was heated in situ from room temperature to 150 °C under vacuum. The solid-state ¹³C CP/MAS NMR spectra were recorded on a Bruker Avance 400 WB spectrometer at 100.61 MHz, respectively. An overall 1000 free induction decays were accumulated. The excitation pulse and recycle time for ¹³C CP/MAS NMR were 6 ms and 2 s, respectively. Chemical shifts were measured relative to a tetramethylsilane standard. CHNS elemental analysis was performed on a Thermo Flash 2000 elemental analyser.

Synthesis of 1-thiol-1,2-bis(triethoxysilyl)ethane.

The thio-acid-ene reaction under photochemical conditions was performed as follows:

2,2-dimethoxy-2-phenylacetophenone (20)mg, 0.078 mmol) and 1,2-(E)bis(triethoxysilyl)ethene (2 mL, 5,67 mmol) (Fig S1 (top). $\delta_{\rm H}$ (300.13 MHz; CDCl₃; CHCl₃): 1.23 (t, 18H, J_{HH}=7 Hz, O-CH₂-CH₃), 3.83 (q, 12H, J=7 Hz, O-CH₂-CH₃), 6.66 (s, 2H, CH=CH)) were shaken in a closed flask until complete dissolution of the photoinitiator. The solution was purged with N₂ for 2 min to assure the elimination of oxygen. A small excess of thioacetic acid (0.52 g, 6.83 mmol, 1.2 eq) was subsequently added to the solution using a syringe. The solution was again purged with N₂ for 2 min. Finally, the mixture was placed in a Metalight Classic UV irradiation chamber fitted with 12 360 nm UV-lamps and was irradiated for 2 h. The yellowish solution (1) was analyzed by ¹H NMR in deuterated chloroform (Fig. S1 (bottom)). $\delta_{\rm H}$ (300.13 MHz; CDCl₃; CHCl₃): 0.87-0.96 (dd, 1H, J_{c,b}= 15.9 Hz, J_{c,a} = 10.8 Hz, CH-CH-SCOCH₃-), 1.21 (t, 18H, J = 7 Hz, O-CH₂-CH₃), 1.27 (dd, 1H, J_{b,c} = 15.9 Hz, J_{b,a} = 4.5 Hz, CH-CH-SCOCH₃-), 2.32 (s, 3H, CH₃-CO-S-CH), 2.4 (s, 3H, CH₃-CO-SH), 2.5 (s, 1H, CH₃-CO-SH), 3.13-3.18 (dd, 1H, J_{a,c} = 10.8 Hz, J_{a,b} = 4.5 Hz, -CH-SCOCH₃), 3.83 (q, 12H, J = 7 Hz, O-CH₂-CH₃).

The aminolysis of the thio-acetyl groups was subsequently carried out by treatment with dry propylamine (2 mL, 24,32 mmol). The propylamine was added slowly to the solution previously cooled in an ice-bath. Then, the unreacted amine was removed using a rotary evaporator to produce a yellow slightly turbid liquid (**2**) (Fig. S2 and S3). This liquid was used directly in the synthesis of the PMO without further purification. $\delta_{\rm H}$ (300.13 MHz; CDCl₃; CHCl₃): 0.89 – 0.98 (m, 3H, -CO-NH-CH₂-CH₂-CH₃), 0.90 (dd, 1H, J_{c,a} = 4.3 Hz, J_{c,b} = 15.6 Hz, CH-CHSH-), 1.23 (tt, 18H, J= 7 Hz, O-CH₂-CH₃), 1.30 – 1.36 (dd, 1H, J_{b,c} = 15.6 Hz, J_{b,a} = 2.5 Hz, CH-CHSH), 1.49 – 1.56 (m, 2H, -CO-NH-CH₂-CH₂-CH₃), 1.98 (s, 3H, CH₃-CO-NH-CH₂-CH₂-CH₃), 2.01 – 2.03 (d, 1H, J = 7.9 Hz, CH-SH), 3.17- 3.24 (m, 2H, -CO-NH-CH₂-CH₂-CH₃), 3.83 (tq, 12H, J = 7 Hz, O-CH₂-CH₃), $\delta_{\rm C}$ (75.48 MHz; CDCl₃; Me₄Si): 11.31 (CH-SH), 14.01 (CH₃-CH₂-CH₂-NH-CO-), 15.35 (Si-CH₂-CHSH-Si), 18.21 (O-CH₂-CH₃), 22.79 (CH₃-CH₂-CH₂-NH-CO-), 23.25 (CH₃-CO-NH-), 41.32 (CH₃-CH₂-CH-NH-CO-), 58.4, 59.2 (O-CH₂-CH₃).

Synthesis of 1-thiol-ethylene-bridged PMO

In a typical synthesis, P123 surfactant (0,42 g) and KCl (2,1 g) were added to a solution of HCl (2,1 mL) in water (14,76 mL). The resulting mixture was vigorously stirred overnight at 45°C. The 1-thiol-1,2-bis(triethoxysilyl)ethane precursor was then added to the resulting clear solution. The reactant molar ratio was 1.0 Si:6.9 KCl:158.5 H₂O:4.9 HCl:0.013 P123. The synthesis mixture was stirred at 45 °C for 24h and subsequently aged at 100 °C for 24h under static conditions. A white solid was recovered by filtration which was thoroughly washed with water. The surfactant was removed by refluxing the as-synthesized material (0,5 g) in a solution of 4 mL of HCl in 150 mL of ethanol for 6h. After repeating this process twice, the solid was filtrated, washed with ethanol and dried under vacuum at 120 °C.

1. C. Vercaemst, M. Ide, B. Allaert, N. Ledoux, F. Verpoort and P. Van Der Voort, *Chem Commun*, 2007, 2261-2263.



Fig. S1: ¹H NMR of 1,2-(E)-bis(triethoxysilyl)ethene (top) and 1-(acetylthio)-1,2-bis(triethoxysilyl)ethane (1) (bottom).



Fig. S2: ¹H NMR of 1-thiol-1,2-bis(triethoxysilyl)ethane (2)



Fig. S3: ¹³C DEPT NMR of 1-thiol-1,2-bis(triethoxysilyl)ethane (2)



Fig. S4: X-Ray diffraction patterns of thiol-ethylene bridged periodic mesoporous organosilicas: as-synthesized (a) and after removal of surfactant (1^{st} extraction (b) and 3^{rd} extraction (c)).



Fig. S5: FT-IR spectrum of 1-thiol-1,2-bis(triethoxysilyl)ethane (up) and DRIFT spectra of thiol-ethylene bridged PMOs: as-synthesized (a) and after removal of surfactant (1^{st} extraction (b) and 3^{rd} extraction (c)).