

Preparation and Characterization of Novel Inorganic–Organic Mesoscopic Ordered Composites with Bridges Formed by Coordination Compounds

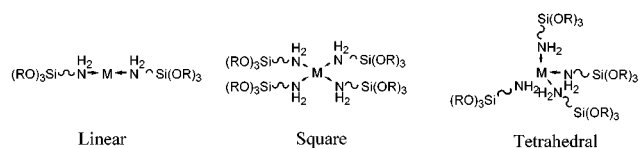
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Breakthroughs^{1–6} in the synthesis of mesoporous materials have resulted in a novel methodology for preparing mesoscopic inorganic materials with highly ordered mesostructures. The basis for this new methodology is the use of molecular self-assemblies of surfactants or related substances as templates during the formation of oxides. The size of the mesoscopic surfactant phase can be precisely tailored from 1.2 to 20 nm, based on surfactant or block copolymer assemblies being used. Recently, Inagaki et al.,⁷ Stein et al.,⁸ and Ozin et al.⁹ have succeeded in preparing uniformly distributed periodic organosilicas by condensation of organosilanes with trialkyloxysilyl groups connected via organic spacers (bridged silsesquioxane) in the presence of structure-directing surfactants. An evaporation-induced self-assembly procedure has been developed by Loy and Brinker and their co-workers¹⁰ to prepare poly(bridged silsesquioxane) mesophases with thin-film morphology. The bridged compounds explored in such syntheses consist of covalently linked and topologically linear organic^{11,12} or organometallic groups.⁹ The fact that the topology of the unique bridge spacers is the key to the success of these syntheses prompted us to consider that other bridged organosilane compounds with different topological structures could also be used to form mesoscopically ordered materials through application of surfactant-mediated synthesis. We have been interested in developing hierarchical materials through templating synthesis with metal ions and surfactants, simultaneously.¹³ Here, we report the successful preparation of new ordered mesoscopic materials using organosilane with trialkyloxysilyl groups connected via linear, square, or tetrahedral bridges of coordination compounds (Scheme 1).^{14,15} In comparison with poly(bridged silsesquioxane) mesophases, the key structural features of our bridged mesoscopic

Scheme 1



materials are as follows: (1) the bridge spacers are formed by noncovalent dative bonds between a metal ion and nonbridged siloxane bifunctional ligands, and (2) the topology of the bridge is generalized to square and tetrahedral linkages. No other sources of silica, such as tetramethyl orthosilicate, are used in our synthesis. A series of new bridged organic–inorganic hybrid mesoporous materials with periodic frameworks and uniformly distributed organic functional ligands, silica, and metal ions has been synthesized. The 3-aminopropyltriethoxysilane (aptes) is used as ligand to form the linear-, square-, or tetrahedral-bridged coordination complexes, which are then introduced as precursors to the inorganic–organic backbones of the mesoscopic solids. These new inorganic–organic mesoscopic hybrid materials contain metal ions as an integral part of their framework structures. Hybrid mesoscopic materials have been synthesized by template-directed co-condensation of tetraalkoxysilanes and functional organotrialkoxysilanes. The drawback associated with this methodology is that it is very difficult to increase the content of the functional organosilane without disrupting mesoporous silica networks.¹⁶

In a typical synthesis, sodium dodecyl sulfate (SDS) was dissolved in 30 g of deionized water. To this solution, the respective inorganic precursors (Table 1) were added with stirring. After a clear solution had formed, aptes [$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3$] was added dropwise, and precipitates appeared immediately.¹⁷ The suspension was aged for 24 h with stirring. The resulting precipitates were then filtered and dried in air for 12 h. The metal ions used in the syntheses were Cd^{2+} , Zn^{2+} , and Ni^{2+} , which are known to form strong coordination bonds with amine ligands.¹⁸ The strong dative bonds are important factors in the preservation of the topological metal-mediated bridge structures during condensation and precipitation reactions. The Ni^{2+} -bridged hybrid sample (Ni–MBH) forms only lamellar structures, while the Cd^{2+} -bridged sample (Cd–MBH) yields only hexagonal structures. The bridge complex of Ni–MBH is expected to be square-planar on the basis of the coordination properties of Ni^{2+} complexes.¹⁹ On the same basis,¹⁹ an octahedral structure can be assigned to the bridge of Cd–MBH. Since the mole ratio of metal ion (M^{2+}) to aptes is very near 1:4,²⁰ the metal-ion centers in Ni–MBH and Cd–MBH are expected to be coordinated by four aptes ligands. There are several stereochemical conformations for four amine ligands around Cd^{2+} . The exact bridge structure should be one of them or the mixture of them. The Zn^{2+} -bridged hybrid sample (Zn–MBH) can form both lamellar and hexagonal structures, depending on the conditions used for syntheses. The

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(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

(3) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.

(4) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 56.

(5) (a) Feng, X.; Fryxell, G. E.; Wang, L. Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923. (b) Fryxell, G. E.; Liu, J.; Hauser, T. A.; Nie, Z.; Ferris, K. F.; Mattigod, S.; Gong, M.; Hallen, R. T. *Chem. Mater.* **1999**, *11*, 2148. (c) Shin, Y.; Liu, J.; Wang, L. Q.; Nie, Z.; Samuels, W. D.; Fryxell, G. E.; Exarhos, G. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2702.

(6) Stein, A.; Melde, B. J.; Schroden, R. C. *Adv. Mater.* **2000**, *12*, 1403.

(7) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611.

(8) Melde, B. J.; Holland, B. T.; Blanford, C. F. A. *Stein Chem. Mater.* **1999**, *11*, 3302.

(9) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867.

(10) Lu, Y.; Fan, H.; Doke, N.; Loy, D. A.; Assink, R. A.; LaVan, D. A.; Brinker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 5258.

(11) (a) Shea, K. J.; Loy, D. A. *Chem. Mater.* **1989**, *1*, 572. (b) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431.

(12) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1420.

(13) (a) Dai, S. *Chem. Eur. J.* **2001**, *7*, 763. (b) Dai, S.; Burleigh, M. C.; Ju, Y. H.; Gao, H. J.; Lin, J. S.; Pennycook, S.; Barnes, C. E.; Xue, Z. L. *J. Am. Chem. Soc.* **2000**, *122*, 992.

(14) Schubert, U. *New J. Chem.* **1994**, *18*, 1049.

(15) Lindner, E.; Schneller, T.; Auer, F.; Mayer, H. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2155.

(16) (a) Macquarrie, D. J. *Chem. Commun.* **1996**, 1961. (b) Fowler, C. E.; Burkett, S. L.; Mann, S. *Chem. Commun.* **1997**, 1769.

(17) Control experiments involving the formulation without metal ions showed no precipitates for 4-h reaction times. Both TEM and XRD indicated that the precipitates formed for long reaction times were not mesoscopic phases.

(18) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1975; Vol. 2.

(19) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1988.

(20) This molar ratio was also verified by quantitative electron energy-dispersive spectroscopy (EDS) analyses. FTIR spectra are very similar to those reported for similar amine complexes. See Supporting Information and Klunkowski, A. M.; Grobelna, B.; Widernik, T.; Jankowska-Frydel, A.; Mozgawa, W. *Langmuir* **1999**, *15*, 5814.

Table 1. Preparation Conditions and Structures of Metal Cation-Mediated Bridged Hybrid Mesoscopic Materials

sample annotation ^a	inorganic precursor (I)	organic precursor (O)	surfactant (S)	I:O:S:H ₂ O	symmetry structure
Ni-MBH-1	Ni(NO ₃) ₂ ·6H ₂ O	aptes	SDS	0.27:1.0:0.06:146	lamellar
Ni-MBH-2	Ni(NO ₃) ₂ ·6H ₂ O	aptes	SDS	0.27:1.0:0.18:146	lamellar
Zn-MBH-1	Zn(NO ₃) ₂ ·6H ₂ O	aptes	SDS	0.27:1.0:0.036:146	hexagonal
Zn-MBH-2	Zn(NO ₃) ₂ ·6H ₂ O	aptes	SDS	0.27:1.0:0.06:146	lamellar
Zn-MBH-3	Zn(NO ₃) ₂ ·6H ₂ O	aptes	SDS	0.54:1.0:0.12:146	hexagonal
Zn-MBH-4	Zn(NO ₃) ₂ ·6H ₂ O	aptes	SDS	0.27:1.0:0.225:146	hexagonal
Zn-MBH-5	Zn(NO ₃) ₂ ·6H ₂ O	aptes	SDS	0.27:1.0:0.36:146	hexagonal
Cd-MBH-1	Cd(OAC) ₂ ·2H ₂ O	aptes	SDS	0.27:1.0:0.09:146	hexagonal
Cd-MBH-2	Cd(OAC) ₂ ·2H ₂ O	aptes	SDS	0.27:1.0:0.12:146	hexagonal
Cd-MBH-3	Cd(OAC) ₂ ·2H ₂ O	aptes	SDS	0.27:1.0:0.225:146	hexagonal

^a MBH: metal cation-mediated bridged hybrid mesoscopic materials.

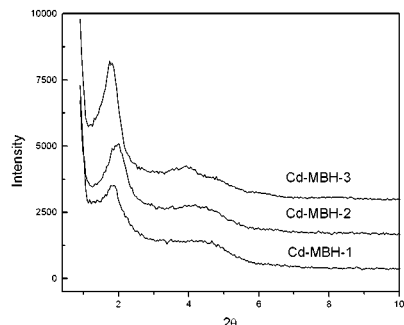


Figure 1. XRD patterns of as-synthesized mesostructured Cd-bridged hybrid materials (Cd-MBH).

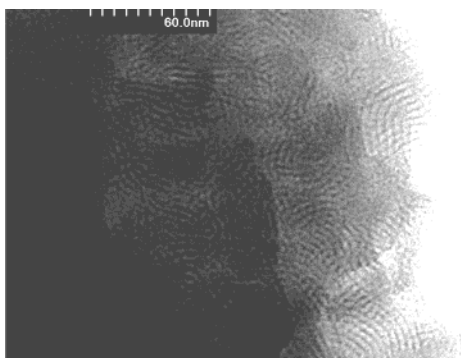


Figure 2. TEM image of as-synthesized Cd-MBH-3.

structure of Zn²⁺ complexes with bulky amine ligands is expected to be tetrahedral.²¹ Figure 1 shows the variations in the X-ray diffraction (XRD) patterns of Cd²⁺-bridged samples with XRD patterns, the phase of the mesoscopic products can be classified as hexagonal. Figure 2 shows a typical transmission electron micrograph (TEM) image of different concentrations of the surfactant template. On the basis of these TEM images of the hexagonal mesoscopic structure of a Cd-MBH sample, the

(21) Greenword, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984.

d-spacing (4.2–3.8 nm) measured by TEM is consistent with that of the XRD measurement.²² No mesoscopic composites were found without the addition of metal ions in the syntheses. Accordingly, the formation of the coordination complex precursors plays a key role in such syntheses. Substitution of the anionic surfactant template with cationic surfactants (e.g., cetyltrimethylammonium bromide) in the synthesis protocol did not lead to any composite mesophases. This indicates that the Coulombic interaction between anionic surfactants and cationic metal complex precursors forms the thermodynamic driving force for assembling the mesophases. Both extraction and calcination of the metal ion-mediated bridged mesoscopic composites resulted in destruction of the mesophases. Therefore, the interaction between cationic bridges and anionic surfactants is very strong, and the stability of the mesoscopic structures strongly depends on this interaction.

In conclusion, a new class of mesoscopic hybrid materials has been synthesized and characterized. The interaction between cation-bridged coordination complexes and anionic surfactants gives rise to the thermodynamic driving force for formation of the mesophases. The bridges are formed by dative bonds instead of covalent bonds. Research is under way to develop solvent-extraction processes to remove the surfactants without destruction of the mesoscopic structures. The resulting materials may have applications in separation sciences.^{5b,c}

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Supporting Information Available: XRD patterns of Zn-MBH and Ni-MBH samples. FTIR and EDS spectra of Cd-MBH, Zn-MBH, and Ni-MBH samples. STEM images of Zn-MBH and Ni-MBH samples. High spatial resolution EDS spectra of Cd-MBH (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(22) We have conducted scanning transmission electron microscopy (STEM or Z-contrast) measurements of our mesoscopically ordered composites (probe size ~0.3 nm). The key point with high annular dark-field imaging is that the intensity of the Rutherford scattered beams is directly proportional to Z², where Z is the atomic number of the scattering element. In situ EDS measurement of the bright area (~0.1 nm²) assigned to the wall structure was conducted. Strong signals from Cd and Si were measured, which indicates the presence of Cd and Si simultaneously in the walls. See Supporting Information.