

## Bifunctional Periodic Mesoporous Organosilica with Large Heterocyclic Bridging Groups and Mercaptopropyl Ligands

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### Experimental

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, Pluronic P123 from BASF), tetraethyl orthosilicate (TEOS from Fluka), tris[3-(trimethoxysilyl)propyl]isocyanurate (Aldrich), (3-mercaptopropyl)trimethoxysilane (Acros Organics) were used without additional purification. In a typical synthesis, 4 g of Pluronic P123 was dissolved in 28 mL of deionized water and 120 mL of 2M HCl under constant stirring for three hours prior to addition of the specified amounts of TEOS, tris[3-(trimethoxysilyl)propyl]-isocyanurate (ICS) and, after 15 minutes, (3-mercaptopropyl)trimethoxysilane (SH) to achieve the desired molar composition of these organosilanes. The temperature of the synthesis mixture was kept constant ~40°C. This mixture was further stirred for 24 hours before hydrothermal treatment at 100°C for 48 hours. The resulting white precipitate was filtered followed by extraction of the polymeric template with ethanol/HCl solution for 24 hours at 60°C. The extraction solution contained 100 mL of 95% ethanol and 4ml of 12M HCl. Extraction was repeated for every sample twice.

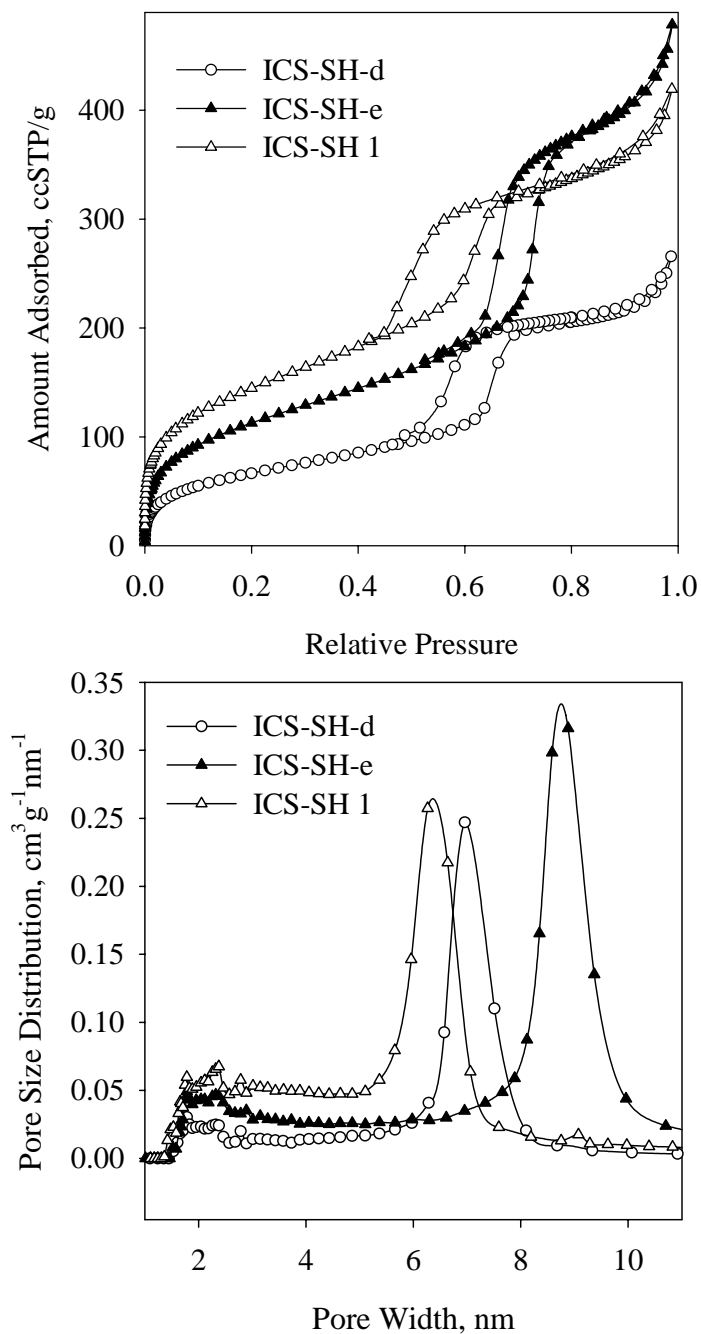
The molar compositions of the synthesis mixtures used to prepare two bifunctional periodic mesoporous organosilicas (PMOs), denoted as ICS-SH 1 and ICS-SH 2, were as follows: 1.0 TEOS: 0.15 SH: 0.14 ICS: 0.02 P123: 229 H<sub>2</sub>O: 7.05 HCl and 1.0 TEOS: 0.11 SH: 0.15 ICS: 0.02 P123: 237 H<sub>2</sub>O: 7.31 HCl, respectively.

For the comparison purpose two bifunctional PMOs were prepared by post-synthesis modification of the PMO sample prepared from TEOS and tris[3-(trimethoxysilyl)-propyl]isocyanurate according to the recipe reported previously (*J. Am. Chem. Soc.*, 2005, **127**, 60). Its molar composition was as follows: 0.917 TEOS: 0.083 ICS: 0.017 P123: 188 H<sub>2</sub>O: 5.8 HCl. The first sample was prepared by post-synthesis modification of the aforementioned PMO-ICS sample extracted prior modification with ethanol/HCl solution to remove polymeric template. About 0.2 g of this extracted PMO-ICS sample was reacted with 0.448ml of (3-mercaptopropyl)trimethoxysilane in toluene as solvent. The reaction was carried out under reflux conditions at the boiling temperature of the solvent for 24 hours. The reacted sample was washed many times on the glass filter with small portions of isopropanol and toluene, dried in the vacuum oven for 24 hours at 80°C. This sample was denoted as ICS-SH-e. The percentage of nitrogen and sulfur, found in this sample by elemental analysis, was 2.81 and 6.20%, respectively.

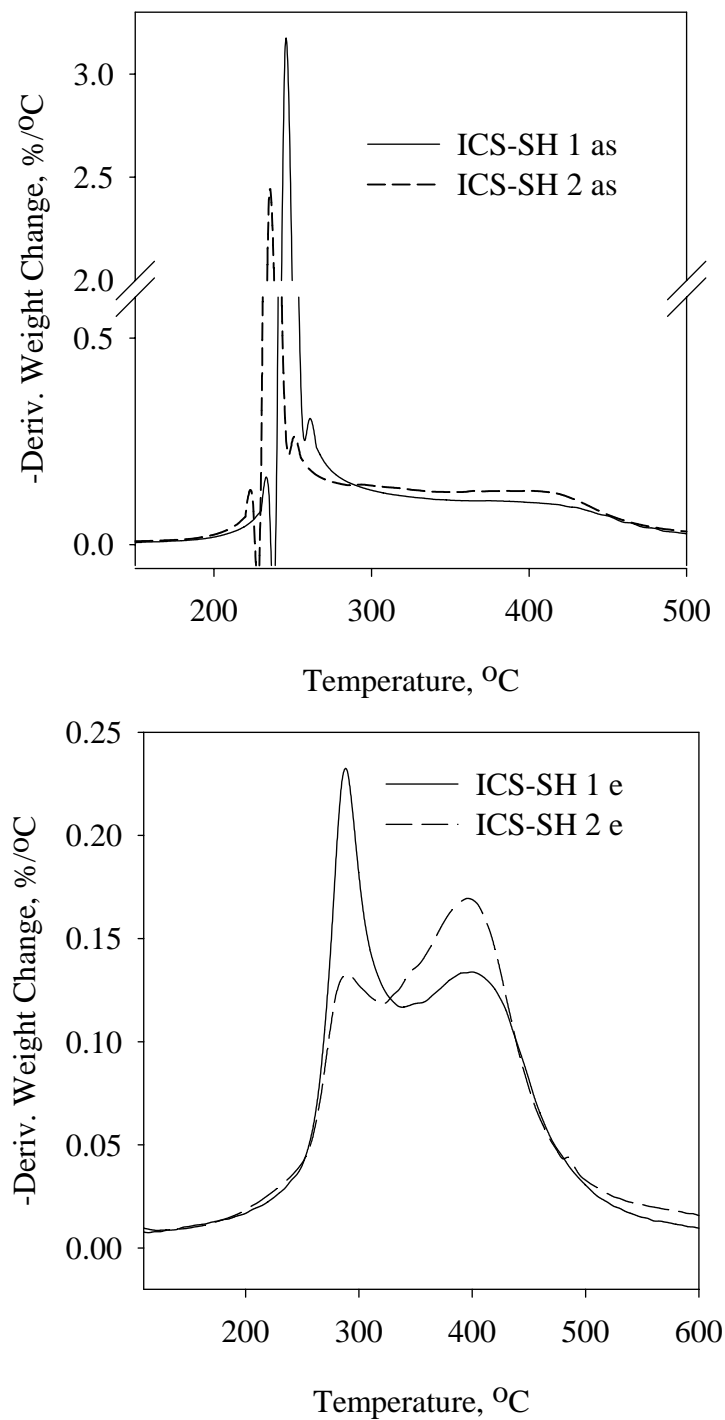
The second sample was prepared by post-synthesis modification of as-synthesized PMO material with (3-mercaptopropyl)trimethoxysilane. This procedure was analogous to that used for the post-synthesis modification of the extracted PMO. In this case the polymeric template is displaced by (3-mercaptopropyl)trimethoxysilane, which simultaneously is attached to the surface of mesopores. This sample was denoted as ICS-SH-d. The elemental analysis data reveals 1.93% of nitrogen and 4.37% of sulfur in the resulted sample.

**Table 1S.** Gel compositions used for the synthesis of PMO-ICS-SH materials and the elemental analysis data and ligand concentrations for the resulting PMO samples.

Sample	Synthesis gel composition					Elemental analysis of the PMO samples with ICS and SH groups			
	ICS, mol	SH, mol	TEOS, mol	%N	%S	%N	%S	ICS, mmol/g	SH, mmol/g
ICS-SH 1	0.083	0.092	0.825	3.55	2.98	3.08	2.86	0.73	0.89
ICS-SH 2	0.117	0.088	0.795	4.45	2.58	4.15	1.89	0.99	0.59



**Figure 1S.** Nitrogen adsorption isotherms measured at  $-196^{\circ}\text{C}$  and corresponding pore size distributions for the bifunctional PMOs prepared via three different synthesis routes: (i) direct co-condensation of tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS), (3-mercaptopropyl)trimethoxysilane and TEOS (sample ICS-SH 1), (ii) post-synthesis modification of extracted PMO-ICS with (3-mercaptopropyl)-trimethoxysilane (sample ICS-SH-e) and (iii) post-synthesis modification of as-synthesized PMO-ICS with (3-mercaptopropyl)trimethoxysilane (sample ICS-SH-d).



**Figure 2S.** Differential thermogravimetric (DTG) curves for as-synthesized (ICS-SH 1 as, and ICS-SH 2 as) and extracted (ICS-SH 1e, and ICS-SH 2e) samples.