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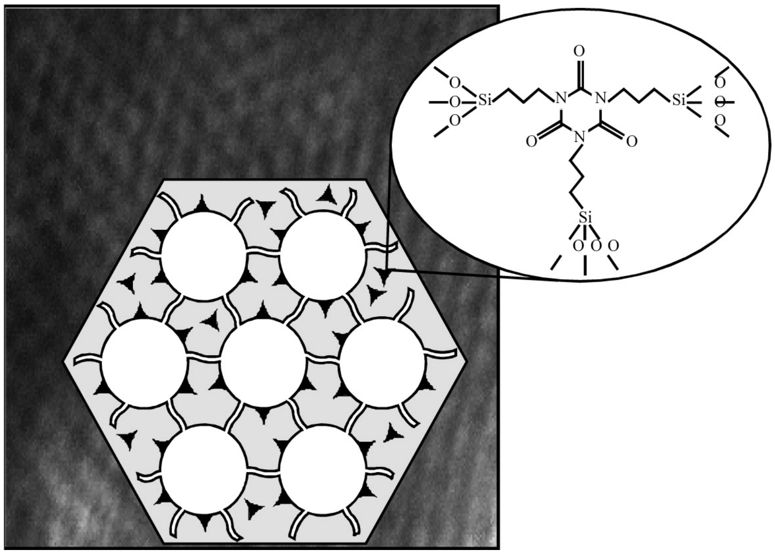

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Periodic Mesoporous Organosilica with Large Heterocyclic Bridging Groups

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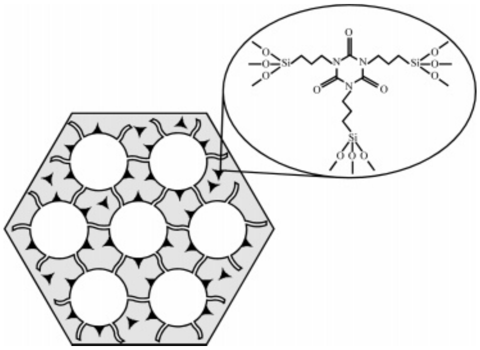
Since the publication of the first paper in 1992 on the self-assembly of silica and surfactant species,[1] impressive progress has been made in the chemistry of nanomaterials. One of the significant breakthroughs in this area was the discovery of periodic mesoporous organosilicas (PMOs),[2] which contain organic groups instead of oxygen in siloxane bridges of the silica framework. This discovery opened almost unlimited possibilities to design novel PMOs with uniformly distributed organic and organometallic groups within silica framework and to tailor their density, chemical reactivity, and thermal stability as well as their surface, electronic, optical, and mechanical properties (see reviews[3] and references therein). Initially, PMOs were synthesized with relatively small aliphatic and aromatic bridging groups, such as ethane, ethylene, phenylene, methylene, and thiophene, by using ionic surfactants as templates.[2,4] Analogous large-pore PMOs were prepared by using nonionic block copolymers as templates.[5] Also, several attempts have been made to synthesize PMOs with large bridging groups, such as bipyridine, biphenylene, tetraazacyclotetradecane, and Schiff−base complexes.[6] However, these attempts afforded PMOs with small percentage bridging groups and often with poor ordering. Only Ozin et al.[7] reported successful incorporation of benzene groups integrated with three silicon atoms and $[Si(CH_2)]_3$ rings into the silica framework.

Here, we report the incorporation of a heterocyclic bridging group with large molecular weight (MW = 615.85), that is, tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS), into the silica framework. The core of this bridging group is an isocyanurate ring integrated with three trimethoxysilyls through flexible propyl chains (see Scheme 1). This molecule is commercially available and is often used as a cross-linker, a sol−gel precursor, and a glass coating agent.[8]

This novel PMO, denoted PMO−ICS, was synthesized by self-assembly of tris[3-(trimethoxysilyl)propyl]isocyanurate (Aldrich), tetraethyl orthosilicate (TEOS from Aldrich), and the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (Pluronic 123 from BASF) under acidic conditions analogous to those used to obtain SBA-15.[9] The molar composition of the synthesis gel was $(1 - x)$M TEOS:xM ICS:0.017 M polymer:188 M H_2O:5.8 M HCl, where x denotes the number of moles of ICS. The synthesis of the PMO−ICS-p materials was performed using a different percentage of ICS expressed per silicon atom to one mole of silica precursors (i.e., $p = 100(3x)\% = 10, 25, 50, 75$, and 90). The as-synthesized nanocomposites were extracted with a hydrochloric acid/ethanol solution to remove the polymeric template and to make the mesoporous structure accessible for adsorption (see Supporting Information for other details of the synthesis).

Nitrogen adsorption isotherms, measured at −196 °C for the PMO samples synthesized up to ~30% ICS, feature a sharp capillary condensation step and a slightly delayed parallel desorption branch, characteristic for the SBA-15-type ordered mesoporous silicas (Figure 1). Narrow pore-size distributions (Figure 1), calculated from adsorption branches of the isotherms using the modified BJH algorithm,[10] confirm uniformity of mesopores in the PMO studied. The structural ordering of mesopores in the samples synthesized up to ~30% ICS was confirmed by transmission electron microscopy (see TEM images for PMO−ICS-25 in Figure 2). Small-angle X-ray scattering (SAXS) spectrum for the same sample reveals four distinct peaks characteristic for a hexagonal structure of *P*6*mm* symmetry (see Figure 1S in Supporting Information).

Scheme 1. Schematic Illustration of the PMO−ICS Material[a]



[a] Large white circles denote ordered mesopores interconnected by irregular micropores (thin white ribbons). Black triangles represent ICS bridging groups incorporated into the silica framework.

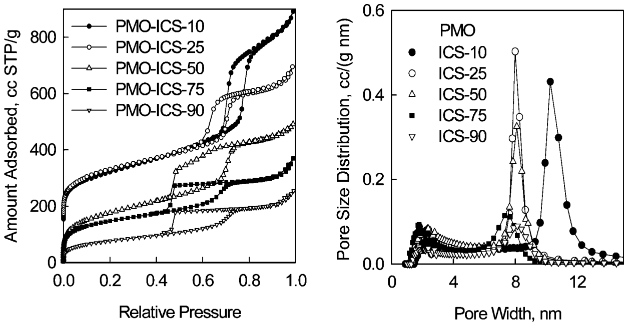


Figure 1. Nitrogen adsorption isotherms at −196 °C for the PMO−ICS materials synthesized using a different percentage of tris[3-(trimethoxysilyl)-propyl]isocyanurate. The isotherms for PMO−ICS-10 and PMO−ICS-25 are offset vertically by 150 cm^3 STP/g.

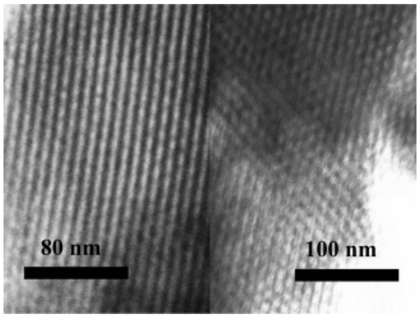


Figure 2. High-resolution TEM images for PMO−ICS with 25% tris[3-(trimethoxysilyl)propyl]isocyanurate used in the synthesis.

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It was possible to synthesize mesoporous organosilicas up to 90% of tris[3-(trimethoxysilyl)propyl]isocyanurate, which was unexpected due to the fact that the isocyanurate ring is integrated with three trimethoxysilyl groups through flexible propyl chains. As shown in Figure 1, nitrogen adsorption isotherms for the samples with 50, 75, and 90% ICS exhibit sharp condensation steps, which indicate narrow pore-size distributions (i.e., uniform mesoporosity). However, for these samples, the adsorption−desorption loops close at the lower limit of hysteresis, indicating the presence of pore constrictions/entrances less than ~5 nm.[11] It is interesting that the percentage increase of ICS up to 75% did not cause a significant decrease in the pore width and specific surface area of the resulting materials, but their pore volume decreased gradually from 1.1 to 0.5 cm^3/g (see Table 1S in Supporting Information). However, a substantial drop in the pore volume and surface area was observed for the samples synthesized with 75−90% ICS.

The TEM analysis of the organosilica studied showed that the samples synthesized with a higher percentage of ICS have a wormlike structure (see Figure 2S in Supporting Information for the sample with 50% ICS). Also, the intensity of SAXS peaks decreases with an increasing percentage of ICS (Figure 3S in Supporting Information).

The elemental analysis was used for quantitative estimation of organic functionality incorporated into the silica framework. As can be seen from Supporting Information Figure 4S, when the percentage of ICS used in the synthesis increased, the percent of C and N obtained from elemental analysis increased accordingly. The percentage values of N (Table 2S in Supporting Information) were used to estimate the isocyanurate concentration within mesopore walls because the C percentage data were slightly overestimated due to the presence of a small amount of template, which was not completely removed during the extraction process. In addition, the incorporation of ICS into the silica framework was monitored by high-resolution thermogravimetry (TG). The TG weight-change curves and the corresponding differential (DTG) curves are shown for the extracted samples in Supporting Information Figures 5S and 6S, respectively. Disappearance of the characteristic peak for polymer removal at 170 °C (see Figure 7S) on the DTG curves obtained for extracted samples (Figure 6S) indicates a successful extraction of the polymeric template with a hydrochloric acid/ethanol solution. However, a gradual increase in the weight loss in the range between 250 and 450 °C is proportional to the amount of the incorporated organic bridging group.

Chelating properties of the isocyanurate bridging group make the materials studied attractive adsorbents for heavy metal ions. This potential application was tested for adsorption of mercury(II) ions from aqueous solutions. Adsorption experiments performed for the samples with a different percentage of incorporated ICS suggest formation of complexes with several mercury ions per one isocyanurate group. The distribution coefficients obtained for mercury adsorption on these materials are on order of 10^8. This high affinity of the isocyanurate group toward mercury ions resulted in very high adsorption capacity of these materials; for example, maximum adsorption of mercury on the PMO−ICS-75 sample was ~1.8 g of Hg^{2+} per gram of the adsorbent. This high adsorption capacity was achieved because co-condensation synthesis allowed for the incorporation of a high percentage of multifunctional bridging groups into the silica mesostructure, which consists of large uniform mesopores interconnected by complementary micropores. For instance, the postsynthesis modification of SBA-15 silica with tris[3-(trimethoxysilyl)propyl]isocyanurate gave material with much smaller pore volume and comparable pore size, which indicates that the postsynthesis functionalization mostly occurred on the external surface (see Figure 8S in Supporting Information).

It is shown that large organic bridging groups of complex chemical structure, consisting of a heterocyclic ring integrated through flexible alkyl chains with three trimethoxysilyls, can be incorporated into the silica framework. Since it was possible to introduce the high percentage of these chelating groups into the silica framework, the resulting materials are expected to have high affinity toward heavy metal ions, which was evidenced by high adsorption capacity of these materials obtained for mercury ions.

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Supporting Information Available: Figures (8) with TEM images (1), SAXS patterns (2), nitrogen adsorption data (1), TG and DTG curves (3), and elemental analysis data (1). Tables (2) with adsorption parameters and chemical composition data. Experimental with description of synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710−712.
(2) (a) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611−9614. (b) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater*. **1999**, *11*, 3302−3308. (c) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867−871.
(3) (a) Asefa, T.; Yoshina-Ishii, C.; MacLachlan, M.; Ozin, G. A. *J. Mater. Chem.* **2000**, *10*, 1751−1755. (b) Sayari, A.; Hamoudi, S. *Chem. Mater*. **2001**, *13*, 3151−3168. (c) Kickelbick, G. *Angew. Chem., Int. Ed*. **2004**, *43*, 3102−3104.
(4) (a) Yoshina-Ishii, C.; Asefa, T.; Coombs, N.; MacLachlan, M. J.; Ozin, G. *Chem. Commun*. **1999**, 2539−2540. (b) Asefa, T.; MacLachlan, M. J.; Grondey, H.; Coombs, N.; Ozin, G. A. *Angew. Chem., Int. Ed*. **2000**, *39*, 1808−1811. (c) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304−307. (d) Kapoor, M. P.; Yang, Q.; Inagaki, S. *J. Am. Chem. Soc*. **2002**, *124*, 15176−15177. (e) Wang, W.; Zhou, W.; Sayari, A. *Chem. Mater*. **2003**, *15*, 4886−4889. (f) Lee, B.; Luo, H.; Yuan, C. Y.; Linc, J. S.; Dai, S. *Chem. Commun*. **2004**, 240−241.
(5) (a) Muth, O.; Schellbach, C.; Froba, M. *Chem. Commun*. **2001**, 2032. (b) Zhu, H.; Jones, D. J.; Zajac, J.; Dutartre, R. *Chem. Commun*. **2001**, 2568. (c) Burleigh, M. C.; Markowitz, M. A.; Wong, E. M.; Lin, J.-S.; Gaber, B. P. *Chem. Mater*. **2001**, *13*, 4411−4412. (d) Matos, J. R.; Kruk, M.; Mercuri, L. P.; Jaroniec, M.; Asefa, T.; Coombs, N.; Ozin, G. A.; Kamiyama, T.; Terasaki, O. *Chem. Mater*. **2002**, *14*, 1903−1905. (e) Goto, Y.; Inagaki, S. *Chem. Commun*. **2002**, 2410−2411.
(6) (a) Corriu, R. J. P.; Mehdi, A.; Reye, C.; Thieuleux, C. *Chem. Commun*. **2002**, 1382−1383. (b) Baleizao, C.; Gigante, B.; Das, D. D.; Alvaro, M.; Garcia, H.; Corma, A. *Chem. Commun*. **2003**, 1860−1861. (c) Corriu, R. J. P.; Lancelle-Beltran, E.; Mehdi, A.; Reye, C.; Brandes, S.; Guilard, R. *Chem. Mater*. **2003**, *15*, 3152−3160. (d) Baleizao, C.; Gigante, B.; Das, D. D.; Alvaro, M.; Garcia, H.; Corma, A. *J. Catal*. **2004**, *223*, 106−113.
(7) (a) Kuroki, M.; Asefa, T.; Whitnal, W.; Kruk, M.; Yoshina-Ishii, C.; Jaroniec, M.; Ozin, G. A. *J. Am. Chem. Soc*. **2002**, *124*, 152−155. (b) Landskron, K.; Hatton, B. D.; Perovic, D. D.; Ozin, G. A. *Science* **2003**, *302*, 266−269.
(8) (a) Matisons, J. G.; Jokinen, A. E.; Rosenholm, J. B. *J. Colloid Interface Sci*. **1997**, *194*, 263−268. (b) Norstrom, A. E. E.; Mikkola, P. J.; Matisons, J. G.; Rosenhol, J. B. *J. Colloid Interface Sci*. **2000**, *232*, 149−155. (c) Ni, H.; Skaja, A. D.; Sailer, R. A.; Soucek, M. D. *Macromol. Chem. Phys.* **2000**, *201*, 722−732.
(9) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc*. **1998**, *120*, 6024−6036.
(10) Kruk, M.; Jaroniec, M.; Sayari, A. *Langmuir* **1997**, *13*, 6267−6273.
(11) Kruk, M.; Jaroniec, M. *Chem. Mater.* **2003**, *15*, 2942−2949.

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