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Self-Organization of Organosilica Solids with Molecular-Scale and Mesoscale Periodicities[†]

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This review focuses on the self-organization of organic–inorganic hybrid materials with molecular-scale and mesoscale periodicities. It describes organosilicas with molecular periodicity of organic units formed by self-organization of bissilylated organic monomers without employing templates, as well as porous organosilicas with mesoscale periodicity, i.e., periodic mesoporous organosilicas (PMOs). Moreover, PMOs with molecular-scale periodicity in the framework are discussed. Relevant uses of PMOs in diverse applications are summarized in the final chapter.

1. Introduction

The well-ordered mesoporous materials M41S[1,2] and FSM-16 [3,4] were discovered and developed in 1991–1993. Researchers reported the successful synthesis of mesoporous silicas with hexagonal and cubic symmetries through the use of surfactant micellar structures as template or organizing agents. These materials exhibit a large specific surface area and narrow pore-size distribution ranging from 2 to 10 nm. Today, a large number of mesoporous materials of varying composition, pore size, and wall thickness are available, derived using anionic, cationic, neutral, Gemini, and triblock copolymers and oligomers under a wide range of acidic and basic conditions. Calcination yields empty channels with exposed silanol groups, making the materials particularly attractive as covalent scaffolding hosts for many applications. These mesoporous solids also provide an excellent opportunity for organosilicon chemistry. The integration of organic functionality within these mesoporous solids has greatly expanded and advanced their applications, and many fruitful experiments have demonstrated the versatility and usefulness of mesoporous organosilicas in catalysis, drug delivery, and optical applications. In particular, mesoporous organosilica materials can be prepared from molecular building blocks that contain a variable organic component attached to two or more functional silyl groups. The Si−C bond is stable enough to provide a homogeneous material in which the organic moieties bound to two SiO$_{1.5}$ units are uniformly distributed as elementary building blocks.

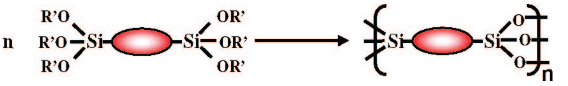

Figure 1. Hydrolytic polycondensation of organic-bridged trialkoxysilane.

For instance, bridged organoalkoxysilanes are well-known as precursors of highly cross-linked hybrid organosilica materials. The use of organo-bridged trialkoxysilanes [(R′O)$_3$Si−R−Si(OR′)$_3$] in sol–gel processing is a fascinating bottom-up approach to fabricating new functional hybrid materials with numerous applications; the R group is an organic unit that directly links two Si atoms through Si−C covalent bonds (Figure 1).

Bridged polysilsesquioxanes can be prepared with a broad range of organic bridging groups incorporated into the network. Arylenes, alkylenes, cyclams, crown ethers, porphyrins, polymers, and so on have been used as the organic component. This diversity of organic moieties enables modification of bulk properties such as the porosity, thermal stability, optical clarity, refractive index, chemical resistance, hydrophobicity, and dielectric constant. In addition, organic–inorganic hybrid materials reveal the excellent thermal and chemical stability of the Si−O−Si network, wherein the Si−O−Si network is easily accessible and shows excellent transparency for selected optical applications. Furthermore, bissilylated organic precursors have a special property, namely, a high ability for self-organization, higher than that of monosilylated organic precursors [R−Si(OR′)$_3$]. This property is a great advantage in forming highly organized structures such as crystal-like structures in organosilica and mesoporous organosilica materials. The self-organization of bissilylated organic precursors could be exploited to construct new functional hybrid materials with unique properties that are due to the crystal-like periodic structure of organosilicas. Moreover, the construction of mesoscale porous structures

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

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988.

(4) Inagaki, S.; Fukushima, Y.; Kuroda, K. *Chem. Commun.* **1993**, 680.

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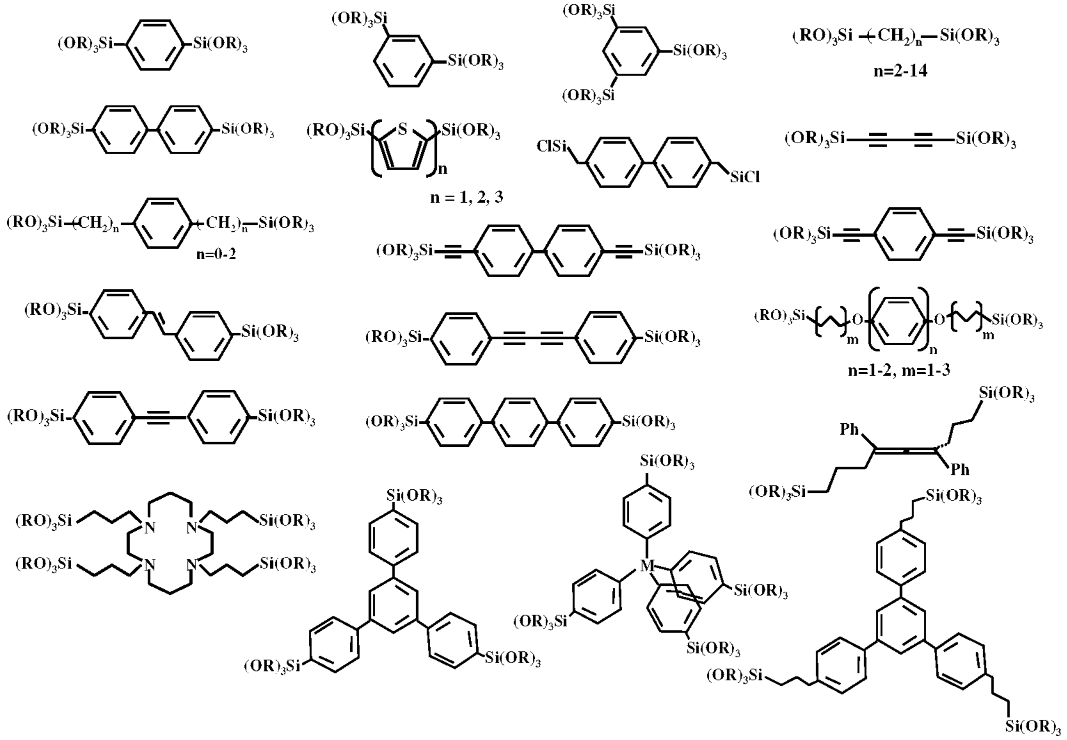
Scheme 1. Representative Organo-Bridged Precursors Resulting in Self-Organized Hybrid Materials



with molecular periodicity of organic units has opened up many interesting possibilities. Thus, numerous studies have been devoted to the self-organization of bissilylated organic precursors or mesoporous materials obtained via supramolecular self-assembly of bridged silsesquioxane monomers.

This review first outlines the self-organization of molecular units using bridged organoalkoxysilane monomers and gives an overview of the synthesis and properties of periodic mesoporous organosilicas (PMOs). The main focus will be on PMOs with molecular-level periodicity. Finally, an overview of functionalized PMOs and their applications will be presented.

2. Self-Organization of Bridged Organosilicas

In the 1990s, bridged trialkoxysilane precursors, $[(R'O)_3Si-R-Si(OR')_3]$, were widely used for the synthesis of numerous organisilica xerogels (bridged polysilsesquioxanes) by the sol–gel process.[5–7] The amorphous silica signals detected by X-ray diffraction (XRD) measurements revealed the bridged polysilsesquioxane xerogels to be amorphous solids.

However, birefringence and XRD measurements conducted by Corriu's group suggested the possibility of local organization for $O_{1.5}SiC{\equiv}CC_6H_4C{\equiv}CSiO_{1.5}$,[8,9] $O_{1.5}Si(C_6H_4)_nSiO_{1.5}$ ($n = 1-3$), $O_{1.5}Si(C_4H_2S)_nSiO_{1.5}$ ($n = 1$ and 3),[10] $O_{1.5}Si(CH_2)_5O(C_6H_4)_nO(CH_2)_5SiO_{1.5}$ ($n = 1$ and 2),[11] $O_{1.5}SiC{\equiv}CC{\equiv}CSiO_{1.5}$ xerogels.[12] XRD of these xerogels did not exhibit any sharp Bragg signals. However, broad signals were frequently observed, along with a signal attributed to the Si−O−Si distance ($d = 3.5–3.7$ Å). For instance, the $O_{1.5}SiC{\equiv}CC_6H_4C{\equiv}CSiO_{1.5}$ xerogel showed a broad diffraction at $d = 11.4$ Å, which was close to the estimated Si−Si distance in the organic spacer [d(Si−Si) = 11.45 Å]. Similarly, the Si−Si distances in the organic spacer for $O_{1.5}Si(C_6H_4)_nSiO_{1.5}$ ($n = 1-3$) are 7.8, 12.3, and 15.7 Å, respectively, corresponding to values determined by molecular simulation (7.8, 12.5, and 16.3 Å for $n = 1-3$).[13,14] Self-organization on a nanometer scale occurs in solution during the initial stage of the sol–gel process, and the organized structure is fixed by the irreversible Si−O−Si bond formation. The organized structure in xerogels is completely different from crystalline order, as evidenced by the fact that the XRD peaks are broader than those of crystalline materials. In general, it is difficult to form highly ordered structures in xerogels similar to those found in crystalline materials owing to the chemistry of sol–gel processes. Scheme 1 shows organo-bridged precursors that yield self-organized hybrid materials.

Boury et al.[15] and Muramatsu et al.[16] reported a rather different strategy to synthesize highly ordered organosilica materials from bridged organosilane precursors. They syn-

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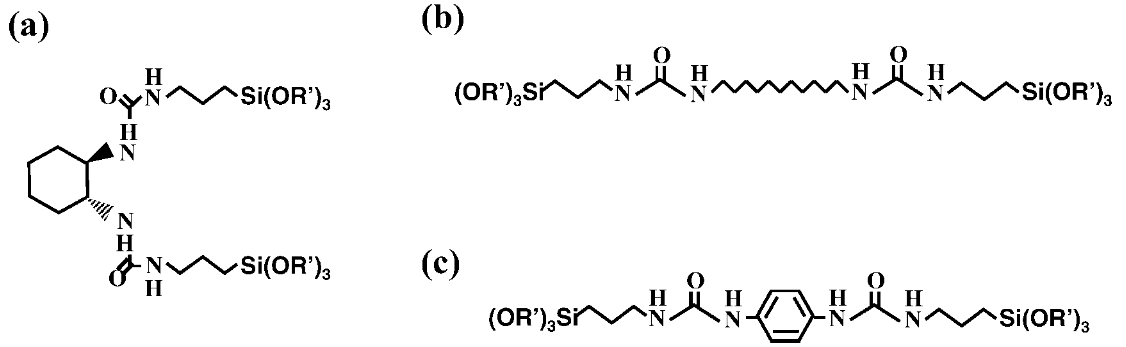
(5) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431.
(6) Corriu, R. J. P. *Angew. Chem., Int. Ed* **2000**, *39*, 1376.
(7) Loy, D. A.; Shea, K. J. *Chem. Mater.* **2001**, *13*, 3306.
(8) Boury, B.; Corriu, R. J. P.; Le Strat, V.; Delord, P.; Nobili, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3172.
(9) Boury, B.; Corriu, R. J. P.; Delord, P.; Le Strat, V. *J. Non-Cryst. Solids* **2000**, *265*, 41.
(10) Ben, F.; Boury, B.; Corriu, R. J. P.; Le Strat, V. *Chem. Mater.* **2000**, *12*, 3249.
(11) Ben, F.; Boury, B.; Corriu, R. J. P. *Adv. Mater.* **2002**, *14*, 1081.
(12) Boury, B.; Corriu, R. J. P. *Chem. Commun.* **2002**, 795.
(13) Lerouge, F.; Cerveau, G.; Corriu, R. J. P. *New J. Chem.* **2006**, *30*, 1364.
(14) Boury, B.; Ben, F.; Corriu, R. J. P.; Delord, P.; Nobili, M. *Chem. Mater.* **2002**, *14*, 730.
(15) Boury, B.; Ben, F.; Corriu, R. J. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2853.
(16) Muramatsu, H.; Corriu, R. J. P.; Boury, B. *J. Am. Chem. Soc.* **2003**, *125*, 854.

Scheme 2. Precursors with Hydrogen-Bonding Interactions between Urea Groups



thesized hybrid materials by solid-state hydrolysis/polycondensation of bis(trichlorosilyl)dibenzyl and 1,4-bis[5-(trimethoxysilyl)-1-pentenoxy]biphenyl without any solvent or catalyst. First, the precursor molecules were crystallized without condensation. The crystallized precursor solids, which showed sharp peaks in XRD, were contacted with water and HCl in the liquid or gas phase to induce condensation. The structures of the materials obtained by the solid-state process exhibited much higher periodicity than that of a corresponding solid prepared by sol–gel hydrolytic polycondensation. For instance, XRD showed a high periodicity for $O_{1.5}Si(CH_2)_5O(C_6H_4)_2O(CH_2)_5SiO_{1.5}$. The peaks at $d = 24.8$ and 12.4 Å corresponded to the length of the organic spacer (25.3 Å) and half of the length of the organic spacer. However, the level of condensation was low because of the increased difficulty for water to diffuse and increased number of Si−O−Si units that progressively hindered the movement required for condensation. Cerveau et al. reported the formation of three-dimensional (3D) Si−O−Si networks by solid-state thermal polycondensation at 180 °C of 4,4′-bis(trihydroxysilyl)stilbene, 4,4′-bis(trihydroxysilyl)diphenylacetylene, and 4,4′-bis(trihydroxysilyl)diphenylbuta-1,3-diyne.[17] The materials obtained, viz., $O_{1.5}SiC_6H_4C{=}CC_6H_4SiO_{1.5}$, $O_{1.5}SiC_6H_4C{\equiv}CC_6H_4SiO_{1.5}$, and $O_{1.5}SiC_6H_4C{\equiv}CC{\equiv}CC_6H_4SiO_{1.5}$, had long-range periodicity and lamellar ordering.

Cerveau et al. showed that self-organization of hybrid materials is not limited to a ridged or linear organic spacer using 1,3-bis(propyltrimethoxysilyl)-1,3-diphenylallene as a twisted allenic precursor.[18] Furthermore, they synthesized hybrid xerogels by sol–gel hydrolysis/polycondensation of 1,3,5-tris[*p*-(triethoxysilyl)phenyl]benzene with a rigid structure and 1,3,5-tris[[*p*-(trimethoxysilyl)propyl]phenyl)benzene with a planar core connected to three short, flexible arms.[19] The resulting materials exhibited molecular periodicity induced by a van der Waals type interaction, which is not limited to linear or ridged organic spacers. Precursors with a ridged tetrahedral geometry have been studied in order to determine the limits of self-organization using tetrakis[4-(triisopropoxysilyl)phenyl]germane and tetrakis[4-(triisopropoxysilyl)phenyl]tin, which have a tetrahedral germanium or tin central atom.[20]

Another example is the specific properties of chelating units in hybrid materials prepared from cyclam precursors.[21–24] Cyclam allows hybrid materials to be obtained in which self-organization is evidenced by the ability of chelating units to complex lanthanides (Eu^{3+}, Er^{3+}, and Gd^{3+}) corresponding to the incorporation of one lanthanide per two cyclam units. The formation of dinuclear copper complexes in which two cyclam rings are in a face-to-face geometry was observed by the incorporation of copper salts within cyclam-containing hybrid materials.

Moreau et al. synthesized a soluble organosilane compound with specific urea groups as a precursor for hydrolysis in an acidic solution (Scheme 2), producing self-structured bridged silsesquioxanes with interesting morphologies such as helical fibers, hollow tubes and spheres, and long-range-ordered lamellar structures.[25–28] These hybrids are formed through hydrogen-bonding interactions promoted by the urea groups within the organic bridged fragment, and self-organization by hydrogen bonds is an attractive feature of these materials. The hydrolysis of chiral units, capable of association by hydrogen bonding, allowed the fabrication of right- and left-handed helical hybrid silica fibers without an ordered structure, according to the (*R*,*R*) or (*S*,*S*) configuration of the 1,2-diureidocyclohexane unit (Scheme 2a).[25] However, Moreau et al. reported the first synthesis of self-organized hybrid materials with a long-range-ordered lamellar structure using (triethoxysilyl)ureidoalkylene or diureidophenylene derivatives as precursors (Scheme 2b,c).[26–28] For example, peaks assigned to the (001)−(004) directions

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(17) Cerveau, G.; Chappellet, S.; Corriu, R. J. P. *J. Mater. Chem* **2003**, *13*, 1905.

(18) Cerveau, G.; Corriu, R. J. P.; Framery, E.; Lerouge, F. *Chem. Mater.* **2004**, *16*, 3794.

(19) Cerveau, G.; Corriu, R. J. P.; Framery, E.; Lerouge, F. *J. Mater. Chem.* **2004**, *14*, 3019.

(20) Lerouge, F.; Cerveau, G.; Corriu, R. J. P. *J. Mater. Chem.* **2006**, 16–90.

(21) Corriu, R. J. P.; Imbert, F.; Guari, Y.; Reye, C.; Guilard, R. *Chem.—Eur. J.* **2002**, *8*, 5732.

(22) Corriu, R. J. P.; Mehdi, A.; Reye, C.; Thieuleux, C. *New J. Chem.* **2003**, *27*, 905.

(23) Dubois, G.; Reye, C.; Corriu, R. J. P.; Brandes, S.; Denat, F.; Guilard, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1087.

(24) Goulon, C.; Goulon-Ginet, A.; Rogalev, A.; Wilhelm, F.; Jaouen, N.; Cabaret, D.; Joly, Y.; Dubois, G.; Corriu, R. J. P.; David, G.; Brandes, S.; Guilard, R. *Eur. J. Inorg. Chem.* **2005**, *13*, 2714.

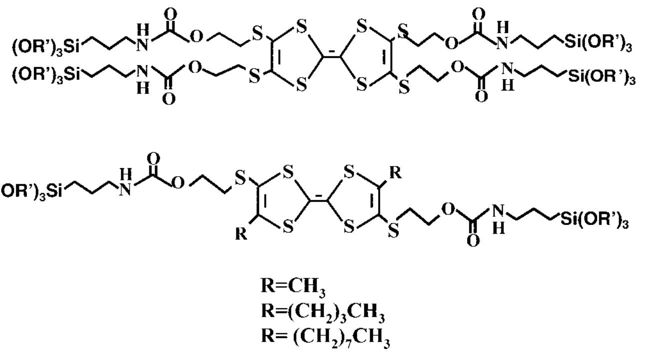
(25) Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C. *J. Am. Chem. Soc.* **2001**, *123*, 1509.

(26) Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C.; Bantignies, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 7957.

(27) Moreau, J. J. E.; Pichon, B. P.; Wong Chi Man, M.; Bied, C.; Pritzkow, H.; Bantignies, J. L.; Dieudonne, P.; Sauvajol, J. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 203.

(28) Moreau, J. J. E.; Pichon, B. P.; Bied, C.; Wong Chi Man, M. *J. Mater. Chem.* **2005**, *15*, 4943.

Scheme 3. Precursors with TTF Groups



of a lamellar structure with a basal spacing of 0.215 Å^{-1} were observed for alkylene-bridged hybrid materials.

Furthermore, Cerveau et al.[29] and Bellec et al.[30] reported that tetrasubstituted tetrathiafulvalene (TTF) derivatives, substituted via a spacer group containing a carbamate function by two or four trialkoxysilyl hydrolyzable groups, led to self-organized hybrid materials (Scheme 3). In this case, the carbamate groups play an important role in the self-organization by hydrogen bonding. Barboiu et al. reported new hybrid organic–inorganic materials based on macrocyclic receptors self-organized in tubular superstructures prepared by sol–gel using urea-based precursors.[31] Bantignies et al. reported using Fourier transform IR spectroscopy to probe the organization of organic units in lamellar-bridged silsesquioxanes with organic substructures based on alkylene chains of various lengths and urea groups $O_{1.5}Si(CH_2)_3NHCONH(CH_2)_3SiO_{1.5}$ (n = 6 and 8–12).[32] The intrinsic self-assembly properties of organic units involving hydrophobic interactions between adjacent alkylene spacers and hydrogen bonding between urea groups were determined by IR spectroscopy. The strength and directionality of the hydrogen bonding were directly correlated to the crystallinity of the hybrid materials.

Shinkai et al. established new concepts for the molecular design of porphyrin-based gelators on the basis of hydrogen-bonding and $\pi-\pi$-stacking interactions, leading to their immobilization in new organic–inorganic hybrid materials.[33] They used porphyrins bearing four urea-linked dodecyl groups or four urea-linked (triethoxysilyl)propyl groups as precursors and synthesized hybrid materials consisting of one- and two-dimensional (1D and 2D) molecular assemblies. Furthermore, Lerouge et al. reported self-organization of porphyrin moieties induced by a magnetic field during the sol–gel process.[34] 5,10,15,20-Tetrakis[4-(3-triethoxysilyl)phenyl]porphyrinzinc and 5,10,15,20-tetrakis[[4-[3-(triethoxysilyl)propyl]ureido]phenyl]porphyrin were used as precursors. According to small-angle X-ray scattering (SAXS) measurements, the resulting hybrid materials exhibited stacks of porphyrin rings.

Inagaki et al. showed the self-organization of phenylene– and biphenylene–silica hybrid solids with crystal-like long-range-ordered structure (Figure 2) using 1,4-bis(triethoxysilyl)benzene, 1,3-bis(triethoxysilyl)benzene, and 4,4′-bis(triethoxysilyl)biphenyl as organosilica precursors in a basic solution.[35]

The hybrid materials have a lamellar structure in which phenylene and biphenylene groups are packed in a head-to-tail manner within silicate sheets. The XRD patterns of these materials exhibited sharp peaks due to the lamellar structure. For example, 1,4- and 1,3-phenylene–silica hybrid materials produced sharp peaks at d = 7.6, 3.8, and 2.5 Å. These peaks can be indexed as (001), (002), and (003) of a lamellar structure with a basal spacing of 7.6 Å. The 4,4′-biphenylylene–silica hybrid material exhibited similar XRD patterns with peaks at d = 11.9, 5.9, 3.9, 2.9, and 2.4 Å, corresponding to a lamellar structure with a basal spacing of 11.9 Å. The hydrophobic–hydrophilic or $\pi-\pi$ interactions between precursor molecules direct the organization of lamellar structures. Likewise, Luo et al. reported the self-directed assembly of photoactive perylenediimide-bridged silsesquioxane into a superlong tubular structure.[36] The XRD pattern shows multiple orders of (00l) (where l = 1, 2, 3, 4, ..., 24) peaks, indicative of highly ordered lamellar stacks with a d spacing of 2.94 nm. More recently, Romeo et al. reported the self-organization of a new family of bridged silsesquioxanes containing a pendant hydrophobic chain in the organic bridge.[37] The precursor of this hybrid was obtained by the reaction of glycidoxypropyl(trimethoxysilane) with dodecylamine. The basic structure of ordered domains consisted of hybrid organic–inorganic multilayers separated by hydrophobic regions with a thickness equal to the length of a tail-to-tail association of dodecylamine chains in all-trans conformation.

On the other hand, there are few examples of self-organization of monosilylated organic precursors.[38–44] Kuroda's group reported the formation of multilayered hybrids via the hydrolysis and condensation of alkyltrimethoxysilanes $[C_nH_{2n+1}(CH_3)_mSi(OCH_3)_3$, where m = 0–2 and n = 8–12] or alkoxytrichlorosilanes (n-$C_nH_{2n+1}OSiCl_3$, where n = 12–20) as precursors. The products exhibited the XRD patterns indicative of layered structures depending on the alkyl chain length. More recently, Menaa et al. reported crystallization in hybrid organic–inorganic materials induced by self-organization of (3-glycidoxypropyl)trimethoxysilane

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(29) Cerveau, G.; Corriu, R. J. P.; Lerouge, F.; Bellec, N.; Lorcy, D.; Nobili, M. *Chem. Commun.* **2004**, 396.
(30) Bellec, N.; Lerouge, F.; Pichon, B. P.; Cerveau, G.; Corriu, R. J. P.; Lorcy, D. *Eur. J. Org. Chem.* **2005**, 136.
(31) Barboiu, M.; Cerneaux, S.; Lee, A.; Vaughan, G. *J. Am. Chem. Soc.* **2004**, *126*, 3545.
(32) Bantignies, J. L.; Vellutini, L.; Maurin, D.; Hermet, P.; Dieudonne, P.; Wong Chi Man, M.; Bartlett, J. R.; Bied, C.; Sauvajol, J. L.; Moreau, J. J. E. *J. Phys. Chem. B* **2006**, *110*, 15797.
(33) Kishida, T.; Fujita, N.; Sada, K.; Shinkai, S. *Langmuir* **2005**, *21*, 9432.
(34) Lerouge, F.; Cerveau, G.; Corriu, R. J. P.; Stern, C.; Guilard, R. *Chem. Commun.* **2007**, 1553.
(35) Okamoto, K.; Goto, Y.; Inagaki, S. *J. Mater. Chem.* **2005**, *15*, 4136.
(36) Luo, Y.; Lin, J.; Duan, H.; Zhang, J.; Lin, C. *Chem. Mater.* **2005**, *17*, 2234.
(37) Romeo, H. E.; Fanovich, M. A.; Williams, R. J. J.; Matejka, L.; Plestil, J.; Brus, J. *Macromolecules* **2007**, *40*, 1435.
(38) Parikh, A. N.; Schivley, M. A.; Koo, E.; Seshadri, K.; Aurentz, D.; Mueller, K.; Allara, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 3135.
(39) Shimojima, A.; Sugahara, Y.; Kuroda, K. *J. Am. Chem. Soc.* **1998**, *120*, 4528.
(40) Cabibil, H. L.; Pham, V.; Lozano, J.; Celoi, H.; Winter, R. M.; White, J. M. *Langmuir* **2000**, *16*, 10471.
(41) Shimojima, A.; Mochizuki, D.; Kuroda, K. *Chem. Mater.* **2001**, *13*, 3603.
(42) Shimojima, A.; Umeda, N.; Kuroda, K. *Chem. Mater.* **2001**, *13*, 3610.
(43) Shimojima, A.; Kuroda, K. *Langmuir* **2002**, *18*, 1144.
(44) Fujimoto, Y.; Shimojima, A.; Kuroda, K. *Chem. Mater.* **2003**, *15*, 4768.

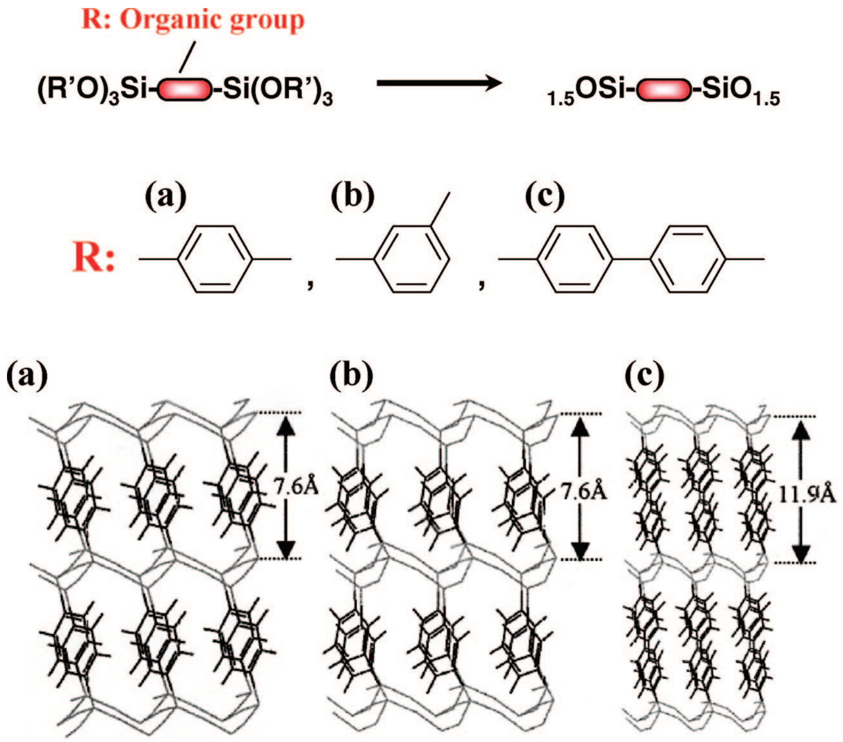

Figure 2. Simulated structure models of (a) 1,4-phenylene−silica, (b) 1,3-phenylene−silica, and (c) 4,4′-biphenylylene−silica hybrid materials.

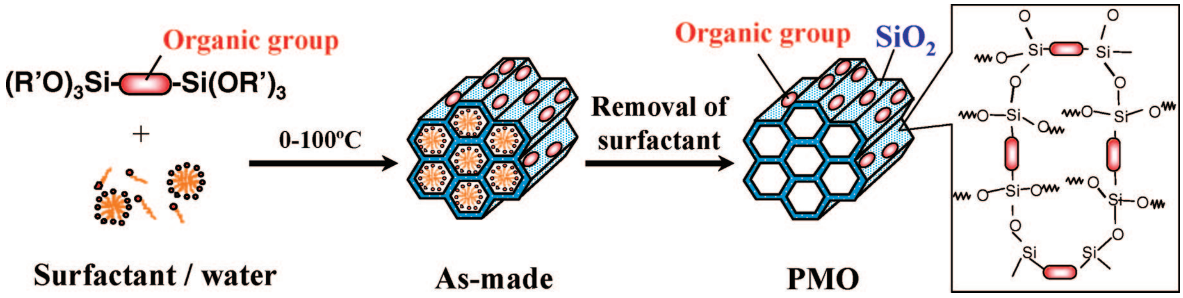

Figure 3. Synthesis of a PMO from an organic-bridged silsesquioxane precursor.

in strong basic conditions.[45] The crystalline structure was formed by epoxy ring opening and self-condensation, resulting in a pillared-type organic–inorganic hybrid structure with the Si-substituted 2,5-bis(propoxymethyl)-1,4-dioxane organic spacer as the pillar ($d = 19.5$ Å).

3. Periodic Mesoporous Organosilicas (PMOs)

The surfactant-mediated synthesis strategy has been successfully applied to bridged polysilsesquioxane materials derived from bissilylated organic precursors, and an entirely new class of bridged polysilsesquioxanes, so-called PMOs, were developed. PMOs have a highly ordered mesostructure with well-defined hexagonal and cubic structures, uniform pore-size distribution, and high surface area. XRD patterns of PMOs show sharp peaks at very low angles corresponding to $d = 2$–10 nm due to the ordered pore arrangement. On the other hand, organic-functionalized mesoporous silicas have been synthesized by a surfactant-mediated strategy from monosilylated organic precursors [$R-Si(OR')_3$] and alkoxysilane [$Si(OR')_4$)]. These have a heterogeneous structure composed of a silica framework with an organic layer grafted onto the silica framework. The bissilylated organic precursors yield mesoporous materials, in which the organic components are distributed homogeneously in the framework at a molecular level (Figure 3).

Furthermore, there are indications that it is advantageous to use organosilane precursors with two or more silyl groups for the formation of mesoporous organosilicas. Highly ordered mesoporous organosilicas have been synthesized from 100% bissilylated organic precursors, while the maximum incorporation of monosilylated organic precursors has been around 20−25 mol %, owing to the additional tetraethoxysilane (TEOS) silica required for full condensation into the rigid framework. Moreover, monosilylated organic precursors have often yielded materials with a lower degree of structural ordering because of sharing of the same confined channels by organic functional moieties that tend to perturb the micellar template structure.

In the present section, we review the synthesis of various PMO materials. The enormous choice of polysilylated molecular precursors each having a different organic linker

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(45) Menaa, B.; Takahashi, M.; Innocenzi, P.; Yoko, T. *Chem. Mater.* **2007**, *19*, 1946.

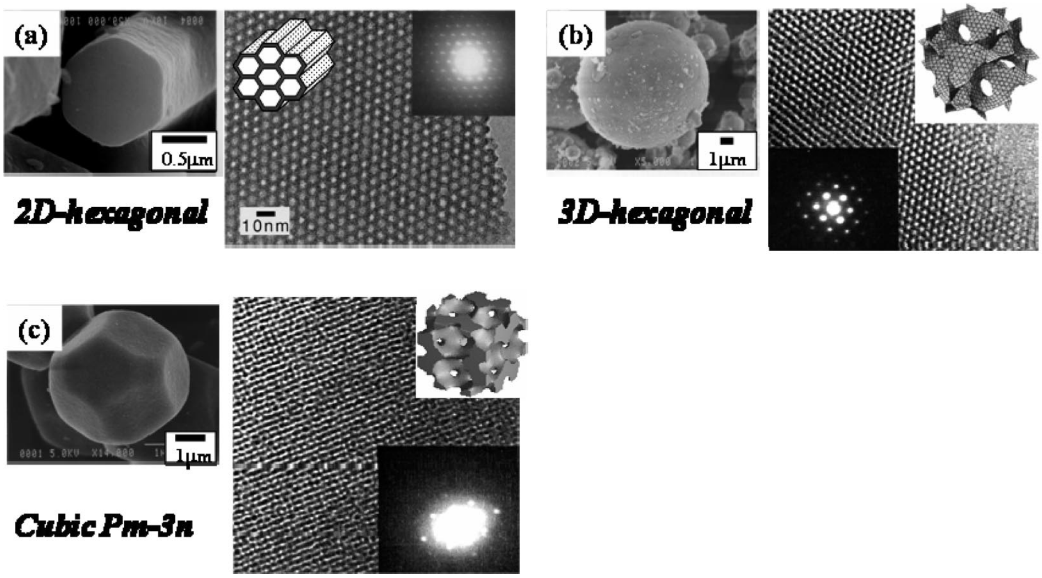

Figure 4. SEM and TEM images of ethane−silica hybrid materials with (a) 2D hexagonal, (b) 3D hexagonal, and (c) cubic $Pm\bar{3}n$.

R provides a broad range of capabilities to precisely control the unique surface properties without disturbing the periodic pore structure. A diversity of organic spacers have been successfully employed in the synthesis of mesoporous organosilicas using a variety of surfactants in basic, acidic, or neutral media, and various chemical, electrical, and optical functionalities have been integrated within the mesoporous network. Hexagonal, cubic, and wormhole framework structures have been reported.

The first studies on PMOs were conducted by three independent groups in 1999.[46–49] The first of these was by Inagaki et al., who used 1,2-bis(trimethoxysilyl)ethane as the framework precursor and octadecyltrimethylammonium chloride as the surfactant under basic conditions.[46] They obtained a highly ordered 2D hexagonal phase and 3D hexagonal mesosphase depending on the synthesis temperature and alkyl chain length of the surfactants (Figure 4a,b).

Nitrogen physisorption measurements revealed specific inner surface areas of 750 m^2/g (2D hexagonal) and 1170 m^2/g (3D hexagonal) and pore diameters of 3.1 nm (2D hexagonal) and 2.7 nm (3D hexagonal). ^{29}Si NMR measurements showed that the Si−C bond was not cleaved during the synthesis. Stein et al. reported PMOs with ethane and ethylene groups synthesized using 1,2-bis(triethoxysilyl)-ethane and 1,2-bis(triethoxysilyl)ethylene organosilane precursors in the presence of the surfactant hexadecyltrimethylammonium.[47] The resulting materials had a comparatively low long-range order, which was wormhole-like, rather than strictly parallel 2D hexagonally arranged pores. Further, Ozin et al. reported the synthesis of PMOs using an ethylene-bridged precursor mixed in different ratios with TEOS in the presence of the surfactant hexadecylammonium bromide in basic media.[48,49] The ethene-bridged PMO material exhibited a 2D hexagonally ordered pore system with a specific surface area of 600 m^2/g and a pore diameter of 3.9 nm. That the C═C bonds were incorporated into the silica framework was confirmed by the bromination reaction.[47] Elemental analysis showed a degree of bromination (10%) relative to the C═C bond content. Further, an ethane-bridged PMO with cubic symmetry ($Pm\bar{3}n$), which is analogous to the SBA-1 pure silica phase, has been synthesized by Guan et al.[50] and Sayari et al.[51] The crystal-like external morphology of these hybrid materials, as revealed by scanning electron microscopy (SEM), was described as a decaoctahedron comprising 6 squares and 12 hexagons (Figure 4c). Kapoor and Inagaki presented a unique route for the synthesis of ethane-bridged mesoporous silica with cubic symmetry using 1,2-bis(trimethoxysilyl)ethane and binary surfactant mixtures of octadecyltrimethylammonium chloride and the oligomeric Brij-30 surfactants [$C_{12}H_{25}(EO)_4OH$] as structure-directing agents under basic conditions.[52] Highly ordered ethane silicas with cubic ($Pm\bar{3}n$) symmetry akin to SBA-1 were obtained. The pore size and specific surface area were 2.8 nm and 740 m^2/g, respectively. The influence of the chain length of the surfactant on the synthesis of ethane-bridged PMOs was researched by Hamoudi et al.[53] The length of the alkyl chain in the surfactant varied between C_{10} and C_{18}. The pore size increased with increasing chain length of the surfactant. Liang and Anwander first described the synthesis of ethane-bridged organosilica using a binary mixture of Gemini (C_{18-3-1}) and cationic (C_{16}) surfactants as the template. The resultant materials exhibited a relatively low structural order and poor long-range order with a broad low-

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

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

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

(49) Yoshina-Ishii, C.; Asefa, T.; Coombs, N.; MacLachlan, M. J.; Ozin, G. A. *Chem. Commun.* **1999**, 2539.

(50) Guan, S.; Inagaki, S.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 5660.

(51) Sayari, A.; Hamoudi, S.; Yang, Y.; Moudrakovsk, I. L.; Ripmeester, J. R. *Chem. Mater.* **2000**, *12*, 3857.

(52) Kapoor, M. P.; Inagaki, S. *Chem. Mater.* **2002**, *14*, 3509.

(53) Hamoudi, S.; Yang, Y.; Moudrskoviski, I. L.; Lang, S.; Sayari, A. *J. Phys. Chem. B* **2001**, *105*, 9118.

angle Bragg reflection.[54] The synthesis of ethane-bridged PMOs could also be achieved under acidic conditions. The reaction pathway was different in this case. The "$S^+X^-I^+$" route was adopted in acidic conditions in contrast to the usual "S^+I^-" route under basic conditions. However, the acid-based approach produced poorly ordered mesoporous materials. Ren et al.[55] used 1,2-bis(triethoxysilyl)ethane as the precursor in the presence of cetylpyridinium bromide as the structure director. Others[56,57] have described in detail the synthesis of average pore ethane-linked mesoporous organosilicas under acidic conditions in the presence of biodegradable Brij-56 [$(EO)_{10}C_{16}H_{33}$] and Brij-76 [$(EO)_{10}C_{18}H_{37}$] oligomers as structure directors. The material showed a long-range-ordered pore system with hexagonal symmetry and a pore diameter of 4.5 nm. Burgleigh et al. showed the synthesis of ethane-bridged organosilica using both Brij-56 and Brij-76 surfactants under a wide range of acid concentrations.[58–60] The structural ordering of the resultant ethane mesoporous organosilica was higher with Brij-76 (pore diameter: 4.2−4.5 nm) than with Brij-56 (pore diameter: 3.6−3.9 nm), while synthesis performed in the presence of oligomeric surfactants with larger head groups such as Brij-58 and Brij-78 resulted in disordered materials with wide pore-size distributions.

Fröba et al. used a neutral Pluronic P123 triblock copolymer as the structure-directing agent and 1,2-bis(trimethoxysilyl)ethane as the organosilica source under acidic conditions.[61] Their material exhibited hexagonal symmetry akin to SBA-15 silica with large pores (6.5 nm). A well-ordered PMO with large, cagelike pores (12 nm) was obtained using the triblock polymer surfactant B50-6600 ($EO_{39}BO_{47}EO_{39}$) and 1,2-bis(triethoxysilyl)ethane as precursors under acidic conditions.[62] Guo et al. found that the addition of a salt such as NaCl improves the degree of ordering of the materials.[63] Cho and Char achieved the synthesis of large-pore and thick-pore-wall (4.2 nm) ethane-bridged organosilicas with 2D hexagonal symmetry using the triblock copolymer [$EO_{16}(L_{28}G_3)EO_{16}$].[64] The material showed enhanced thermal and hydrothermal stability and low microporosity. Meanwhile, Zhu et al. synthesized enlarged-pore ethane-bridged organosilica using preexisting lyotropic liquid-crystal phases as templates in the binary Pluronic P123/water system to obtain monolithical mesoporous material with a specific surface area and a pore size of 950 m^2/g and 7.7 nm, respectively.[65] Recently, Guo et al. reported that the addition of a large amount of K_2SO_4 to a synthesis mixture containing 1,2-bis(trimethoxysilyl)ethane and Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) under acidic conditions affords a high-quality cubic ($Im\bar{3}m$) ethane silica mesophase with large cavities of 9.8 nm in diameter and a specific surface area of 980 m^2/g.[66] Furthermore, Cho et al. attempted the synthesis of large-pore ethane-bridged organosilica akin to SBA-16 by a cocondensation process using an ethane-bridged precursor (less than 10 mol%) and TEOS in the presence of the triblock copolymer F127.[67] More recently, Djojoputro et al. successfully synthesized ethane-bridged PMO hollow spheres, with diameters in the 100–1000 nm range and a tunable wall thickness, by a dual-templating approach using a fluorocarbon surfactant and cetyltrimethylammonium bromide.[68]

The most commonly studied typical organic linker group is ethane ($-CH_2-CH_2-$) because 1,2-bis(trialkoxysilyl)ethane is a widely available silsesquioxane precursor. However, the ethane linker group has limited chemical functionality. Thus, other linker groups have been used to form bissilyl hybrid mesophases: methylene ($-CH_2-$), ethenylene ($-CH{=}CH-$), butylene ($-CH_2CH_2CH_2CH_2-$), phenylene ($-C_6H_4-$), thiophenylene ($-C_4H_2S-$), biphenylene ($-C_6H_4C_6H_4-$), tolyl, xylyl, dimethoxyphenyl, and vinyl. An overview of the structures of silsesquioxane precursors that were successfully used to create PMOs is presented in Scheme 4.

For example, Asefa et al. reported the synthesis of the shortest organic bonded periodic mesoporous materials with 2D hexagonal mesophases containing a methylene linker, which is isoelectronic with the O atoms in MCM-41s materials.[69] The synthesis of ethenylene-bridged mesoporous organosilica was also reported, showing the wide range of opportunities for further surface modifications based on olefin chemistry. Melde et al. synthesized mesoporous ethylene silica with 2.4-nm wormhole-like channels, and pure ethylene silica mesoporous solids having 4-nm pores with hexagonal symmetry were synthesized in basic conditions.[47] Wang et al. prepared high-quality ethenylene silica mesophases under acidic conditions with varying pore sizes using oligomeric (4–5 nm) and triblock copolymer (8–9 nm) surfactant templates.[70] They found that the addition of butanol to the polymeric reaction mixture improved the structural order and narrowed the pore-size distributions. Burgleigh et al. reported a synthesis using a ethenylene-bridged precursor and Brij-76 surfactant under acidic conditions,[60] while Nakajima et al. detailed the synthesis of ethenylene-bridged mesoporous silicas with large pores using P123.[71–73] Recently, Zhou et

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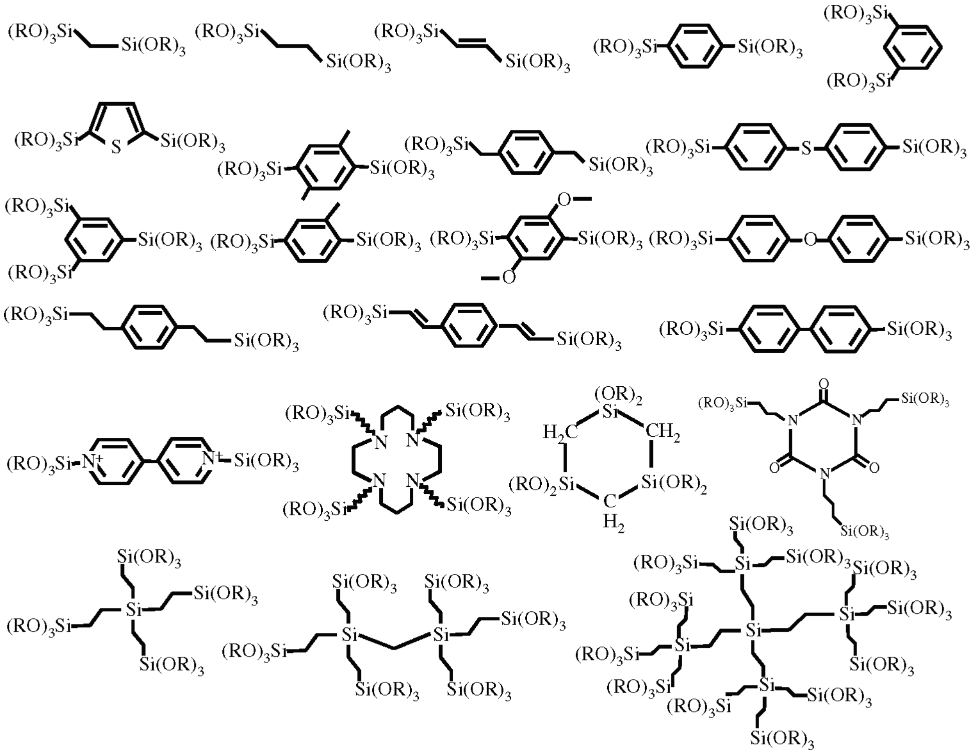
(54) Liang, Y.; Anwander, R. *Microporous Mesoporous Mater.* **2004**, *72*, 153.
(55) Ren, T.; Zhang, X.; Suo, J. *Microporous Mesoporous Mater.* **2002**, *54*, 139.
(56) Sayari, A.; Yang, Y. *Chem. Commun.* **2002**, 2582.
(57) Hamoudi, S.; Kaliaguine, S. *Chem. Commun.* **2002**, 2118.
(58) Burleigh, M. C.; Jayasundera, S.; Thomas, C. W.; Spector, M. S.; Markowitz, M. A.; Gaber, B. P. *Colloid Polym. Sci.* **2004**, *282*, 728.
(59) Burleigh, M. C.; Markowitz, M. A.; Spector, M. S.; Gaber, B. P. *J. Phys. Chem. B* **2002**, *106*, 9712.
(60) Burleigh, M. C.; Markowitz, M. A.; Jayasundera, S.; Spector, M. S.; Thomas, C. W.; Gaber, B. P. *J. Phys. Chem. B* **2003**, *107*, 12628.
(61) Muth, O.; Schellbach, C.; Fröba, M. *Chem. Commun.* **2001**, 2032.
(62) Matos, M. P.; Kurk, M.; Mercuri, L. P.; Jeroniec, M.; Asfa, T.; Coombs, N.; Ozin, G. A.; Kamiyama, T.; Terasaki, O. *Chem. Mater.* **2002**, *14*, 1903.
(63) Guo, W.; Park, J.-Y.; Oh, M.-O.; Jeong, H.-W.; Cho, W.-J.; Kim, I.; Ha, C.-S. *Chem. Mater.* **2003**, *15*, 2295.
(64) Cho, E. B.; Char, K. *Chem. Mater.* **2004**, *16*, 270.
(65) Zhu, H.; Jones, D. J.; Zajac, J.; Rozière, J.; Dutartre, R. *Chem. Commun.* **2001**, 2568.
(66) Guo, W.; Kim, I.; Ha, C.-S. *Chem. Commun.* **2003**, 2692.
(67) Cho, E. B.; Kwon, K.-W.; Char, H. *Chem. Mater.* **2001**, *13*, 3837.
(68) Djojoputro, H.; Zhou, X. F.; Qiao, S. Z.; Wang, L. Z.; Yu, C. Z.; Lu, G. Q. *J. Am. Chem. Soc.* **2006**, *128*, 6320.
(69) Asefa, T.; MacLachlan, M. J.; Grondey, H.; Coombs, N.; Ozin, G. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1808.
(70) Wang, W.; Xie, S.; Zhou, W.; Sayari, A. *Chem. Mater.* **2004**, *16*, 1756.
(71) Nakajima, K.; Lu, D.; Tomita, I.; Inagaki, S.; Hara, M.; Hayashi, S.; Domen, K.; Kondo, J. N. *Adv. Mater.* **2005**, *17*, 1839.
(72) Nakajima, K.; Tomita, I.; Hara, M.; Hayashi, S.; Domen, K.; Kondo, J. N. *J. Mater. Chem.* **2005**, *15*, 2362.

Scheme 4. Representative Polysilsesquioxane Precursors Used for the Synthesis of PMOs



al. successfully synthesized highly ordered ethylene-bridged PMO (face-centered cubic *Fm*$\bar{3}$*m*) with an ultralarge pore size of up to 14.7 nm using triblock copolymer F127 as the template and 1,3,5-trimethylbenzene as the swelling agent.[74]

A new structural class of macromolecules, dendritic polymers, has attracted the attention of the scientific community. These nanometer-sized polymeric systems are hyperbranched materials having compact hydrodynamic volumes in solution and a high surface functional group content. This unique combination of properties makes them ideal candidates for nanotechnology applications in both biological and materials sciences. Landskron and Ozin reported dendritic mesoporous organosilica compositions from the self-assembly of various dendrimer building blocks under ionic and nonionic surfactant routes using octadecyltrimethylammonium chloride or triblock copolymer surfactant templates.[75] This was clearly an application of the structural Aufbau principle to materials science technology; the presence of intact $Si-C_4$ building blocks was confirmed by magic-angle-spinning ^{29}Si NMR.

In an analogous PMO group, a variety of nonsilica-based mesoporous materials have been successfully synthesized using phosphonic acid in the presence of surfactants. Surface functionalization techniques using organophosphorus coupling molecules have been established by Kimura and Kato[76–78] and Mutin et al.[79] Ordered mesoporous aluminum organophosphonates were obtained using aluminum chloride, methylene, ethylene, and propylene phosphonates, and the triblock copolymers P123, F68, and F127 as surfactants.

Further, several attempts have been made for the synthesis of an aromatic-bridged PMO to introduce an enhanced functionality in mesoprous materials. Ozin et al. described the synthesis of phenylene-bridged mesophases using cetylpyridinium chloride as a structure director and a 1,4-bis(triethoxysilyl)benzene precursor in an acidic medium.[49] The pore diameter was 2.0 nm with a very high surface area (1360 m^2/g), although Si−C bond cleavage could not be completely avoided. They also reported mesophases from 1,4-bis(triethoxysilyl)-2-methylbenzene, 1,4-bis(triethoxysilyl)-2,5-dimethylbenzene, and 1,4-bis(triethoxysilyl)-2,5-dimethoxybenzene precursors using cetylpyridinium chloride as the surfactant under acidic conditions and also by adding ammonium fluoride as the catalyst after neutralization.[80] Further, their group reported the synthesis of mesoporous 1,3,5-phenylene−silica with three-point attachment.[81] Burgleigh et al.[59] and Sayari et al.[56,82] reported a similar synthesis using benzene-bridged precursors in the presence of Brij-type surfactants. Hunks and Ozin synthesized 4-phenyl ether and 4-phenyl sulfide bridged periodic mesoporous silicas using bis[4-(triethoxysilyl)phenyl] ether and bis[4-(triethoxysilyl)phenyl] sulfide precursors in the presence of the oligomeric surfactant Brij-76.[83] The addition of a small amount of NaCl salt assisted the interaction between hydrophilic head groups of the oligomeric template and the

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(73) Nakajima, K.; Tomita, I.; Hara, M.; Hayashi, S.; Domen, K.; Kondo, J. N. *Catal. Today* **2006**, *116*, 151.

(74) Zhou, X.; Qiao, S.; Hao, N.; Wang, X.; Yu, C.; Wang, K. L.; Zhao, D.; Lu, G. Q. *Chem. Mater.* **2007**, *19*, 1870.

(75) Landskron, K.; Ozin, G. A. *Science* **2004**, *306*, 1529.

(76) Kimura, T. *Chem. Mater.* **2003**, *15*, 3742.

(77) Kimura, T. *Chem. Mater.* **2005**, *17*, 5521.

(78) Kimura, T.; Kato, K. *J. Mater. Chem.* **2007**, *17*, 559.

(79) Mutin, P. H.; Guerrero, G.; Vioux, A. *J. Mater. Chem.* **2005**, *15*, 3761.

(80) Temtsin, G.; Asefa, T.; Bittner, S.; Ozin, G. A. *J. Mater. Chem.* **2001**, *11*, 3202.

(81) Landskron, K.; Hatton, B. D.; Perovic, D. D.; Ozin, G. A. *Science* **2003**, *302*, 266.

(82) Wang, W.; Zhou, W.; Sayari, A. *Chem. Mater.* **2003**, *15*, 4886.

(83) Hunks, W. J.; Ozin, G. A. *Chem. Commun.* **2004**, 2426.

inorganic species. The materials showed a single low-angle peak in the XRD patterns. When this was combined with the transimission electron microscopy (TEM) results, it was concluded that the material had a wormhole-type structure. The channel wall thickness was approximately 3.0 nm, while the pore diameter ranged from 2 to 3 nm. The specific surface area was 630 m^2/g. Similarly, periodic mesoporous structures with aryl−methylene bridging groups could be obtained from the corresponding 1,4-(triethoxysilyl)$(CH_2)_nC_6H_4$ ($n = 1$ or 2) precursors in the presence of the surfactant Brij-56 under acid conditions.

In addition to the above-mentioned aromatic-bridged mesoporous silicas, the synthesis of thiophene-bridged periodic mesoporous silicas was also reported. Ozin's group described the synthesis using the precursor 2,5-bis(triethoxysilyl)thiophene in the presence of cetyltrimethylammonium bromide as the surfactant template.[49] The Si−C bonding was found to cleave under basic conditions, while mild acidic conditions were shown to promote stability. Recently, Morell et al. synthesized very high-order thiophene-bridged periodic mesoporous materials using a 2,5-bis(triethoxysilyl)thiophene precursor in the presence of the triblock copolymer surfactant Pluronic P123.[84] The pore size ranged between 5 and 6 nm with a specific surface area of up to 550 m^2/g. ^{29}Si NMR and Raman spectroscopy confirmed that, under the conditions used (even though a highly acidic medium was used), only less than 4% of the Si−C bond was cleaved. Furthermore, Morell et al. successfully synthesized highly ordered bifunctional PMOs containing different amounts of aromatic thiophene and benzene groups using the triblock copolymer Pluronic P123 and the oligomeric surfactant Brij-76 under acidic conditions.[85] They employed 2,5-bis(triethoxysilyl) thiophene and 1,4-bis(triethoxysilyl)benzene as organosilica precursors. The bifunctional aromatic PMO materials exhibited a 2D hexagonal mesostructure with a pore size of ~5.4 nm. Furthermore, Fröba's group determined the vibrational spectroscopic features of ethane-, thiophene-, benzene-, and biphenyl-bridged PMO by IR and Raman spectra.[86] Corriu's group synthesized functional mesoporous organosilica containing chelating groups in the framework and reactive functional groups in the pores.[87] This material was obtained in one step by direct synthesis using cocondensation of TEOS and a bridged organosilica with chelating properties, 1,4,8,11-tetrakis[(triethoxysilyl)propyl]-1,4,8,11-tetraazacyclotetradecane, in the presence of the nonionic triblock copolymer P123 used as the surfactant. The content of the organic component of the framework was up to 33 wt %. A highly ordered mesostructure was not obtained, but monodisperse channel pores (pore size ~11 nm) with no long-range order were formed.

4. PMOs with Crystal-like Pore Walls

The bridge organic component in the PMOs described above is arranged randomly in the walls, and the chemical functionality of pore-wall surfaces is limited. By contrast, the inherent potentials of electronic, optical, and sensors are enhanced in the case of molecular periodicity in the walls. In this section, several research studies about PMO materials combining an ordered mesoporous structure and molecular periodicity within pore walls will be discussed.

The first report on PMOs with crystal-like pore walls came from Inagaki et al.[88] They reported the first surfactant-mediated synthesis of ordered benzene-bridged hybrid mesoporous organosilicas using 1,4-bis(triethoxysilyl)benzene and alkyltrimethylammonium chloride as surfactants (Figure 5).

The benzene-bridged hybrid mesoporous organosilicas showed a hexagonal array of mesoporous and crystal-like pore walls, observed as molecular periodicity in the walls along the channel directions due to the $\pi-\pi$ stacking of benzene bridging groups. The resulting material had a hexagonal array of mesopores with a lattice constant of 52.5 Å and exhibited an atomic-scale periodicity with a spacing of 7.6 Å along the channel direction within all pore walls. In addition to three peaks in the small-angle scattering regime ($2\theta < 10°$) with d spacings of 45.5, 26.0, and 22.9 Å, the material also showed four sharp diffraction peaks at d spacings of 7.6, 3.8, 2.5, and 1.9 Å in the medium-angle scattering region ($2\theta = 10$–$50°$). The higher-order reflections with a spacing of 7.6 Å, the TEM images of stacked lattice fringes with a uniform basal spacing of 7.6 Å, along with the corresponding electron diffraction spot confirmed the atomic-scale periodicity in the pore walls (Figure 5b). The Brunauer−Emmett−Teller (BET) specific surface area and pore size were 818 m^2/g and 3.8 nm, respectively. Figure 6 shows the pore surface structure of mesoporous phenylene−silica with crystal-like pore walls.

Benzene rings are aligned in a circle around the pore, fixed at both sides by silicate chains. The silicate chains are terminated by silanol (Si−OH) at the surface. Hydrophobic benzene layers and hydrophilic silicate layers are arranged alternately at an interval of 7.6 Å along the channel direction. The periodically arranged hydrophobic−hydrophilic surface is highly suitable for use as a catalyst and a host material for inclusion chemistry because it could enable structural orientation of guest molecules or clusters enclosed in the pores. Later, Bion et al. reported the synthesis of benzene-bridged hybrid mesoporous solids having crystal-like pore walls with varying pore diameters by using C_{14} to C_{18} trimethylammonium halide surfactants under basic conditions.[89] The pore diameters ranged from 2.3 to 2.9 nm depending on the alkyl chain length of the respective surfactant. Onida et al. conducted an IR and ab initio molecular modeling study to deduce the surface properties of mesoporous phenylene−silica hybrid materials with

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(84) Morell, J.; Wolter, G.; Fröba, M. *Chem. Mater.* **2005**, *17*, 804.
(85) Morell, J.; Gungerich, M.; Wolter, G.; Jiao, J.; Hunger, M.; Klar, M. J.; Fröba, M. *J. Mater. Chem.* **2006**, *16*, 2809.
(86) Hoffmann, F.; Gungerrich, M.; Klar, P. J.; Fröba, M. *J. Phys. Chem. C* **2007**, *111*, 5648.
(87) Alauzun, J.; Mehdi, A.; Reye, C.; Corriu, R. J. P. *J. Mater. Chem.* **2007**, *17*, 349.
(88) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304.
(89) Bion, N.; Ferreira, P.; Valente, A.; Goncalves, I. S.; Rocha, J. *J. Mater. Chem.* **2003**, *13*, 1910.

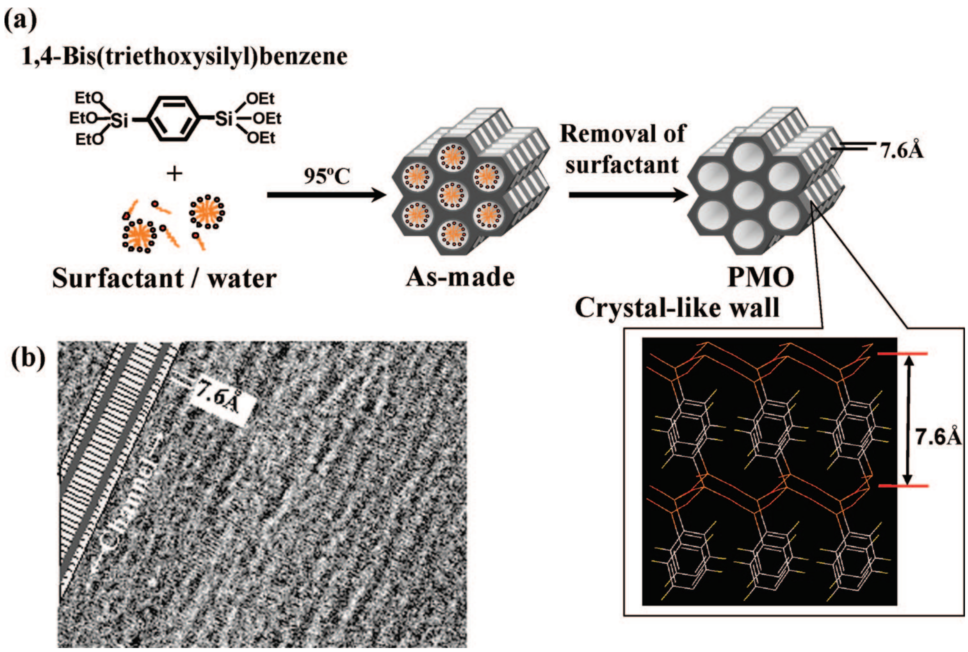

Figure 5. Synthesis of mesoporous organosilica with a crystal-like pore-wall structure. (b) TEM image of molecular-scale periodicity in the pore walls.

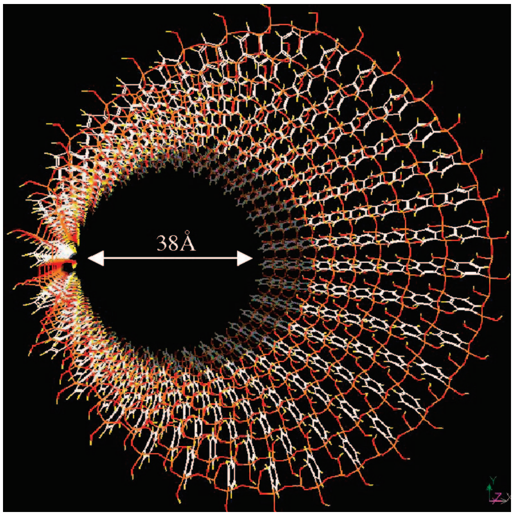

Figure 6. Simulated image of the crystal-like pore-wall structure of surfactant-free mesoporous phenylene–silica with crystal-like pore walls.

crystal-like pore walls.[90,91] Goto et al. reported the postsynthesis treatment for the formation of molecular-scale periodicity within the pore walls of mesoporous organosilica derived using the triblock copolymer surfactant Pluronic P123.[92] Since the discovery of this first benzene-bridged mesoporous hybrid material with crystal-like pore walls, the number of mesoporous hybrid materials exhibiting molecular-scale periodicity has increased. Kapoor et al.[93] have also demonstrated a similar arrangement using 1,3-bis(triethoxysilyl)benzene, a nonlinear symmetrically bridged organosilica precursor, in a synthesis route similar to that described by Inagaki et al.[88] This material also showed similar atomic-scale periodicity at 7.6 Å, as well as its higher-order diffractions. The series of PMOs with crystal-like pore walls was researched using organosilica precursors by Mokaya et al.,[94] Sayari and Wang,[95] and Fröba et al.[96] (Table 1).

Moyaka et al. synthesized an ethylene-containing PMO with crystal-like pore walls using 1,2-bis(triethoxysilyl)ethylene and cetyltrimethylammonium bromide as templates under basic conditions.[94] This material exhibited a molecular-level periodicity because of the lamellar ordering of the ethylene groups with a basal spacing of 5.6 Å and a high surface area (1300 m^2/g) with a pore size of 4 nm. Sayari and Wang used 1,4-bis[(triethoxysilyl)ethyl-2-vinyl]benzene as the precursor and alkyltrimethylammonium chloride as the surfactant under basic conditions to obtain 2D hexagonal 1,4-vinylbenzene PMO materials.[95] Fröba et al. synthesized the same vinylbenzene-bridged PMO with a pore size of 2.7 nm and a specific surface area of 800 m^2/g.[96] Another mesoporous hybrid system that showed periodically ordered mesopores as well as molecular-scale periodicity in the entire pore-wall region was synthesized by Kapoor et al. using 4,4′-bis(triethoxysilyl)biphenyl as the organosilica precursor, in which hydrophilic silicate layers alternated with hydrophobic biphenylene layers.[97] These results clearly demonstrated that such a unique arrangement in the pore walls can also be obtained in other hierarchically ordered mesoporous solids by changing the nature of the organic linkers. The material showed a molecular-scale pore-surface periodicity along the channel direction with a basal spacing of 11.6 Å (Table 1). The pore diameter and BET surface area were determined

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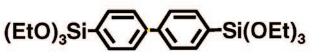
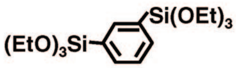
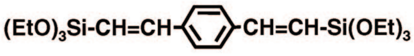
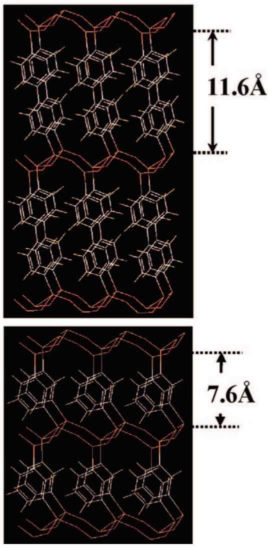
(90) Onida, B.; Borello, L.; Busco, C.; Ugliengo, P.; Goto, Y.; Inagaki, S.; Garrone, E. *J. Phys. Chem. B* **2005**, *109*, 11961.
(91) Onida, B.; Camarota, B.; Ugliengo, P.; Goto, Y.; Inagaki, S.; Garrone, E. *J. Phys. Chem. B* **2005**, *109*, 21732.
(92) Goto, Y.; Okamoto, K.; Inagaki, S. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 932.
(93) Kapoor, M. P.; Yang, Q.; Inagaki, S. *Chem. Mater.* **2004**, *16*, 1209.
(94) Xia, Y.; Wang, W.; Moyaka, R. *J. Am. Chem. Soc.* **2005**, *127*, 790.
(95) Sayari, A.; Wang, W. *J. Am. Chem. Soc.* **2005**, *127*, 12194.
(96) Cornelius, M.; Hoffman, F.; Fröba, M. *Chem. Mater.* **2005**, *17*, 6674.
(97) Kapoor, M. P.; Yang, Q.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 15176.

Table 1. Extension of Crystalline Mesoporous Organosilicas

Precursors	Periodicity in the walls (Å)
	7.6Å
	11.6Å
	7.6Å
$(EtO)_3Si\text{-}CH{=}CH\text{-}Si(OEt)_3$	5.6Å
	11.9Å



to be 3.5 nm and 869 m^2/g, respectively. Furthermore, Morell et al. reported the in situ synchrotron SAXS/XRD measurement of the formation of an ordered mesoscopic hybrid biphenyl-bridged PMO with crystal-like pore walls.[98] They demonstrated the formation of the mesostructure and the periodicity within pore walls.

In another attempt, Inagaki et al. reported the synthesis of lamellar mesophases of phenylene− and biphenylylene−silica composites with periodicity within the silicate layers from mixtures of bridged organosilane precursors and surfactants at room temperature.[99] Figure 7 shows a representative structure model of lamellar mesophase phenylene−silica hybrid materials. Interestingly, the phenylene−silica layers of the lamellar mesophase include a 4.2 Å periodicity that is different from the 7.6 Å periodicity observed in the pore walls of crystal-like mesoporous phenylene−silicas. A periodicity of 4.2 Å, which is very close to the phenylene−phenylene distance (4.4 Å), was also observed in the simulated model of the 2D hexagonal mesophase of phenylene−silica. It was shown that the periodic lamellar mesophases within the layers can also be obtained by refluxing the initial mixture at 55 and 75 °C, indicating that stable lamellar mesophases are likely to be formed under a wide range of condensation temperatures. In addition, the intercalation of a biphenylylene−silica mesophase with toluene also demonstrated the uniquely flexible features of these expandable interlayered materials (Figure 7). The diffraction peaks at *d* spacings of 30.0 and 14.9 Å confirm the lamellar lattice in the material. The 4.2-Å periodicity observed in the lamellar biphenylylene−silica mesophase was relatively lower compared to the lamellar phenylene−silica mesophase. The XRD peaks at *d* spacings of 46.7 and 23.4 Å indicate the swelling of the interlayer region of the lamellar hybrid material. This study is the first report on a lamellar mesophase organosilica hybrid with a crystal-like sheet structure. Its potential applications are eagerly anticipated.

5. PMOs with Crystal-like Pore Walls Obtained from Allyl Precursors

A wide range of synthetic routes to PMOs with different mesophases and morphologies have been reported using organosilica precursors, which consist of trialkoxy groups such as bridged organosilicon molecules $(R'O)_3SiRSi(OR')_3$. However, the range of suitable alkoxysilane precursors is limited because alkoxysilane precursors are difficult to obtain in high purity owing to the limitations in distillation and chromatographic separation, namely, that alkoxysilane precursors are highly reactive toward hydrolysis, rendering the silicon compounds difficult to handle under hydrolytic conditions and during purification by silica gel chromatography. For example, the precursor 1,4-bis[(diallylethoxy)silyl]benzene is preferable to 1,4-bis(triethoxysilyl)benzene in terms of their handling and purification during synthesis. Shimada et al. have demonstrated a new method for functionalizing the surface of mesoporous silica using allylorganosilane, which is stable under regular hydrolytic conditions.[100,101] Recently, Inagaki's group has presented the preparation of a new family of bridged allylorganosilane precursors that, upon surfactant-assisted assembly under basic conditions, afford ordered mesoporous organosilica having crystal-like pore walls with molecular-scale periodicity (Figure 8).[102]

The XRD patterns of the as-synthesized benzene−silica hybrid mesoporous material derived from 1,4-bis[(dial-

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(98) Morell, J.; Teixeira, C. T.; Cornelius, M.; Rebbin, V.; Tiemann, M.; Amenitsch, H.; Fröba, M.; Linden, M. *Chem. Mater.* **2004**, *16*, 5564.

(99) Okamoto, K.; Kapoor, M. P.; Inagaki, S. *Chem. Commun.* **2005**, 1423.

(100) Shimada, T.; Aoki, K.; Shinoda, Y.; Nakamura, T.; Tokunaga, N.; Inagaki, S.; Hayashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 4688.

(101) Aoki, K.; Shimada, T.; Hayashi, T. *Tetrahedron: Asymmetry* **2004**, *15*, 1771.

(102) Kapoor, M. P.; Inagaki, S.; Ikeda, S.; Kakiuchi, K.; Suda, M.; Shimada, T. *J. Am. Chem. Soc.* **2005**, *127*, 8174.

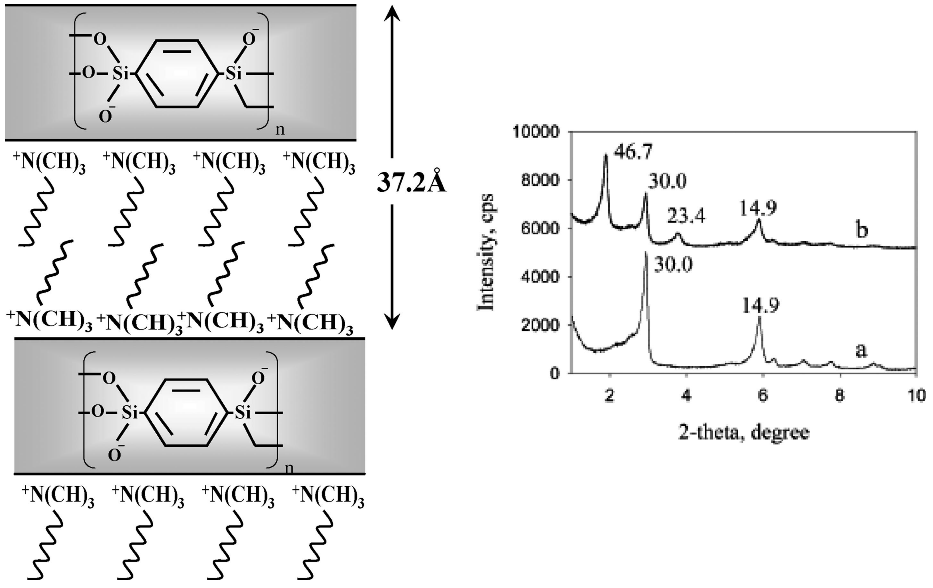

Figure 7. Representative structural models of the lamellar mesophase phenylene−silica hybrid material (left) and XRD patterns of lamellar mesophase of biphenylylene−silica hybrids (right) (a) before and (b) after treatment with toluene.

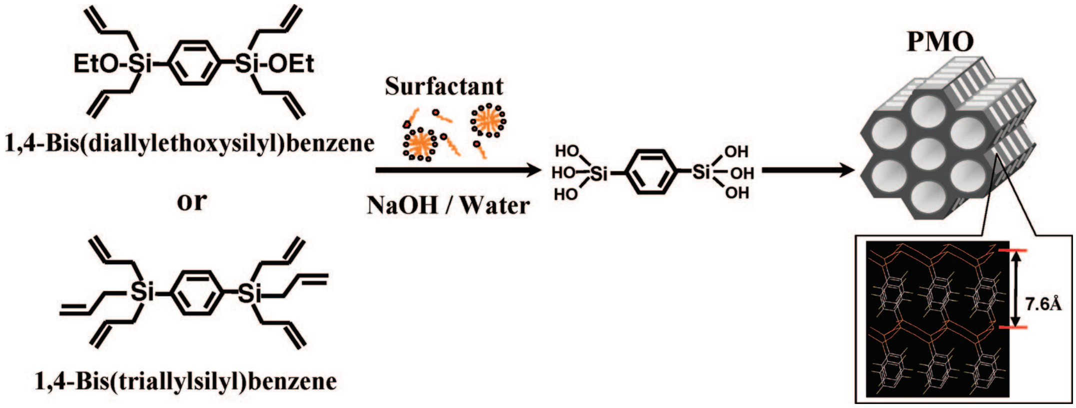

Figure 8. Alternate route for the synthesis of mesoporous phenylene−silicas from allylorganosilane precursors.

lylethoxy)silyl]benzene show a d_{100} reflection peak at 41.6 Å and sharp peaks at $d = 7.6$, 3.8, and 2.5 Å at intermediate scattering angles ($2\theta = 10$–$40°$), indicating that the pore walls are composed of crystal-like domains with a spacing of 7.6 Å in the channel direction. The surfactant-free material also exhibited a well-defined pattern with diffraction peaks in the low-angle region (d_{100} spacing of 45.7 Å). The molecular-scale periodicity was fully retained upon surfactant removal, indicating substantial framework ordering with crystalline pore walls. The final material was identical with the materials synthesized from the alkoxy derivative of the benzene-bridged precursor [1,4-bis(triethoxysilyl)benzene], which exhibited weaker peaks related to molecular-scale periodicity.[88] The Barrett−Joyner−Halenda (BJH) pore diameter, BET surface area, and mesopore volume were 23.5 Å, 744 m^2/g, and 0.53 cm^3/g, respectively. Furthermore, Inagaki's group has synthesized a stable 1,4-bis(triallylsilyl)benzene precursor without any alkoxy terminal group and attempted to form mesostructures under basic conditions. The XRD pattern clearly shows the successful formation of a mesostructure with a d_{100} spacing of 35.5 Å. The other two broad reflections at $d = 9.5$ and 4.4 Å were due to the molecular-scale periodicity of the pore walls. This material exhibits structural ordering, with a BET surface area of 960 m^2/g and a BJH pore diameter of 23.2 Å. Kapoor et al. have reported the synthesis of a 3D ($Pm\bar{3}n$) cubic phenylene-bridged hybrid mesoporous silica material using the allylorganosilane precursor 1,4-bis(triallyl)phenylene and cetyltrimethylammonium chloride (C_{16}TMACl) as structure-directing agents in an acidic medium.[103] The specific surface area and pore size of this material are 680 m^2/g and 37.7 Å, respectively. Finally, the methodology of PMO formation using both the alkoxy derivative of the precursors and the allylorganosilane precursors themselves is unique. This achievement represents a new step toward the discovery of alternative organosilane precursors for the synthesis of mesoporous organosilica, to replace the existing precursors that are difficult to obtain in high purity.

6. Functionalized PMOs

A variety of functionalized periodic mesoporous materials have been obtained in the past decade. In general, organic

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(103) Kapoor, M. P.; Yanagi, M.; Kasama, Y.; Yokohama, T.; Inagaki, S.; Shimada, T.; Nanbu, H.; Juneja, L. R. *J. Mater. Chem.* **2006**, *16*, 3305.

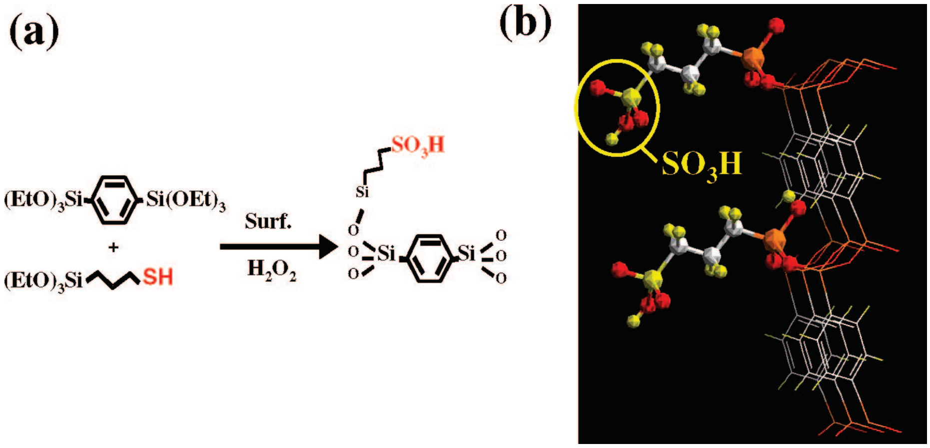

Figure 9. (a) Direct synthesis of sulfonic acid functionalized phenylene−silica by cocondensation of 1,4-bis(triethoxysilyl)benzene and (3-mercaptopropyl)-trimethoxysilane and the oxidation of thiol groups to sulfonic acid groups and (b) a CG image of a surface functionalized with propylsulfonic groups.

functionalized mesoporous silicas have been prepared by two pathways. The first is the grafting approach, where the organic functionalities are bound on the silica surface by a postsynthesis treatment, and the second is the cocondensation method of tetraalkoxysilanes and terminal organotrialkoxysilanes in the presence of supramolecular structure-directing agents. In contrast to the organofunctionalized mesoporous silica, the organic units in PMOs are two-point-attached within the silica matrix through covalent bonds and are completely homogeneously distributed. PMO materials exhibit ordered pore arrangements accompanied by sharp pore-size distributions because structure-directing agents are employed for their synthesis. By variation of the organic moieties of the organosilica precursors, the chemical and physical properties of PMOs can be tailored to specific needs. Because of their ordered and uniform porosity, functionalized PMOs are attractive for applications such as catalysis, adsorption, photonics, chromatography, electrochemiluminescence, gas storage, and host–guest chemistry.

6.1. Multifunctionalized PMOs. Ozin's group reported bifunctionalized PMOs with bridging ethyl groups in their walls and vinyl groups protruding into their channels.[104] In addition, hierarchically ordered mesophases with crystal-like pore walls could be fabricated with interactive bridging organic spacers inside the pore walls; these mesophases allowed modification of the organic functional groups via further chemical transformations for versatile applications.[105] For instance, Yang et al. developed sulfuric acid functionalized mesoporous phenylene−silica by cocondensation of 1,4-bis(triethoxysilyl)benzene and (3-mercaptopropyl)-trimethoxysilane using a cationic surfactant template in a basic medium, followed by oxidative transformation of the thiol (−SH) group to (−SO_3H) using HNO_3.[106] The resulting materials showed a molecular-scale periodicity (7.6 Å) similar to that previously observed for benzene-bridged mesoporous materials. Characterization results revealed that the mercaptopropyl group (C_3H_6SH) or its oxidized derivatives ($C_3H_6SO_3H$) are linked to silicate layers of the hybrid mesoporous solids (Figure 9). The degree of oxidation of −SH to −SO_3H was 41.7%, and the sulfonic acid group concentration was 0.70 mequiv/g. The materials were found to be very reactive toward esterification of acetic acid with ethanol, and the catalytic results showed a higher conversion compared to commercially available Nafion-H.[107]

Further, the synthesis of sulfuric acid functionalized biphenyl-bridged mesoporous materials with similar characteristics is also interesting because these materials have an equimolar ratio of phenylene to silica, which would enhance hydrophobicity in catalytic applications. The materials were synthesized by cocondensation of a 4,4′-bis(triethoxysilyl)biphenyl precursor and (3-mercaptopropyl)trimethoxysilane in a basic medium and a cationic surfactant followed by an oxidation treatment similar to that described for benzene-bridged functionalized materials. The presence of −SO_3H groups was confirmed by acid titration. The sulfonic acid group concentration was significantly higher (0.99 mequiv/g) than those obtained for benzene-bridged mesoporous materials (0.70 mequiv/g).[108] This method yields highly hydrophobic biphenyl-bridged bifunctional hybrid mesoporous solids with sulfonic acid functionalities and crystalline pore walls, which may be useful for potential applications.

Burleigh et al. obtained bifunctionalized PMOs having both ethane and benzene bridging groups via cocondensation of the corresponding ethane- and benzene-bridged monomer precursors in the presence of the surfactant Brij-76.[109] Depending on the molar ratio of the two monomer precursors in the initial reaction gel, a well-ordered mesoporous material with hexagonal symmetry could be formed. Adjustment of the hydrolysis and condensation rates of individual precursors was rather difficult; however, elemental analysis revealed that the amount of benzene moieties was higher than that of ethane moieties in the resultant mesoporous organosilicas.

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(104) Asefa, T.; Kruk, M.; MacLachlan, J.; Grondey, H.; Jaroniec, M.; Ozin, G. A. *J. Am. Chem. Soc.* **2001**, *123*, 8520.

(105) Yang, Q.; Kapoor, M. P.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 9694.

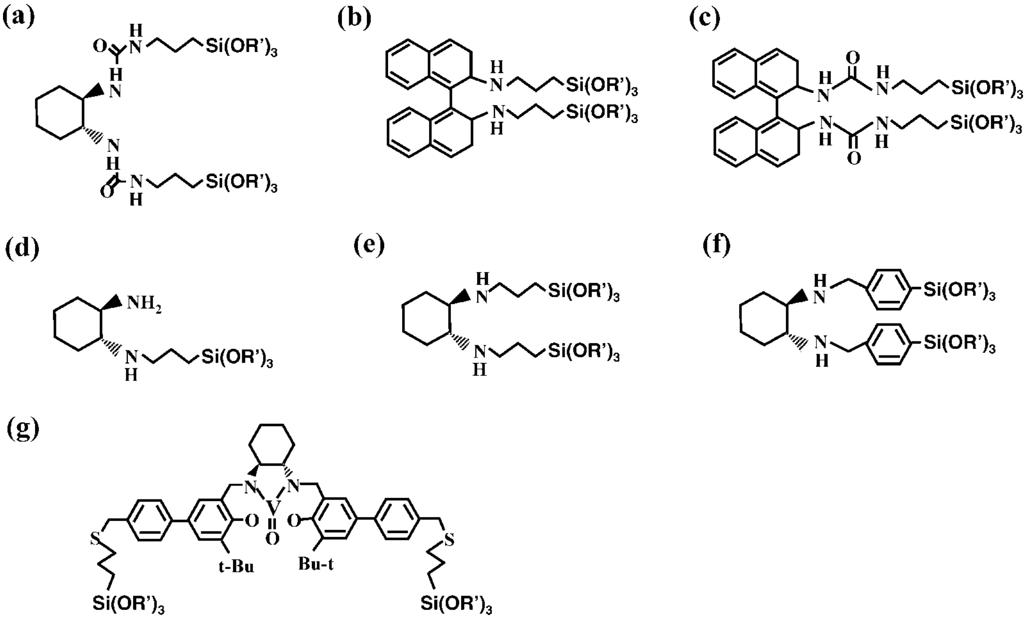
(106) Yang, Q.; Liu, J.; Yang, J.; Kapoor, M. P.; Inagaki, S.; Li, C. *J. Catal.* **2004**, *228*, 265.

(107) Yang, Q.; Kapoor, M. P.; Inagaki, S.; Shirokura, N.; Kondo, J. N.; Domen, K. *J. Mol. Catal. A: Chem.* **2005**, *230*, 85.

(108) Kapoor, M. P.; Yang, Q.; Goto, Y.; Inagaki, S. *Chem. Lett.* **2003**, *32*, 914.

(109) Burleigh, M. C.; Jayasundera, S.; Spector, M. S.; Thomas, C. W.; Markowitz, M. A.; Garer, B. P. *Chem. Mater.* **2004**, *16*, 4.

Scheme 5. Precursors of Chiral PMOs



Furthermore, the possibility of the formation of multifunctional PMOs having four bridging moieties such as methane, ethane, ethylene, and benzene was explored, and a material with a somewhat low order was obtained. In addition, materials combining the two aromatic bridging moieties were synthesized using phenylene and thiophene bridging monomer precursors. Corriu et al. synthesized a bifunctional mesoporous material with an acidic ($-SO_3H$) framework and basic ($-NH_2$) channel pores by cocondensation of a ternary mixture of bis(trimethoxysilyl)-4,5-dithiooctane $(MeO)_3(CH_2)_3SS(CH_2)_3Si(OMe)_3$, TEOS, and 3-[[(*tert*-butoxycarbonyl)amino]propyl]trimethoxysilane $(MeO)_3Si(CH_2)_3NHBoc$ in the presence of P123. The material exhibited a worm-like structure with a specific surface area of 560 m^2/g and a pore size of 8.9 nm.[110] Furthermore, they reported the direct synthesis of bifunctional mesoporous organosilicas containing chelating groups in the framework and reactive functional groups ($-CN$, $-SH$, and $-Cl$) in the channel pores. The bridged organosilicas used 1,4,8,11-tetrakis[(triethoxysilyl)propyl]-1,4,8,11-tetraazacyclotetradecane and the corresponding copper(II) chloride complex as chelating precursors.[87]

6.2. Chiral PMOs. There are a few examples of PMOs with chiral moieties either in the mesopore or in the mesoporous framework prepared by the cocondensation method.[111–115] Alvaro et al. synthesized chiral organic bridges into MCM-41 analogous hybrid materials by using mixtures of bissilylated binaphthyl or cyclohexadiyl precursors (Scheme 5a–c) and TEOS.[111] Li et al. synthesized mesoporous ethane–silicas with *trans*-(1*R*,2*R*)-diaminocyclohexane in the mesopores by the cocondensation of 1,2-bis(trimethoxysilyl)ethane and a chiral precursor (Scheme 5d).[112] The resulting materials had an ordered mesoporous structure with a pore diameter of ~3.3 nm, a specific surface area of ~890 m^2/g, and a ligand loading of up to 0.57 mmol/g. The chiral diamino groups were located in the mesopores of PMOs and were attached on the pore walls through the propyl linkages. These PMOs, after complexing with $(Rh(cod)Cl)_2$, exhibited ~96% conversion and ee values of around 23% ee for the asymmetric transfer hydrogenation of acetophenone. Owing to the ethane bridges in the PMOs, the hydrophobic surface enhanced the catalytic activity. Li et al. also synthesized PMOs that incorporated the chiral diaminocyclohexane moiety by cocondensation of chiral precursors (Scheme 5e,f) with trimethoxysilane.[113,114] These materials have highly ordered mesostructures with a pore size of ~2.3 nm, a specific surface area of ~1070 m^2/g, and a ligand loading of up to 1.02 mmol/g. The catalyst $(Rh(cod)Cl)_2$ incorporated by the chiral diamino groups with phenyl groups as linkers in the framework of the PMO exhibited 97% conversion and an ee value of ~30% for the asymmetric transfer hydrogenation of ketones. Baleizão et al. reported that PMOs with a chiral vanadyl Schiff base complex in the framework showed enantioselectivity for the asymmetric catalytic cyanosilylation of benzaldehyde (Scheme 5g).[115] Recently, Polarz and Kuschel[116] and Ide et al.[117] synthesized functionalized mesoporous ethylene–silicas from 100% chiral borated ethylene-bridged disilane precursors prepared by enantioselective hydroboration.

6.3. Metal-Complexed PMOs. Corriu et al. incorporated large chelating agents into mesoporous silica (Scheme 6a).[118] They induced a cyclam derivative into the framework of silica

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(110) Alauzun, J.; Mehdi, A.; Reye, C.; Corriu, R. J. P. *J. Am. Chem. Soc.* **2006**, *128*, 8718.

(111) Alvaro, M.; Benitez, M.; Das, D.; Ferrer, B.; Gracia, H.; Corma, A. *Chem. Mater.* **2004**, *16*, 2222.

(112) Jiang, D. M.; Yang, Q. H.; Yang, J.; Zhang, L.; Zhu, G. R.; Su, W. G.; Li, C. *Chem. Mater.* **2005**, *17*, 6154.

(113) Jiang, D. M.; Yang, Q. H.; Yang, J.; Zhu, G. R.; Li, C. *J. Catal.* **2006**, *239*, 65.

(114) Li, C.; Zhang, H.; Jiang, D.; Yang, Q. *Chem. Commun.* **2007**, 547.

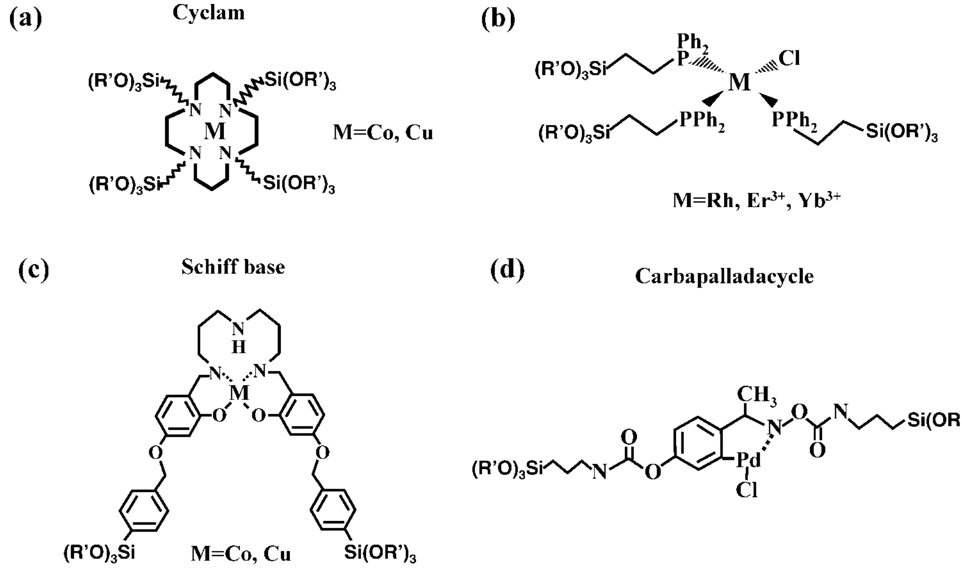
(115) Baleizão, C.; Gigante, B.; Das, D.; Álvaro, M.; Garcia, H.; Corma, A. *J. Catal.* **2004**, *223*, 106.

(116) Polarz, S.; Kuschel, A. *Adv. Mater.* **2006**, *18*, 1206.

(117) Ide, A.; Voss, R.; Scholz, G.; Ozin, G. A.; Antonietti, M.; Thomas, A. *Chem. Mater.* **2007**, *19*, 2649.

(118) Corriu, R. J. P.; Mehdi, A.; Reye, C.; Thieuleux, C. *Chem. Commun.* **2003**, 1564.

Scheme 6. Precursors of Metal-Complexed PMOs



materials through the neutral synthetic route with P123 and F127. The material obtained exhibited only a low mesoscopic order; however, it was able to bind a large concentration of the metal ions Cu^{2+} and Co^{2+}. Corriu et al. also reported functionalization of mesoporous organosilicas by rare-earth complexes.[119] A mesoporous material containing free phosphine oxide ligands in the pore walls was prepared. The phosphine oxide ligands were proven to operate as templates for Er^{3+} and Yb^{3+} ion complexation (Scheme 6b). Similarly, Dufaud et al. synthesized SBA-3 incorporating phosphine-ligated transition-metal complexes.[120] In another attempt, Corriu et al. synthesized hybrid materials containing metal Schiff base complexes (Scheme 6c).[121] Corma et al. reported PMO containing a carbapalladacycle complex as a heterogeneous catalyst for Suzuki cross-coupling (Scheme 6d).[122] Zhu et al. reported the synthesis of propylethylenediamine bridging group functionalized ethane-bridged organisilicas via cocondensation of the ethane-bridged precursor [1,2-bis(triethoxysilyl)ethane] and the Cu^{2+}-complexed precursor bis[(3-trimethoxysilyl)propyl]ethylenediamine in the presence of the triblock copolymer surfactant Pluronic P123.[123] The pore size of the resultant-functionalized materials could be varied from 11 to 21 nm by changing the initial mole ratios of the two precursors (complex/ethane) from 0.1 to 0.3. The materials also allowed reversible change or substitution of Cu^{2+} ions by other ions, such as Zn^{2+}. Furthermore, functionalized PMOs have found application as absorbents. Zhang et al. prepared a tetrasulfide-bridging mesoporous silica, which showed a high affinity for Hg^{2+} cations as well as some affinity for other cations such as Cd^{2+}, Zn^{2+}, Pb^{2+}, and Cu^{2+}.[124] Meanwhile, Olkhovyk and Jaroniec integrated the isocyanurate group into PMOs for high affinity to Hg^{2+} (1.8 g of Hg^{2+}/g of adsorbent).[125]

6.4. Photoactive PMOs. Several studies have dealt with photochemical PMOs (Scheme 7).[126–130] Garcia et al. synthesized a PMO containing electron-acceptor viologen units using the precursor 4,4′-bipyridinium (Scheme 7a).[126] The ability of bipyridinium units to act as electron-acceptor termini has been demonstrated by observation of the radical cation in the photochemical and thermal activation of as-made materials. Corriu et al. reported a photoresponsive PMO, introducing a bridged azobenzene moeity using 4,4′-[[(triisopropoxysilyl)propyl]oxy]azobenzene as the precursor (Scheme 7b).[127] Minoofar et al. reported the synthesis of a PMO containing luminescent molecules and verified their locations by luminescence lifetime measurement (Scheme 7c).[128] Furthermore, Alvaro et al. and Peng et al. synthesized PMOs containing triphenylenepyrylium and diacetylene moieties, respectively (Scheme 7d,e).[129,130] For instance, Peng et al. produced a unique PMO embedded with polydiacetylene via cooperative assembly of cetyltrimethylammonium bromide and diacetylene-bridged silsesquioxane.[130] The diacetylenic molecules spontaneously organized around the surfactant liquid-crystalline structure, forming a mesoscopically ordered composite with molecularly aligned diacetylenic units. Surfactant removal followed by polymerization yielded a polydiacetylene−PMO with a 2D hexagonal mesostructure (*P*6*mm*) and a pore size of 5 nm. The reversible chromatic rapid responses to external stimuli were demonstrated by subjecting this material to thermal cycles between 20 and 103 °C.

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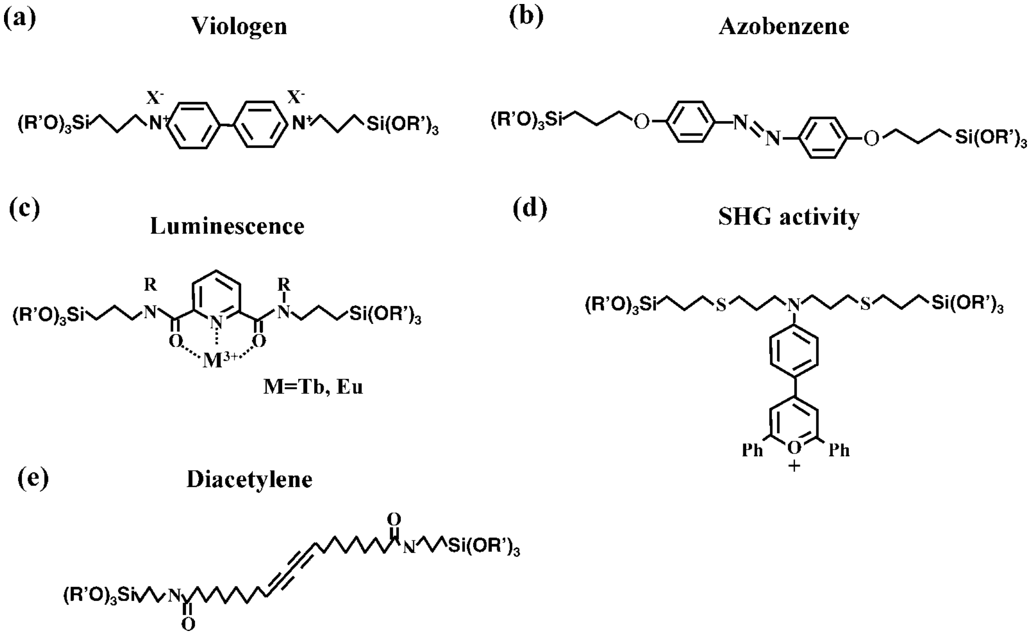
(119) Besson, E.; Mehdi, A.; Reye, C.; Corriu, R. J. P. *J. Mater. Chem.* **2006**, *16*, 246.
(120) Dufaud, V.; Beauchesne, F.; Bonneviot, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 3475.
(121) Corriu, R. J. P.; Lancelle-Beltran, E.; Mehdi, A.; Reye, C.; Brandes, S.; Guilard, R. *Chem. Mater.* **2003**, *15*, 3152.
(122) Corma, A.; Das, D.; Garcia, H.; Leyva, A. *J. Catal.* **2005**, *229*, 322.
(123) Zhu, H.; Jones, D. J.; Zajac, J.; Dutartre, R.; Rhomari, M.; Roziere, J. *Chem. Mater* **2002**, *12*, 4886.
(124) Zhang, L.; Zhang, W.; Shi, J.; Hua, Z.; Li, Y.; Yan, J. *Chem. Commun.* **2003**, 210.
(125) Olkhovyk, O.; Jaroniec, M. *J. Am. Chem. Soc.* **2005**, *127*, 60.
(126) Alvaro, M.; Ferrer, B.; Fornes, V.; Garcia, H. *Chem. Commun.* **2001**, 2546.
(127) Besson, E.; Mehdi, A.; Lerner, D. A.; Reye, C.; Corriu, R. J. P. *J. Mater. Chem.* **2005**, *15*, 803.
(128) Minoofar, P. N.; Hernandez, R.; Chia, S.; Dunn, B.; Zink, J. I.; Franville, A.-C. *J. Am. Chem. Soc.* **2002**, *124*, 14388.
(129) Alvaro, M.; Aprile, C.; Benitez, M.; Bourdelande, J. L.; Garcia, H.; Herance, J. R. *Chem. Phys. Lett.* **2005**, *414*, 66.
(130) Peng, H.; Tang, J.; Yang, L.; Pang, J.; Ashbaugh, H. S.; Brinker, C. J.; Yang, Z.; Lu, Y. *J. Am. Chem. Soc.* **2006**, *128*, 5304.

Scheme 7. Precursors of Photoactive PMOs



6.5. Catalysis. Numerous studies of catalysis using functionalized PMO have been reported. For instance, Yang et al. showed the benefits of periodic pore surface structures in which the ethane linker served to enhance the selectivity and activity during esterification.[131] Similarly, in another study, they have evaluated the catalytic properties of sulfonic acid functionalized ethane and benzene bridging mesoporous organosilicas derived from the oligomeric surfactant Brij-76, synthesized by a cocondensation and subsequent grafting procedure in the condensation of phenol with acetone to form Bisphenol A.[106] In the same study, they presented comparative results on mesoporous benzene−silica materials with and without crystal-like pore-wall structures. The higher catalytic activity of mesoporous benzene−silica materials functionalized via grafting was explained by the fact that sulfonic acid sites on the surface or near the pore mouth are easily accessible for the reactants in the catalytic reaction. Bisphenol is an important precursor in resin and polymer chemistry.

Recently, the structural properties of hydrothermally stable sulfonic acid functionalized ethane-bridged mesoporous organosilicas derived from a triblock copolymer surfactant (Pluronic P123) template were presented. The positive influence of ethane bridging groups on the catalytic behavior of the materials was described.[132] In another report, the hydrolysis of sugars on ethane- and phenylene-bridged mesoporous hybrid materials was described.[133] Kapoor et al. have shown that sulfonic acid functionalized derivatives of 3D ($Pm\bar{3}n$) cubic phenylene-bridged hybrid mesoporous silica materials derived from the precursor 1,4-bis(triallyl)phenylene are effective in Friedel−Craft acylation reactions.[103] Nakajima et al. showed the esterification and pinacol−pinalcolone rearrangement reactions using a new type of functionalized PMO, in which the ethenylene sites on the surface were modified to phenylenesulfonic acid via a Diels–Alder reaction.[71–73]

Furthermore, isomorphous substitution of heteroatoms in the organosilica framework would be useful to enhance the catalytic properties. For instance, Kapoor et al. synthesized a new class of titanium-containing hybrid silsesquioxane mesophases with integral ethane organic functionality from a single organosilane source, in which the titanium is necessarily incorporated, along with the ethane constituents, into the channel wall as molecularly dispersed bridging ligands.[134–136] Gold nanoparticles supported on a highly hydrophobic ethane-bridged titanium-incorporated mesoporous material were reported for enhanced vapor-phase epoxidation of propene using H_2 and O_2.[135] Hughes et al. recently presented the synthesis of ethane-bridged mesoporous silicas with incorporated aluminum, which could offer new prospects for the application of such hybrid silicas to acid catalysis.[137] However, Yang et al. presented the synthesis of aluminum-containing mesoporous phenylene−silicas with crystal-like pore walls and demonstrated their application in alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol.[138] Fukuoka et al. showed the improved catalysis of PMO-embedded palladium nanowires for measuring the reaction rate of CO oxidation in the presence of excess O_2.[139]

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(131) Yang, Q.; Kapoor, M. P.; Shirokura, N.; Ohashi, M.; Inagaki, S.; Kondo, J. N.; Domen, K. *J. Mater. Chem.* **2005**, *15*, 666.

(132) Liu, J.; Yang, Q.; Kapoor, M. P.; Setoyama, N.; Inagaki, S.; Yang, J.; Zhang, L. *J. Phys. Chem.* **2005**, *109*, 12250.

(133) Dhepe, P. L.; Ohashi, M.; Inagaki, S.; Ichikawa, M.; Fukuoka, A. *Catal. Lett.* **2005**, *102*, 163.

(134) Kapoor, M. P.; Bhaumik, A.; Inagaki, S.; Kuraoka, K.; Yazawa, T. *J. Mater. Chem.* **2002**, *12*, 3078.

(135) Kapoor, M. P.; Sinha, A. K.; Seelan, S.; Inagaki, S.; Tsubota, S.; Yoshida, H.; Haruta, M. *Chem. Commun.* **2002**, 2902.

(136) Bhaumik, A.; Kapoor, M. P.; Inagaki, S. *Chem. Commun.* **2003**, 470.

(137) Hughes, B. J.; Guilbaud, J. B.; Allix, M.; Khimyak, Y. Z. *J. Mater. Chem.* **2005**, *15*, 4728.

(138) Yang, Q.; Yang, J.; Fen, G. Z.; Li, Y. *J. Mater. Chem.* **2005**, *15*, 4268.

(139) Fukuoka, A.; Araki, H.; Sakamoto, Y.; Inagaki, S.; Fukushima, Y.; Ichikawa, M. *Inorg. Chim. Acta* **2003**, *350*, 371.

Recently, Hudson et al. reported that chloroperoxidase was successfully immobilized on PMO. Chloroperoxidase is a versatile heme peroxidase that exhibits halogenase and peroxidative activity.[140] The chloroperoxidase on PMO was formed using bis[3-(trimethoxysilyl)propyl]amine, trimethylbenzene, F127, monochlorodimedon, hydrogen peroxide, and so on. These materials showed significant losses in activity over 20 cycles in a low ionic strength assay.

6.6. Film Formations. The thin-film morphology of PMO is important for patterned lithography, sensors technology, and microelectronic applications. In an attempt to generate low-*k* materials, Lu et al. first demonstrated the applicability of the evaporation-induced self-assembly approach to PMO thin films.[141] Later, Dag et al. showed a significant modification and fabricated thin films with different structures and symmetries from several bissilylated precursors.[142] Park and Ha synthesized high-quality free-standing and oriented ethylene-bridged thin films with a uniform thickness between 180 and 800 nm.[143] Ozin et al. have demonstrated the preparation of periodic mesoporous thin films via the spin-coating method and studied their low dielectric constant properties including some of their mechanical and hydrophobic properties for microelectronic applications.[144] Alvaro et al. reported electrochemiluminescence of PMO films containing 9,10-diarylanthracene units.[145] The benefit for electrochemiluminescence activity of having a large surface area with a periodic porous structure is revealed by the fact that an analogous amorphous material prepared with the same precursors does not exhibit any measurable electrochemiluminescence activity under the same conditions. Ohtani et al. synthesized a self-standing mesoporous organosilica film from a mixture of 1,4-bis(triethoxysilyl)benzene and methyltriethoxysilane or dimethyldiethoxysilane.[146] The addition of methyltriethoxysilane or dimethyldiethoxysilane decreased the cross-linking degree of the siloxane network, resulting in improvement of the flexibility and strength of self-standing films.

6.7. Other Applications. Kapoor and Inagaki were able to synthesize phenylene-bridged periodic mesoporous materials (pore diameters ~2.0 nm) having a spherical morphology with diameters between 0.6 and 1.0 μm under very mild basic conditions by using a dilute ethanolic ammonia solution instead of an aqueous NaOH solution with surfactants.[147] However, the pore walls consisted of a rather poor molecular-scale periodicity compared to conventionally produced phenylene-bridged mesoporous organosilicas. Rebbin et al. have prepared spherical particles (0.4–0.5 μm) of ethane-bridged mesoporous organosilicas using a similar approach.[148,149] Kim et al. also fabricated spheres of an ethane-bridged mesoporous organosilica with a diameter between 1.4 and 2.5 μm, the minimum desired size for high-performance liquid chromatography applications.[150] More recently, Kim et al. reported hydrogen-storage properties for Ni-atom-dispersed benzene−silica hybrid materials.[151] It was demonstrated that this material provided an alternative to reversible hydrogen-storage materials with high hydrogen capacities exceeding 6 wt % at moderate pressure conditions.

In addition, Fukuoka et al. successfully synthesized pure platinum and rhodium and mixed (Pt/Rh, Pt/Pd) necklace-shaped nanowires inside an ethane-bridged PMO and confirmed their results by high-resolution TEM and energy-dispersive X-ray analysis.[152] It was concluded that the mixed metallic nanowires consisted of uniform Pt/Rh alloy phases, while the monometallic platinum and rhodium had mean lengths of about 120 and 48 nm, respectively. Fukuoka et al. also synthesized platinum nanowires, which they isolated by removing the mesoporous silica framework using a dilute aqueous HF solution.[153] The mixed (Pt/Rh, Pt/Pd) nanowires in periodic mesoporous silica exhibit very interesting magnetic properties. The magnetic susceptibility below 90 K was ~3 times higher than expected for the simple sum of the value for bulk platinum and palladium. This was related to the low dimensionality of the metal topology.

7. Summary

In this article, we have mainly discussed the latest developments in self-organization of bridged organosilica precursors resulting in the formation of organosilica solids and PMOs with molecular-scale periodicity in the framework. Since its first synthesis, PMO materials have attracted increasing research attention in materials science because these materials can organize a wide number of chemical units inside silica matrices with almost no limitation. The high loading rate and uniform dispersion of organic groups in their frameworks endow PMO materials with unique advantages over pure mesoporous silica. One interesting characteristic of PMOs is that their polarity, hydrophobicity, and hydrophilicity can be tuned within a certain range by the choice of the organic component, and hence their ability to adsorb other materials can be controlled. Moreover, hybrid mesoporous materials have also shown advantages in the host–guest

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(140) Hudson, S.; Cooney, J.; Hondnett, B. K.; Magner, E. *Chem. Mater.* **2007**, *19*, 2049.

(141) 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.

(142) Dag, Ö.; Yoshina-Ishii, C.; Asefa, T.; MacLachlan, M. J.; Grondey, H.; Coombs, N.; Ozin, G. A. *Adv. Funct. Mater.* **2001**, *11*, 213.

(143) Park, S. S.; Ha, C. S. *Chem. Commun.* **2004**, 1986.

(144) Hatton, B. D.; Landskron, K.; Whitnall, W.; Perovic, D. D.; Ozin, G. A. *Adv. Funct. Mater.* **2005**, *15*, 823.

(145) Alvaro, M.; Benitez, M.; Cabeza, J. F.; Garcia, H.; Leyva, A. *J. Phys. Chem. C* **2007**, *111*, 7532.

(146) Ohtani, O.; Goto, Y.; Okamoto, K.; Inagaki, S. *Mater. Lett.* **2006**, *60*, 177.

(147) Kapoor, M. P.; Inagaki, S. *Chem. Lett.* **2004**, *33*, 88.

(148) Rebbin, V.; Jakubowski, M.; Pötz, S.; Fröba, M. *Microporous Mesoporous Mater.* **2004**, *72*, 99.

(149) Rebbin, V.; Schmidt, R.; Fröba, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 5210.

(150) Kim, D. J.; Chung, J. S.; Ahn, W. S.; Kang, G. W.; Cheongy, W. J. *Chem. Lett.* **2004**, *33*, 422.

(151) Kim, S. Y.; Lee, J. W.; Jung, J. H.; Kang, J. K. *Chem. Mater.* **2007**, *19*, 135.

(152) Fukuoka, A.; Sakamoto, Y.; Guan, S.; Inagaki, S.; Sugimoto, N.; Fukushima, Y.; Hirahara, K.; Iijima, S.; Ichikawa, M. *J. Am. Chem. Soc.* **2001**, *123*, 3373.

(153) Sakamoto, Y.; Fukuoka, A.; Higuchi, T.; Shimomura, N.; Inagaki, S.; Ichikawa, M. *J. Phys. Chem. B* **2004**, *108*, 853.

system, and their ability to adsorb host–guest species that impart interesting properties is now being widely studied; considerable success has already been achieved.

The formation of PMOs with molecular periodicity in their walls advances the development of molecular nanotechnology and nanoscience. Pioneering research in controlling molecular self-organization would allow the use of nanostructured materials in diverse applications and nanodevices. Finally, various challenges still remain; however, we feel it is well worth striving to contribute to the development of mesoporous materials.

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