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Synthesis and characterization of organic–inorganic hybrid mesoporous silica materials with new templates†

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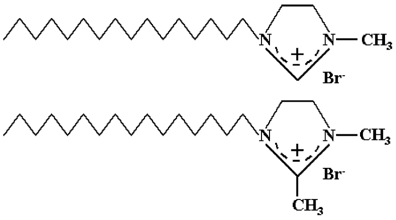
1-Hexadecane-3-methylimidazolium bromide and 1-hexadecane-2,3-dimethylimidazolium bromide were used as new templates for the syntheses of periodic mesoporous organosilica (PMO) materials; using these new templates, ethane-bridged PMO materials were successfully synthesized and characterized under basic conditions.

Since the discovery of mesostructured materials by Mobil[1–2] and Japanese[3] researchers, several types of mesostructured materials were synthesized using different templates and different reaction conditions.[4–7] Using the similar procedure, periodic mesoporous organosilica (PMO) materials were also synthesized by several groups.[8–13] A number of papers have been published recently on the successful synthesis of highly ordered PMOs using a variety of precursors under acidic conditions.[14–19] Unlike the synthesis of mesoporous silica materials, both synthesis conditions and types of surfactant templates are more stringent in the synthesis of PMO materials under basic media. For examples, only worm-hole structured mesoporous materials have been obtained through the use of cetyltrimethylammonium bromide (CTAB) and block copolymers as templates.[10,13] The difficulties associated with the above template syntheses of PMO materials may be attributed to the amphiphilic natures of bridged silsesquioxane precursors. Superior templating surfactants should be optimized for not only the static coulombic interaction between surfactant head groups and silica precursors but also the hydrophobic interaction between surfactant head group and hydrophobic parts of precursor silsesquioxanes. Such self-assembly syntheses through surfactant templates require a carefully tailored structure that balances the competing elements. Here, we report the successful synthesis of mesostructured hybrid silica materials using 1-hexadecane-3-methylimidazolium bromide (C_{16}MIB) and 1-hexadecane-2,3-dimethylimidazolium bromide (C_{16}DMIB) as new surfactant templates. The bridged silsesquioxane used to demonstrate basic synthesis processes is bis(triethoxysilyl)ethane (BTSE).

The new surfactant templates belong to a class of interesting organic salts, which are used for making room-temperature ionic liquids.[20] Ionic liquids are extensively explored as new solvent systems for catalysis and separation.[20] We[21] and others[22] have been interested in using ionic liquids as reaction media for synthesizing advanced materials. The basic molecular structure of the new surfactants is shown in Scheme 1. The head group of such new templates is alkylated imidazolium, which can interact not only with negatively charged silica precursors but also potentially with hydrophobic organic bridges of silsesquioxanes. Compared with CTAB that is usually used for the preparation of mesostructured materials,[1–3] the new templates have larger and flatter head groups. Such unique head groups could lead to optimized interactions with organic–inorganic hybrid silica precursors (*e.g.* BTSE) for the synthesis of PMO materials.



Scheme 1

Another key factor affecting the self-assembly synthesis of PMOs is the ratio between surfactants and hybrid silsesquioxanes.[8] The ratio of C_{16}MIB to BTSE was varied systematically from 0.06 to 0.12 in order to find the optimal composition of the reactants for the synthesis of the periodic mesoporous organosilica containing ethane bridge with C_{16}MIB (**PMO-E-M**). The optimized ratio for such synthesis was 0.1, which was verified by the nitrogen adsorption-desorption measurements. The detailed synthesis conditions are given in supporting materials. By the similar procedure, the optimal composition of reactants for the synthesis of the periodic mesoporous organosilica containing ethane bridge with C_{16}DMIB **(PMO-E-DM)** was also obtained.

Table 1 summarizes the surface areas, pore sizes, and *d* spacings of **PMO-E-M** and **PMO-E-DM**. Both **PMO-E-M** and **PMO-E-DM** showed mesoporosity with the BJH pore diameters of 2.1 and 1.9 nm, respectively (Table 1 and Fig. 1). The SAXS curves of **PMO-E-M** and **PMO-E-DM** are shown in Fig. 2 with a *d* spacing of 3.9 nm for both of them. The transmission electron microscopy (TEM) images of these porous materials indicate that both **PMO-E-M** and **PMO-E-DM** have a nice one-dimensional ordered structure (Fig. 3). Because any lamellar structure would not be stable during the template-removal process *via* solvent extraction, the presence of the ordered mesostructures in the template-removed samples and their SAXS curves are consistent with hexagonal structures for both **PMO-E-M** and **PMO-E-DM.**

In order to verify the unique properties of such imidazolium-based surfactants for the synthesis of PMO materials, both C_{16}MIB and C_{16}DMIB were also used to synthesize mesoporous pure silica materials using TEOS as a silica precursor. Again, several ratios of surfactants to silica precursors in phase diagrams were explored to define the optimal ratio of reactants for the synthesis of mesoporous silica materials (see ESI‡). The nitrogen adsorption-desorption measurements indicates that no ordered mesostructures were observed in the silica materials synthesized using C_{16}DMIB as the micellar template. The surface area of the resulting material is less than 100 $m^2\ g^{-1}$. This observation is consistent with the fact that the C_{16}DMIB surfactant has a relatively hydrophobic head groups, and thus only weakly interacts with the hydrophilic silica precursor. However, the mesoporous silica material (**MS-M**) synthesized

Table 1 Properties of the synthesized mesoporous silica materials: BET surface area, BJH pore diameter, pore volume, and *d* spacing.

	PMO-E-M	PMO-E-DM	MS-M
S.A.$_{BET}$/$m^2\ g^{-1}$	810	817	783
D_{BJH}/nm	2.1	1.9	1.9
P.V./cc g^{-1}	0.45	0.45	0.40
d/nm	3.9	3.9	3.1

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† Electronic supplementary information (ESI) available: synthesis details. See http://www.rsc.org/suppdata/cc/b3/b312178j/

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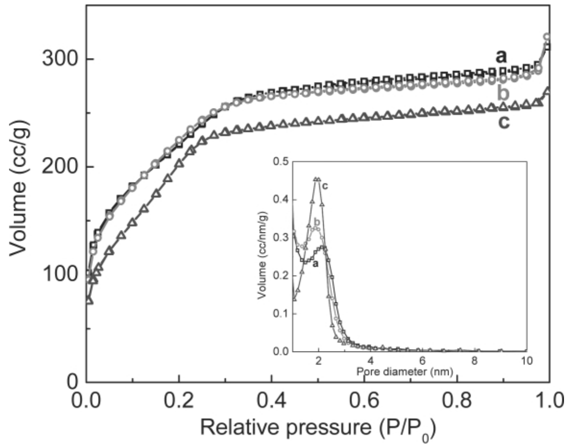

Fig. 1 Nitrogen adsorption-desorption isotherms and BJH mesopore size distributions of a. **PMO-E-M**, b. **PMO-E-DM**, and c. **MS-M**.

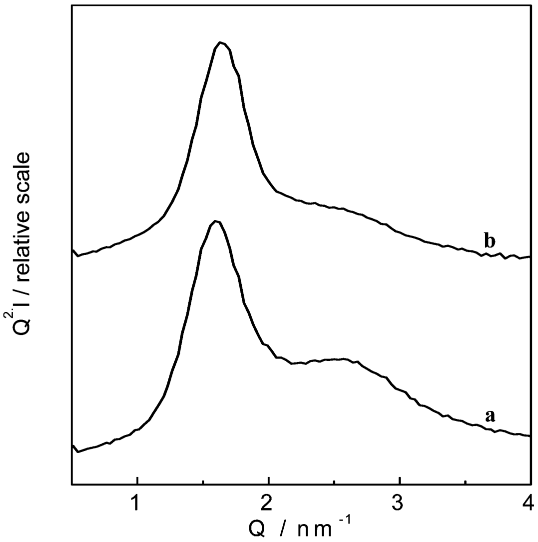

Fig. 2 SAXS spectra of prepared mesoporous silica materials: a. **PMO-E-M** and b. **PMO-E-DM**.

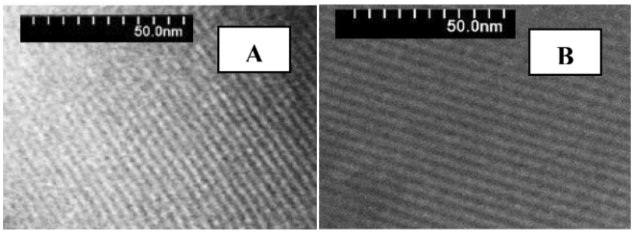

Fig. 3 TEM images of (A) PMO-;E-;M and (B) PMO-;E-;DM.

using C_{16}MIB showed a characteristic feature associated with mesoporous materials (Table 1 and Fig. 1).

In conclusion, we have demonstrated a self-assembly synthesis of mesoporous PMO materials using the imidazolium-based surfactants. The unique surfactant head groups can be the key for the facile formation of the PMO structures. This research clearly opens up a new opportunity of using the imidazolium-based surfactants for synthesizing novel porous materials. The stereochemical properties associated with the head groups of the imidazolium-based surfactants are very different from those of quaternary ammonium surfactants. Currently, the uses of these new templates for the synthesis of PMO materials with other bridged silsesquioxane precursors are being actively investigated.

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