

## REVIEW

# Periodic mesoporous organosilicas for advanced applications

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In 1999, three groups independently developed a novel class of organic–inorganic nanocomposites known as periodic mesoporous organosilicas (PMOs). The organic functional groups in the frameworks of these solids allow tuning of the surface properties and modification of the bulk properties of the material. This paper provides a comprehensive overview of PMOs and discusses their different functionalities, morphology and applications, such as catalysis, drug delivery, sensing, optics, electronic devices, environmental applications (gas sensing and gas adsorption), biomolecule adsorption and chromatography for which PMOs have been used over the past 5 years.

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## INTRODUCTION

To enhance the functionality of mesoporous silica materials, considerable efforts have been made to expand the framework compositions. The hybridization of inorganic and organic species on molecular to mesoscopic scales is a powerful tool for developing functional materials because their cooperative and synergetic effects, as well as the compatibility of different functionalities, can be introduced in the design of such materials.<sup>1</sup>

In this context, three groups (Ozin and co-workers,<sup>2</sup> Inagaki and co-workers<sup>3</sup> and Stein and co-workers<sup>4</sup>) independently developed a novel class of organic–inorganic nanocomposites known as periodic mesoporous organosilicas (PMOs)<sup>2–5</sup> in 1999. In PMOs, the organic groups are located within the channel walls as bridges between the Si centers ((R'O)<sub>3</sub>Si-R-Si(OR')<sub>3</sub> (R' = methyl or ethyl, R = the bridged organic groups)). Organic–inorganic hybrid materials can be synthesized by hydrolysis and condensation reactions of bridged organosilica precursors via the self-assembly process of a structure-directing agent, corresponding to a similar process for the preparation of mesoporous silica materials.

The organic functionalization of these solids permits the tuning of surface properties (hydrophilicity, hydrophobicity and binding to guest molecules), alterations of surface reactivity; protection of the surface from attack; and modification of the bulk properties (for example, mechanical or optical properties) of the material.<sup>6,7</sup>

In the pioneering study of PMOs, the materials were synthesized using single bridged silane as the framework composition. In later studies, two or multiorganosilane precursors were used to obtain PMOs with multifunctional or advanced functionality.

The bridged organosilica precursors have contained heteroelements (N, S, P, O, etc.) in the organic moieties, metal complex and chiral bridges, etc. Generally, these PMOs were obtained with a powder- or film-type morphology.

This is not the first review of PMOs; some excellent reviews of PMOs have been published by a few leading research groups. In 2005, Ozin and co-workers<sup>5</sup> discussed the history of the discovery and development of PMOs, emphasizing the most important advances regarding their compositions and structures, morphologies and properties. Later, Fröba and co-workers,<sup>8</sup> Jaroniec,<sup>9</sup> Inagaki and co-workers,<sup>6</sup> Fujita and Inagaki,<sup>7</sup> Lin and co-workers,<sup>10</sup> Ozin and co-workers<sup>11</sup> and Corma and co-workers<sup>12</sup> published some excellent reviews of PMO studies. The most recent review paper was by Van Der Voort and co-workers,<sup>13</sup> who provided a comprehensive overview of these materials, discussing their functionalities, morphology and applications by referring to approximately 300 works on PMO materials.

This review is limited mainly to the applications of PMOs. We attempted to review most of the recent advances in the applications of PMOs. This publication aims to be a useful resource for experienced researchers in this area, as well as to encourage others to enter this exciting but still young field.

## NEW SYNTHESIS ROUTES AND NEW PRECURSORS FOR THE PREPARATION OF PMOS

A variety of covalent organosilica hybrids have been developed for a wide range of applications, based on the chemical, physical, mechanical and dielectric properties of the materials.<sup>1,2,6</sup> General synthesis

methods for PMOs have been well reviewed in previous review articles.<sup>6,8</sup>

Bis-silane holds an organic functional linker between silicon atoms and has a structure of  $(R'O)_3Si-R-Si(OR')_3$ , with  $OR'$  denoting the hydrolyzable group (usually ethoxy or methoxy groups) and  $R$  the functional linker. The following four pathways were considered for the preparation of PMOs with organic moieties in the frameworks (Figure 1): (1) a single bridged organosilica precursor, (2) more than two bridged organosilica precursors with different functional groups, (3) bridged organosilica and silica precursors with the dangling organic groups and (4) secondary modification by a chemical treatment of the bridged organic moiety after the production of the PMO.

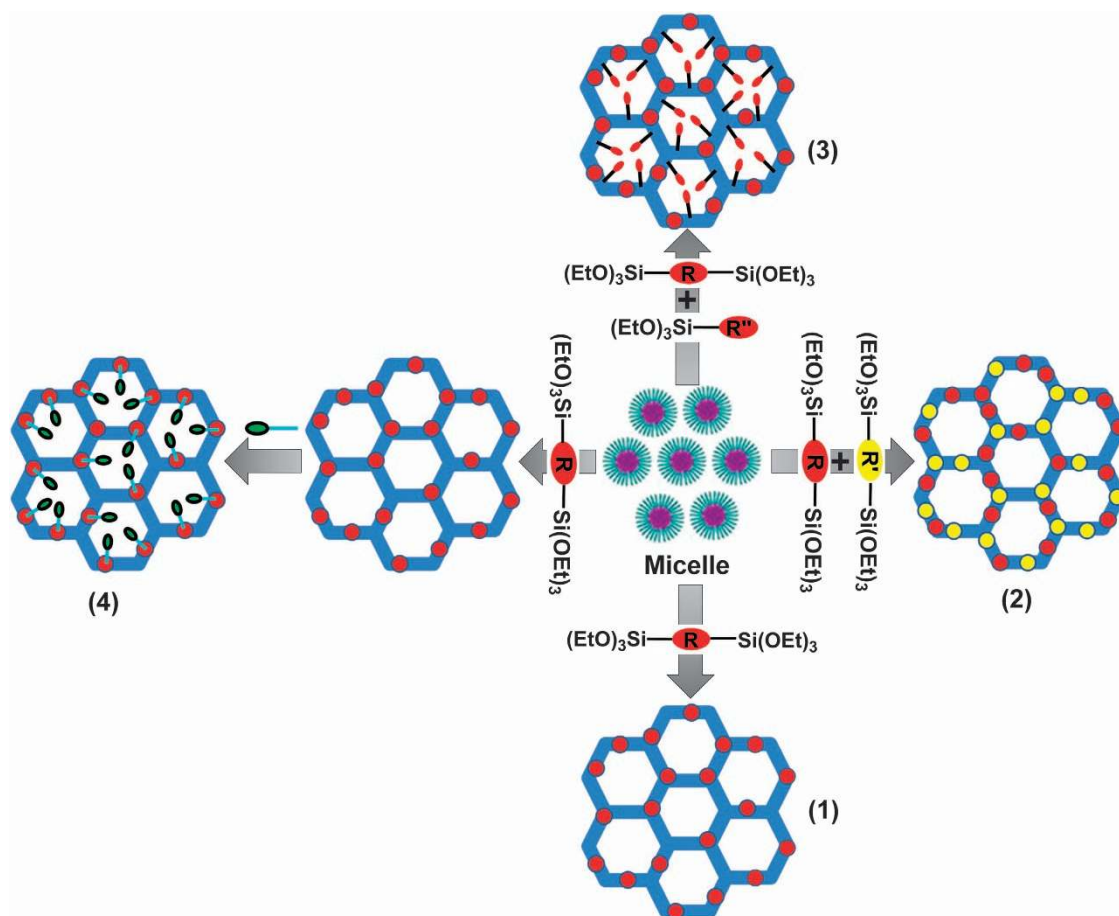
Pathway (1) was discussed in previous review articles.<sup>6,8</sup> Here, pathways (2)–(4) are discussed briefly with a few representative studies. Although mesoporous organosilica composites have been prepared with various functional groups including large-sized functional molecules,<sup>6</sup> there has been little progress on the synthesis of materials with two or more functional groups in a single material system for different or targeted applications with enhanced application efficiency of the materials. In this context, the introduction of two or more functionalities onto the pore surface is an alternative approach to preparing multifunctional materials. Unfortunately, pore surface modifications with different functional groups can easily lead to pore blockage.

An emerging trend is to produce multifunctional mesoporous materials by simultaneous introduction of multifunctional

organosilane molecules with extremely different reactive parts at various ratios into the mesoporous organosilica material pore walls inside the pore framework, without pore blockage.<sup>14–17</sup> For example, Thiel and co-workers<sup>15</sup> generated a PMO material that successfully combined two antagonistic functional groups in a single PMO material, that is, one type of functional group was located in the framework walls and another functional group was directed to the pore channels. The resulting materials possess a hydrophobic phenylene layer and a hydrophilic propylamine layer. Therefore, the materials work as effective catalysts for several aldol-type reactions because they possess two antagonistic functional groups.

In addition, the synthesis of PMOs needs to consider a range of conditions, such as the reaction temperature and time, pH, cosolvent, auxiliary substances and the optimized reactant ratio.<sup>8,17</sup> Better-ordered materials in a wider range of acid concentrations are normally obtained using inorganic salts, such as NaCl, KCl,  $Na_2SO_4$  and  $K_2SO_4$ , and metal ions, such as  $Zr^{4+}$ ,  $Sn^{4+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  and  $Al^{3+}$ .<sup>18</sup> This positive effect of inorganic salts on the long-range ordering of various mesostructures is explained by dehydration of the ethylene oxide (EO) units of the surfactant, which decreases their hydrophilicity and increases the hydrophobicity of the propylene oxide (PO) moieties in the poly(ethylene oxide-*b*-polypropylene oxide-*b*-polyethylene oxide) triblock copolymer ( $EO_n$ - $PO_m$ - $EO_n$ ).

Initial studies of PMOs focused on the incorporation of small aliphatic (ethane and ethene) and aromatic (benzene and thiophene) bridging groups into the walls of the channel-like structures.<sup>1</sup> A range of aromatic bridged PMO precursors (phenyl, biphenyl,



**Figure 1** Four pathways for the preparation of PMOs with organic moieties in their frameworks.

divinylbenzene, acridone and their derivatives) were prepared by several leading groups.<sup>6–8,10,13,14</sup> For example, Inagaki and co-workers<sup>14</sup> produced a PMO material that contains benzene groups in the pore wall framework and the phenylsulfonic acid functionalities ( $\text{C}_6\text{H}_5\text{-SO}_3\text{H}$ ) that face toward the mesopore channels. The sulfonic acid functional groups were derived from the mercaptopropyl groups ( $-\text{C}_3\text{H}_6\text{SH}$ ) by oxidative transformation of surface thiol groups into sulfonic acid groups. The obtained material possesses molecular periodicity even with higher loading of the thiol functional precursor (67 mol% in the initial reaction mixture).

Zhang and co-workers<sup>16</sup> synthesized nanometer-sized PMO materials using bridged organosilane precursors with three types of different functional groups (fluorophores) located in the mesopore walls. The obtained materials show multifluorescent emission by single-wavelength excitation. This type of PMO materials would be useful in the synchronous/asynchronous release of various drugs from different color nanoparticles with tunable color-related drug release.

A remarkable feature of PMOs synthesized from a single precursor is the induction of molecular-scale periodicity in the framework. Mesoporous organosilica materials functionalized with organic groups normally consist of amorphous frameworks. In contrast, the frameworks of PMO materials with bridged aromatic groups can form crystal-like layered structures with molecular-scale periodicity. PMOs have a crystal-like framework with repeating units of alternating organic silica layers (5.6–11.9 Å depending on the organic bridges)<sup>7</sup> (Figure 2).

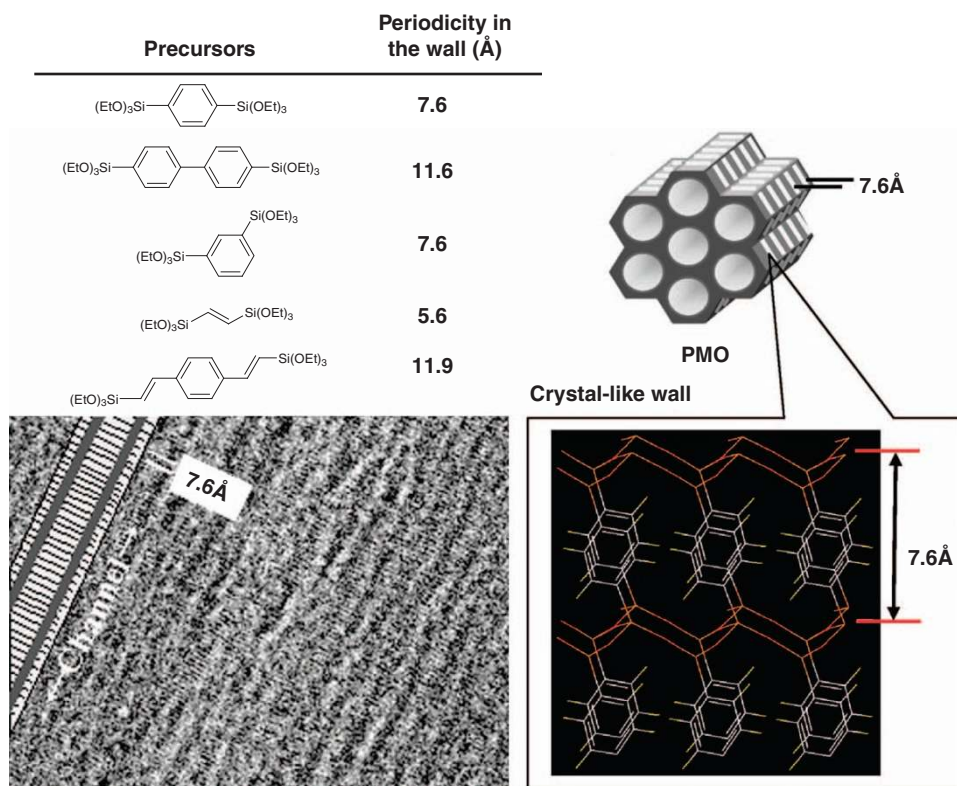
Aromatic-bridged PMOs with crystal-like frameworks can allow tuning of the interactions between the aromatic organic groups and

control of the optical and electrical properties.<sup>6,19</sup> In addition, PMOs with crystal-like frameworks are interesting materials for specific molecular adsorption because their hybrid surfaces consist of regular arrays of aromatic rings and silanols, which exhibit Lewis base and weak Lewis acid characteristics, respectively.<sup>20</sup>

More advanced PMO materials are those with bridges containing hetero atoms such as nitrogen or sulfur.<sup>13,15,21</sup> Long and flexible functionalities are difficult to incorporate into PMOs. In these cases, tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) are added to assist in the formation of more rigid and ordered mesophases. Organosilica precursors with linear bridges containing nitrogen and sulfur atoms were synthesized to produce azobenzene units, diimine Schiff base units, diimine/diacetylenic units, amine units and sulfide units.<sup>13,15</sup>

The sulfide moieties in PMOs are of interest for their high selectivity in adsorbing contaminants. Moreover, these groups can be a source of possible acid functionalities through a postoxidation treatment to provide sulfonic acid moieties. Several researchers<sup>21–23</sup> reported PMO materials incorporating organosilica precursors with nitrogen or oxygen atoms in aliphatic, aromatic or cyclic moieties. These materials are attractive for the development of new types of solid-type host materials with highly selective sorption and separation properties in host–guest chemistry.<sup>22–24</sup>

Other advanced PMO precursors were prepared with ionic bridged organic moieties in the molecular structure ( $(\text{R}'\text{O})_3\text{Si-R}^+-\text{Si}(\text{OR}')_3\text{X}^-$ ) ( $\text{R}' = \text{methyl or ethyl}$ ,  $\text{R}^+ = \text{bipyridinium, imidazolium or dihydroimidazolium units}$ ).<sup>13</sup> These ionic bridged organosilica precursors can lead to advanced materials for heterogeneous catalysis, adsorption and photochemical processes.<sup>13</sup>



**Figure 2** A list of important aromatic organosilane precursors and their periodic arrangement in the mesopore walls of the PMOs, and a transmission electron microscope (TEM) image of a 2,6-naphthylene-bridged PMO with a crystal-like framework (adapted from Fujita and Inagaki,<sup>7</sup> Copyright © 2008 American Chemical Society).

PMO materials with chiral centers have also attracted our interest for their potential in high-technology applications, such as chiral chromatography, chiral separation and asymmetric catalysis. Recently, several researchers synthesized a range of organosilica precursors containing chiral centers (Figure 3)<sup>13</sup> with good properties for asymmetric catalysis.

A variety of metals have been incorporated in PMOs with metal complexes.<sup>13</sup> Metal complexes are particularly interesting in the field of catalysis. These metal complexes can be introduced into PMOs by two approaches: either they can be chelated to the precursor before the PMO synthesis or they can be attached to the PMO surface in a postmodification step.

Various metal complex materials were synthesized though cocondensation after incorporating simple silanes or bis-silanes to obtain PMOs (Figure 4).<sup>13</sup>

Morphological control and the texture of mesoporous materials are also extremely important in many applications. The morphology of materials often controls their function and utility. Dodecahedrons, spheroids, films, monoliths, gyroids, platelets and rod-shaped

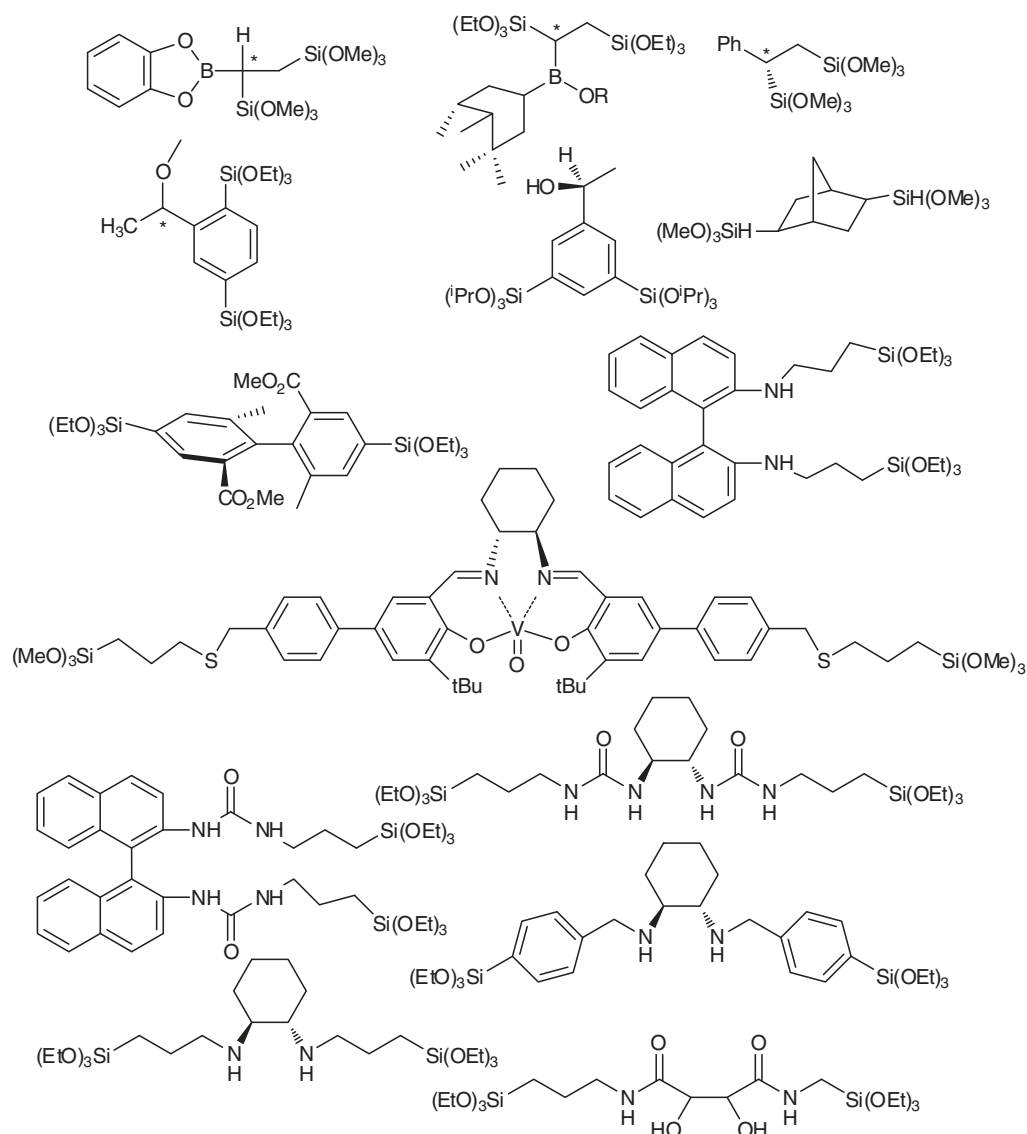
organic–inorganic hybrid mesoporous materials have been reported for practical applications (Figure 5).<sup>17</sup>

Periodic mesoporous hollow spheres are also quite attractive owing to their unique properties, such as large, hollow cavity spaces; high surface areas; well-defined, tunable mesopore wall structures; low density; and good membrane permeability. Owing to their large, hollow cavities, it may be possible to load them with large amounts of cargos, and their release behavior could be well controlled by tuning the silica walls with appropriate functional group modifications. Therefore, the mass transport of the cargos and the membrane permeability could be well controlled. Thus, hollow PMO spheres have been efficiently used in many applications, such as catalysis, and in drug delivery systems, such as microcontainers.<sup>25,26</sup>

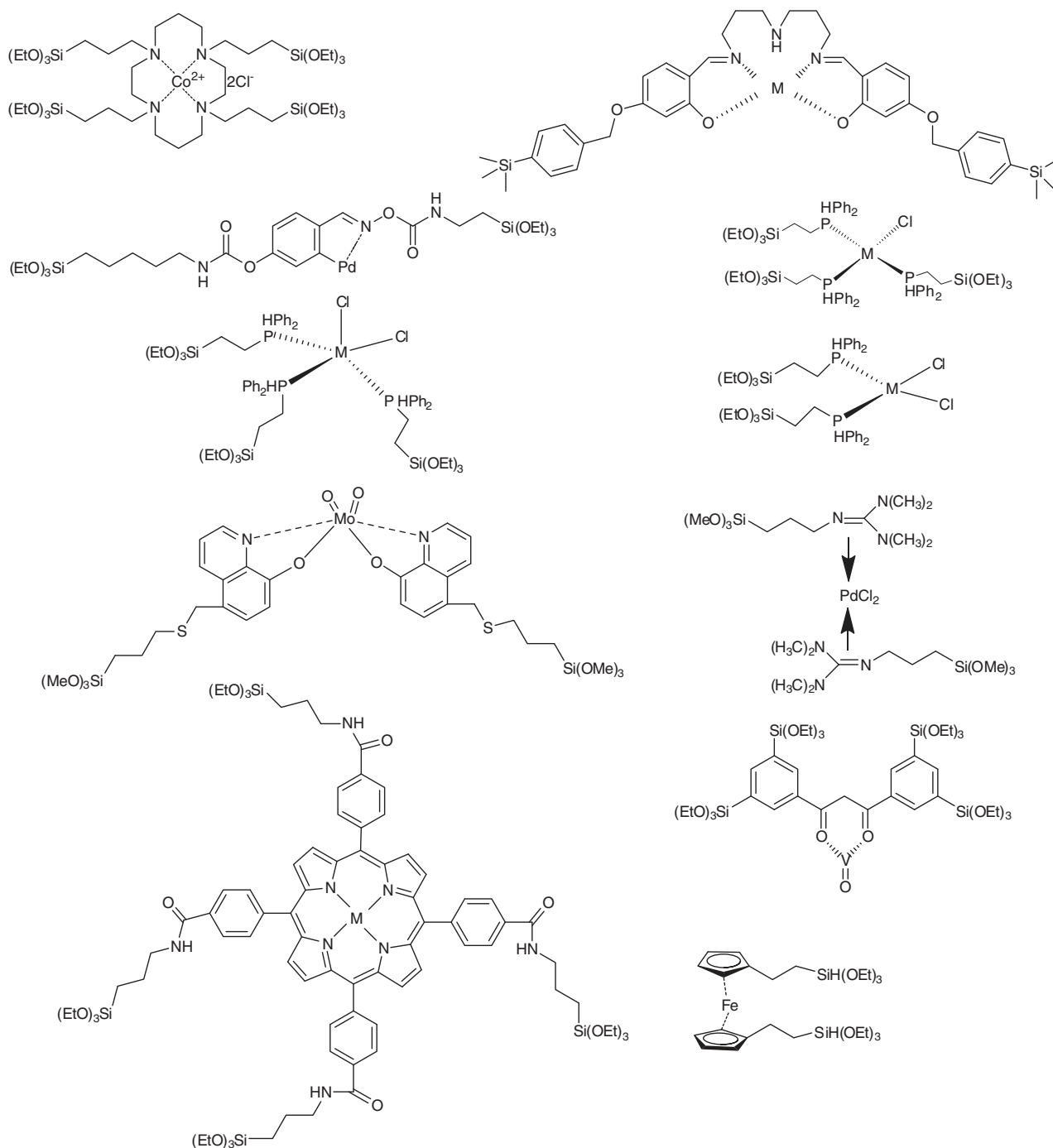
## ADVANCED APPLICATIONS OF PMOS

## Catalysis

Catalysts are of paramount importance. Recent progress regarding the design and synthesis of heterogeneous mesoporous silica catalysts, particularly, PMO catalysts, is quite impressive.



**Figure 3** Bis-silylated chiral precursors used in the synthesis of chiral PMOs.



**Figure 4** Metal complexes included in PMO materials.

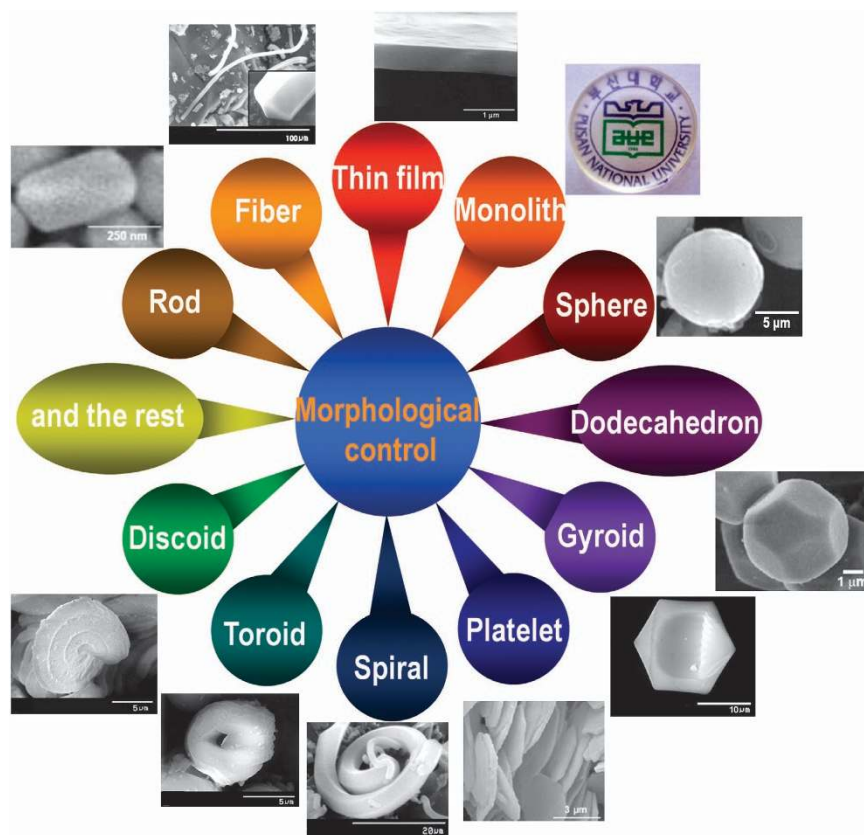
Although PMOs have been periodically reviewed, a limited number of examples illustrate some current trends in the application of the PMO materials in heterogeneous catalysis. To rationalize the catalytic applications of PMOs, this study classified them based on their main catalytic functions.

*Organic group functionalized PMO materials as catalysts.* Several PMO materials have been successfully prepared for catalytic applications. PMO materials containing acid groups have been used widely as acid catalysts because the acidic functional sites act as reaction sites for a range of reactions. Among these, sulfonic acid is one of the

versatile functional groups for acid catalyst applications. Different types of sulfonated PMO materials have been synthesized using cocondensation, direct sulfonation and postfunctionalization methods.<sup>27,28</sup> The prepared sulfonic acid-containing PMO materials exhibited superior catalytic performance in esterification, acetylation and condensation reactions.

The preparation of hollow PMOs using large and flexible organo-silane bridging groups is quite difficult and has not been fully explored. The thermal and mechanical stability of hollow PMOs have not been characterized extensively according to their compositions and structures. Nevertheless, the hollow PMOs deserve consideration





**Figure 5** PMO materials with a range of morphologies.

in future research because the hollow PMOs are the key materials in catalysis applications. Although the catalytic applications of hollow PMOs have not been fully investigated, preliminary results strongly suggest that the unique morphology of hollow PMOs enhances the accessibility of the reactants to the active sites and increases the reactant diffusion rate during the catalytic process.

Wang and co-workers<sup>29</sup> obtained hollow phenylene-bridged PMO (H-PhPMO-Mac) through a hard templating route using hematite nanoparticles as the hard template and applied them as a MacMillan catalyst in asymmetric Diels–Alder reactions. The synthesized H-PhPMO-Mac catalyst exhibited high catalytic activity (98% yield, 81% enantiomeric excess (ee) for endo and 81% ee for exo) in asymmetric Diels–Alder reactions with water as a solvent.

**Metal nanoparticle-supported PMOs as catalysts.** Mesoporous silica solids are beneficial in catalysis owing to their relatively large pore size, which facilitates mass transfer, and high surface area, which allows for a large number of catalytic sites, as well as the incorporation or integration of catalytic organic sites/metal atoms in the framework. On a mesoporous silica matrix, surface-modified catalytic systems have some disadvantages, such as low stability, non-uniform catalytic site distribution and catalytic site leaching. To overcome these problems, PMOs offer a powerful route for catalytic modification with the support of metal nanoparticles, such as Pd,<sup>30–32</sup> Au,<sup>33–36</sup> Ti,<sup>24</sup> Ru,<sup>37</sup> Cu<sup>38</sup> and Cr,<sup>39</sup> etc. Table 1 summarizes the recent studies of PMOs for catalytic applications.

Two representative examples are described briefly in this review. The palladium-catalyzed Heck cross-coupling reaction of alkenes with aryl or vinyl halides is one of the most significant and efficient transformations in chemical processing because palladium has an

important role in the synthesis of key intermediates in asymmetric, pharmaceutical, polymer and industrial chemistry.

Hunt and co-workers<sup>30</sup> produced Pd-containing PMOs with an ionic-liquid framework (Pd@PMO-IL), which exhibited efficient catalytic activity in the Suzuki cross-coupling reaction of aryl boronic acid with a range of aryl halides (Scheme 1). Hunt and co-workers<sup>31</sup> also reported that the PMO-IL can be used effectively for the immobilization and stabilization of Pd nanoparticles with high catalytic efficiency for the selective oxidation of various alcohols, such as benzyl, allylic, alicyclic and aliphatic alcohols in the presence of molecular oxygen/air as the oxidant.

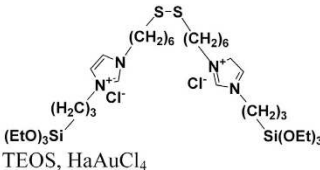
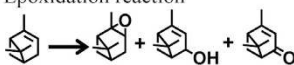
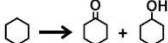
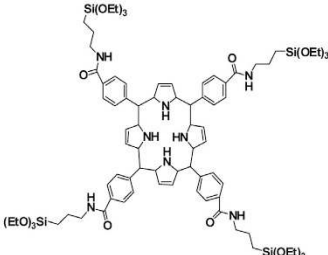
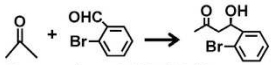
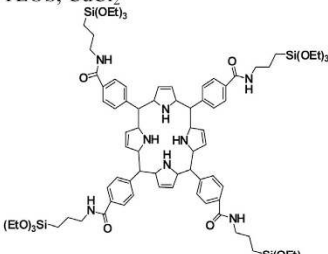

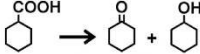
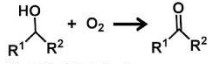
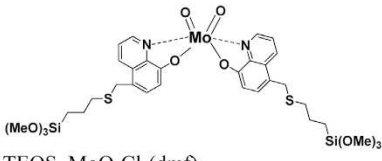
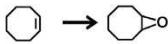
Allyl imidazolium-based PMOs with rhodium metal (Rh@PMO-IL) are suitable for the conversion of a wide range of primary or secondary benzyl alcohols into their corresponding aldehydes or ketones in good to excellent yield. This type of catalyst was reported by Hunt and co-worker<sup>37</sup> (Scheme 2).

Recently, various metals, such as V, Rh and Ir, and molecules, such as porphyrins, have been incorporated into the PMO pore walls with a range of organosilane bridging functional molecules. Although metal complexes can be incorporated onto mesopore silica surfaces using postgrafting methods,<sup>40</sup> it is preferable to incorporate organic groups in the silica walls, because in the former case organic groups offer little resistance to the diffusion of reactants, leading to reduced catalytic efficiency. A range of metal complexes have been integrated in the PMO framework through bridged organosilane–metal complexes.

Recently, the synthesis and preparation of organometallic complexes in heterogeneous forms has become a popular topic that offers great advantages for green catalysis in addition to cost-effectiveness, recovery and reusability of expensive and/or toxic catalysts and the

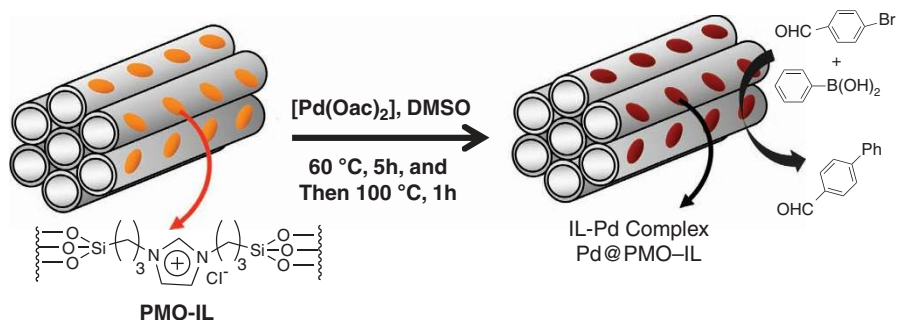


Table 1 Continued

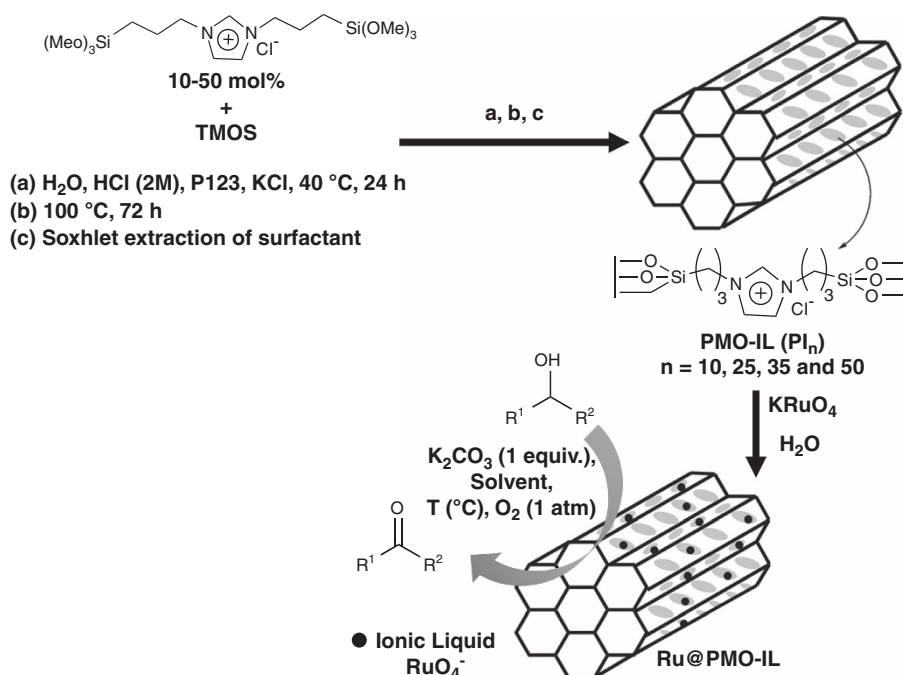
Metal nanoparticles or metal complexes	Precursors	Catalytic effects	Reference
	 <p>TEOS, HaAuCl<sub>4</sub></p>	<p>Epoxidation reaction</p>  <p>Conversion: 11-86 %</p>	33
Cr nanoparticle or Cr complex	<p>(EtO)<sub>3</sub>Si—Si(OEt)<sub>3</sub></p> <p>TEOS, Cr(NO<sub>3</sub>)<sub>3</sub></p>	 <p>Y = &lt;5 % (TBE, H<sub>2</sub>O<sub>2</sub>) 0 % (TBE, <i>t</i>-butyl hydrogen peroxide) Y = 35 % (TBC, H<sub>2</sub>O<sub>2</sub>) 6 % (TBC, <i>t</i>-butyl hydrogen peroxide)</p>	39
Cu complex	 <p>TEOS, CuCl<sub>2</sub></p>	 <p>Conversion: 91% (24 h)</p>	35
Cu, Fe, Sn complex	 <p>TEOS, CuCl<sub>2</sub>, SnCl<sub>2</sub>, FeCl<sub>2</sub></p>	<p>Baeyer-Villiger oxidation</p>  <p>Y = 40.7-100 % (Fe-TCPP-PMO-20%) Y = 3.2-23.7 % (Cu-TCPP-PMO-10%) Y = 1.6-10.4 % (Sn-TCPP-PMO-20%)</p>	42
RuO <sub>2</sub> <sup>2-</sup> complex	<p>(EtO)<sub>3</sub>Si—N<sup>+</sup>—N<sup>+</sup>—Si(OEt)<sub>3</sub></p> <p>TEOS, CuCl<sub>2</sub></p>	 <p>Conversion: 99%</p>	38
	<p>(MeO)<sub>3</sub>Si—(CH<sub>2</sub>)<sub>3</sub>—N<sup>+</sup>—N<sup>+</sup>—Si(OMe)<sub>3</sub></p> <p>TEOS, KRuO<sub>4</sub></p>	 <p>R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, etc R<sup>2</sup> = H, cyclopropyl, Me, Et, C<sub>6</sub>H<sub>4</sub>, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 4-MeO-C<sub>6</sub>H<sub>4</sub>, CH<sub>3</sub>, Me Y = 87-99 % (R<sup>2</sup>=H) Y = 95 % (R<sup>2</sup>=cyclopropyl) Y = 75-96 % (R<sup>2</sup>=Me) Y = &gt;99 % (R<sup>2</sup>=C<sub>6</sub>H<sub>5</sub>) Y = 92 % (R<sup>2</sup>=4-MeO-C<sub>6</sub>H<sub>4</sub>)</p>	37
Mo complex	 <p>TEOS, MoO<sub>2</sub>Cl<sub>2</sub>(dmf)<sub>2</sub></p>	 <p>Y = trace-48.8 %</p>	41

Abbreviations: PMOs, periodic mesoporous organosilicas; TBC, *t*-butyl hydrogen peroxide; TBE, *t*-butyl hydrogen peroxide; TEOS, tetraethyl orthosilicate; TMOS, tetramethyl orthosilicate.





**Scheme 1** Schematic diagram of the preparation and catalysis of the Pd-containing PMOs with an ionic-liquid framework (Pd@PMO-IL) catalyst (adapted from Hunt and co-workers,<sup>30</sup> Copyright © 2010 Wiley-VCH Verlag GmbH KGaA, Weinheim, Germany).



**Scheme 2** Schematic diagram of the preparation and catalysis of Ru@PMO-IL materials (adapted from Hunt and co-workers,<sup>31</sup> Copyright © 2011 Wiley-VCH Verlag GmbH KGaA, Weinheim, Germany).

avoidance of product contamination.<sup>13</sup> For example, bridges, such as bis(8-quinolinolato)dioxo molybdenum (IV) complex<sup>41</sup> and metalloporphyrine<sup>42</sup> (Scheme 3), were more active than homogeneous complexes.

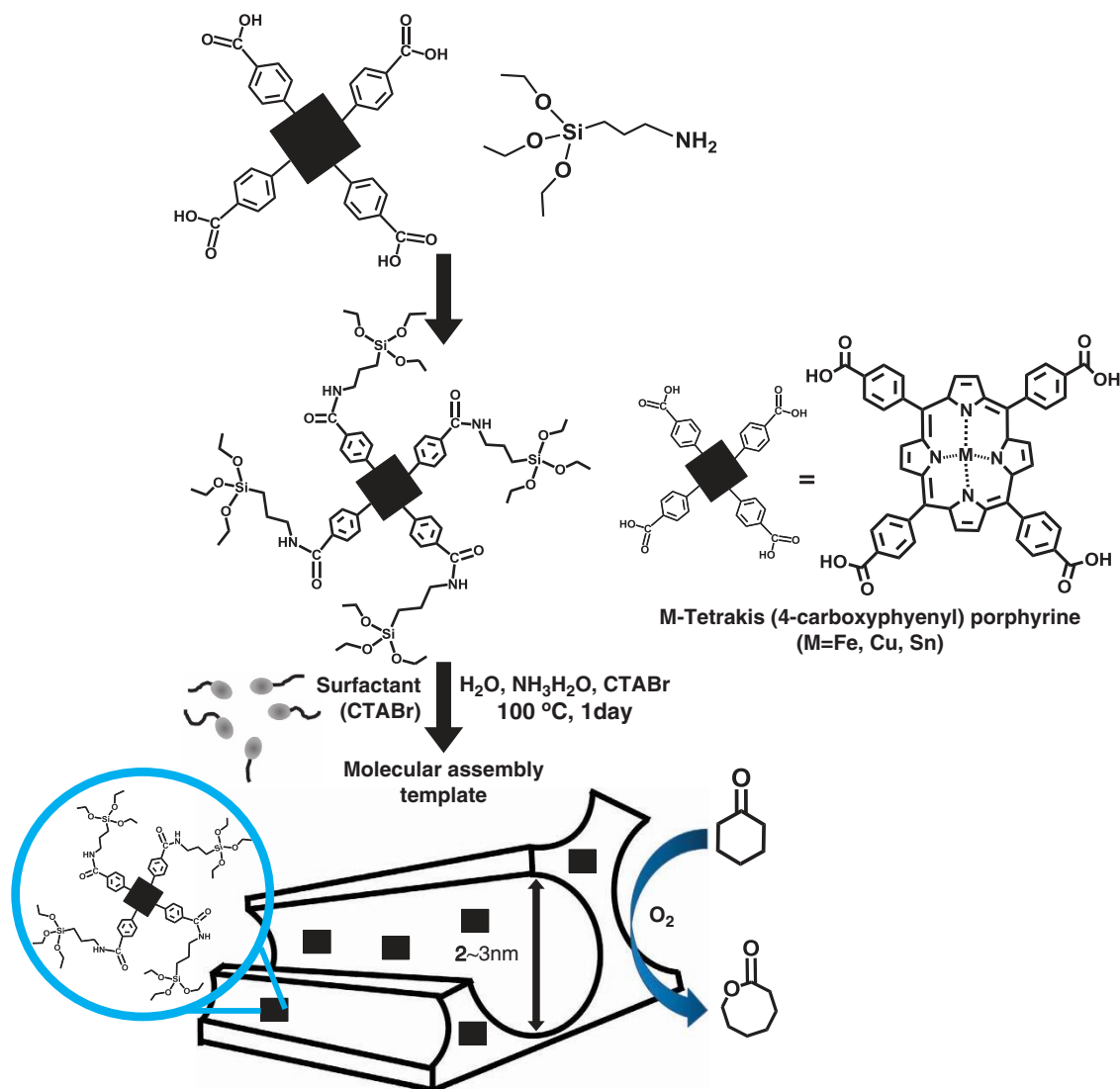
#### PMO materials as hosts for drug and biomolecules

Another exciting field of research in mesoporous organosilicas has been the potential use of PMO materials as efficient drug delivery vehicles. The well-organized mesoporous organosilica network in materials such as organosilane-modified materials and PMOs allows fine control of the adsorption and release of drug molecules in a controlled manner,<sup>43,44</sup> whereas with conventional drug administration such as simple intravenous injection, there are lower drug concentrations in the specific targeted sites because a certain amount of small drug molecules is lost *en route* to the target sites. To use mesoporous organosilica hybrid nanomaterials as an intracellular delivery system, it is important that the drug be released in a controlled manner at the target site. The premature release of loaded cargos can cause severe side effects in healthy cells. In a

perfect scenario, the delivery of toxic anticancer agents would require (i) zero premature release behavior, (ii) a biocompatible drug carrier system and (iii) a controlled and sustained release rate.

Mesoporous organosilica hybrid nanocarriers for drug delivery can be superior to traditional methods because they can be designed to adsorb large amounts of drug molecules by interacting with the organic functionalities and to release only at the specific sites with a controlled release rate. Many studies have examined silica-based organic hybrid mesoporous materials with organosilane, capping molecules/nanoparticles or polymer functional groups for the adsorption and delivery of drugs, genes and enzymes under a range of internal/external stimuli, such as temperature, redox, pH, light, magnetism and ultrasound.<sup>45</sup> However, the studies using PMOs as carriers of drug molecules are still limited.

Lu and co-workers<sup>46</sup> reported the effects of the morphology, wall composition of mesoporous materials and different buffer solutions on the drug delivery profiles. Cisplatin (*cis*-dichlorodiammineplatinum(II), CDDP) is one of the most widely used and effective cytotoxic agents in the treatment of solid tumors because of



**Scheme 3** Synthetic route of M-tetrakis(4-carboxyphenyl)porphyrin-PMOs (adapted from Park and co-workers,<sup>42</sup> Copyright © 2011 American Chemical Society).

its potent DNA crosslinking activity upon entering cells. Hollow PMO spheres were prepared and used as drug carriers; they exhibited higher loading capacity and a slower release rate compared with conventional periodic mesoporous silica spheres and solid spheres of PMO owing to their empty cores. Asefa and co-workers<sup>43</sup> reported an ethane-bridged PMO hybrid carrier for the loading and slow release of hydrophobic drugs (cisplatin). The drug incubation temperature, methods used to remove the surfactant templates from mesoporous materials and the solvents used to place the surface organic functional groups on the materials can affect the adsorption capacity and drug-release properties of potentially useful nanoporous silica and organosilica as drug delivery vehicles. Ethane-bridged PMO also showed a significantly higher adsorption capacity for both rhodamine 6G and cisplatin than the control samples, MCM-41 or SBA-15. Increasing the temperature improved the adsorption capacity of ethane-bridged PMO for both rhodamine 6G and cisplatin.

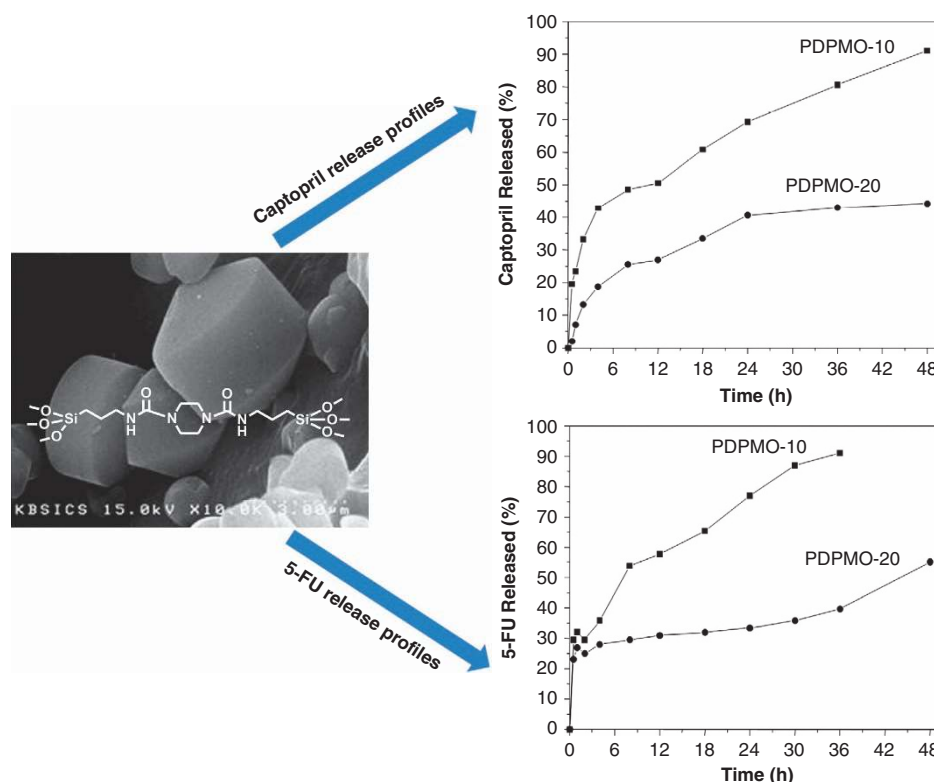
A bis-silylated precursor bearing sulfonamide and urea groups integrated into the PMO framework was prepared for the loading and release of two drugs, captopril and 5-fluorouracil (Figure 6).<sup>47</sup> A PMO material was prepared for the same purpose using ureylene

and piperazine units;<sup>48</sup> PMO materials with bridged organic moieties (bridged amidoxime, bridged pyridine) as nanocarriers were included.<sup>21,49</sup>

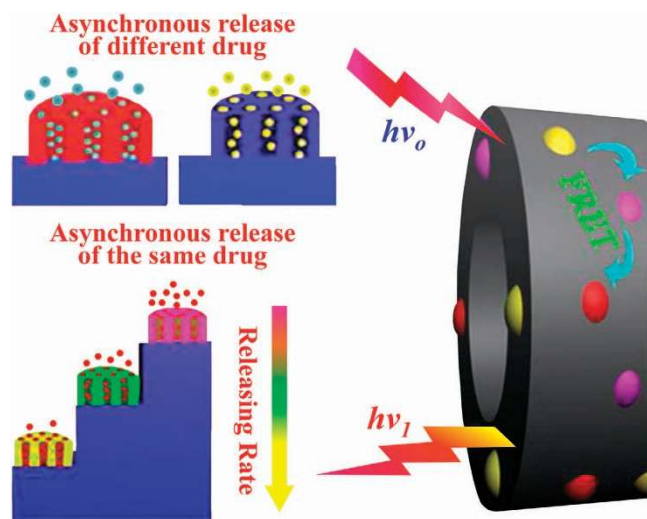
Zhang and co-workers<sup>16</sup> fabricated multifluorescent PMO nanoparticles using a modified and mild Stöber system with bis-silylated biphenyl, anthracene and naphthaleneimide as the multifluorescent organosilane precursors (Figure 7). The prepared multifluorescent material showed finely tunable color-related drug release performance in the effective screening of drugs and therapeutic protocols for diseases.

Recently, Wu and co-workers<sup>44</sup> reported a benzene-bridged PMO material functionalized with a high load of carboxylic acid groups ( $\sim 80\%$ ) in the mesoporous network. The resulting material allowed the controlled loading and release of doxorubicin in cancer therapy.

A recent report by Botella and co-workers<sup>25</sup> described the preparation of spherical poly(lactic-co-glycolic acid) nanoparticles containing hydrophobic molecules covered by redox-responsive amorphous silica via a self-assembly approach with TEOS and a disulfide-bridged silsesquioxane precursor (Scheme 4). The report also showed the feasibility of a bioresponsive drug delivery system.



**Figure 6** Scanning electron microscope (SEM) image of diurelenepiperazine-bridged PMOs, and captopril and 5-fluorouracil release profiles from PDPMOs (adapted from Ha and co-workers,<sup>47</sup> Copyright © 2011 Elsevier).



**Figure 7** Schematic illustration of PMOs with finely tunable color-related drug release performance for the potential applications of fluorescent nanoparticles by fluorescence resonance energy transfer (FRET) in effective screening of drugs and therapeutic protocols for diseases (adapted from Zhang and co-workers,<sup>16</sup> Copyright © 2012 American Chemical Society).

Galla and co-workers<sup>50</sup> prepared new nanocomposite (NC) alginate hydrogels with multiply functionalized PMOs (PMO-alginate) as nanometer-scale particles and nanocontainers, and used the NC hydrogels as the models for three-dimensional scaffolds in cell adhesion experiments. As a proof of principle, the use of the PMO as

a nanocontainer was demonstrated by the release of dye molecules from the pores of the PMO to stain the cell nuclei inside an NC hydrogel.

#### Optical applications: light harvesting, sensing and imprinting

The optical properties of PMOs are also noteworthy for advanced applications. The optical properties of PMOs can be tuned by changing the photoactive bridging organic groups that are incorporated and the synthesis conditions. The optical functions of mesostructured materials are normally obtained by incorporating photoactive species such as dyes into the mesopores by surface immobilization. The surface-immobilized dye molecules might aggregate, resulting in reduced fluorescence, and the incorporation of dye molecules in the mesopore channels might prevent the packing of dye molecules and suppress self-quenching. Consequently, to overcome this limitation, PMOs offer a great potential for higher loading of dye molecules into their pore wall frameworks and show higher quantum efficiency than the surface immobilization on the mesopore channels. The tuning of PMO pore walls with different photoactive species enables energy transfer between two species within a single material.

PMOs with highly efficient light-harvesting properties were achieved by the Inagaki group<sup>51</sup> through energy transfer from the biphenylene groups on the framework to coumarin groups located in the mesopore channels. They also reported PMO materials with an acridone chromophore or 2,6-naphthylene and biphenylene bridging groups for a range of applications, such as light-harvesting and display materials<sup>52–54</sup> Yan and co-workers<sup>55</sup> prepared photoactive lanthanide hybrids bonded covalently with functional PMO materials using calix[4]arene derivatives through the P123 surfactant template sol-gel synthesis process. Further functionalization with lanthanides ( $\text{Tb}^{3+}$ ,  $\text{Eu}^{3+}$ ) was also attempted to obtain luminescent PMO materials.

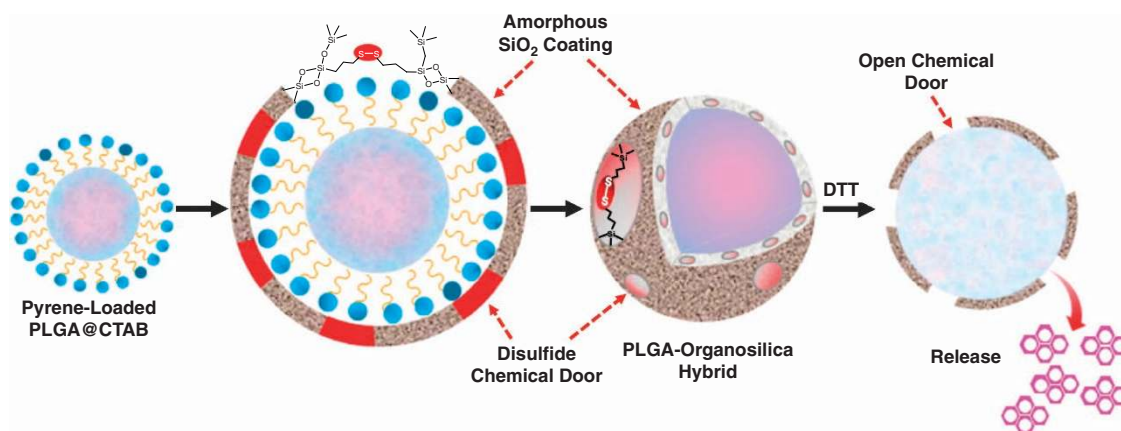
Inagaki and co-workers<sup>56</sup> also constructed a PMO for an artificial photosynthesis system with the three-dimensional organization of molecular parts, such as a light absorber and Re-complex as the multielectron catalyst (Figure 8). The system demonstrated a new conceptual design for enhancing the photocatalytic CO<sub>2</sub> reduction of rhenium (I) complex placed in the mesochannels of PMO with its light-harvesting antenna property by two electron-reduction photocatalysis of CO<sub>2</sub> to CO.

Charge-transporting PMOs with electroactive properties are attractive for a range of applications, such as optical applications, light harvesting, strong light absorption and excitation energy transfer. PMO materials with luminescent properties have significant potential for optical applications. A range of PMOs with different fluorescent chromophores distributed into both the framework (as a bridging groups) and mesopore channels (as a dye dopant) has been reported.<sup>51</sup> The prepared PMOs were reported to exhibit light-harvesting antenna properties with almost no loss of energy transfer.

Energy and electron transfer from the framework of nanoporous or mesoporous materials to guest species in the nano/mesochannels has been considered for photovoltaic devices, luminescent materials and

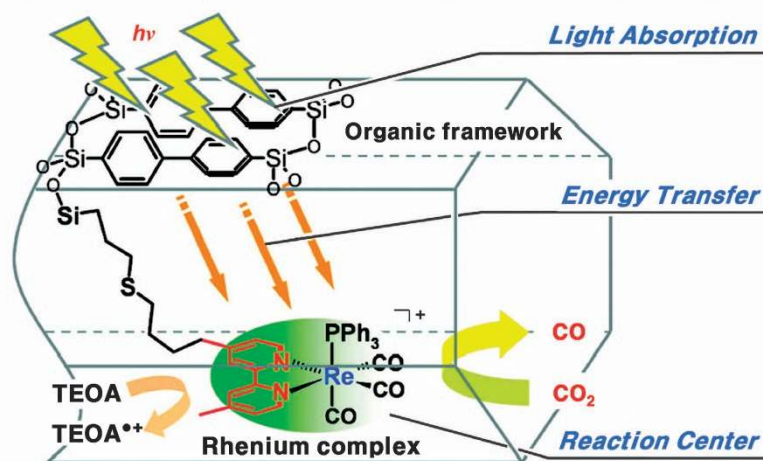
photocatalysts. PMO synthesis was performed with a blue fluorescent tetraphenyl pyrene-silica mesostructured film as the host (energy/electron donor) materials and pyrene bisimide (PBI) dye was selected as the guest (acceptor) molecule.<sup>57</sup> In the film, this fluorescent derivative exhibited strong absorption in the visible light wavelength region, and had a hollow core. Therefore, efficient FRET occurred when the guest pyrene bisimide dye core was located within the critical Förster radius of the tetraphenyl pyrene-pyrene bisimide (donor-acceptor) pairs.

Recent efforts focusing on the synthesis of the luminescent forms of PMOs have targeted the inclusion of large conjugated structures in the mesopore walls. The chromophores in the luminescent PMOs are conjugated  $\pi$  structures. Compared with organic chromophores, photoluminescent inorganic nanocrystals have the advantage of high resistance to photobleaching and tunable size-dependent absorption and emission spectra.<sup>58</sup> Recently, Ozin and co-workers<sup>59</sup> synthesized photoluminescent nanocrystalline silicon PMOs by capping hydride-terminated nanocrystalline SiO<sub>2</sub> with triethoxysilyl ethylene oligomers through hydrosilylation and then coassembled them with TEOS under acidic conditions.



**Scheme 4** Illustration of the preparation and drug delivery of spherical poly(lactic-co-glycolic acid) (PLGA) nanoparticles containing hydrophobic molecules covered by redox-responsive amorphous silica using a self-assembly approach with tetraethyl orthosilicate and disulfide-bridged silsesquioxane precursors (adapted from Botella and co-workers,<sup>25</sup> Copyright © 2013 American Chemical Society).

### Light-harvesting system mimicking the natural photosynthesis



**Figure 8** Enhanced photocatalysis of rhenium(I) complex by a light-harvesting PMO (adapted from Inagaki and co-workers,<sup>56</sup> Copyright © 2010 American Chemical Society).



Organic–inorganic mesoporous silica hybrid materials are attractive for many sensing applications, including heavy metal ions, biomolecules and organic volatiles, because of their stability over a wide range of pH conditions, their inertness in many environments and their transparency in the UV–vis spectrum.<sup>60</sup> Generally, these sensing materials are prepared by the modification of the mesopore surface using alkoxysilanes ((RO)<sub>3</sub>Si-R', R = C<sub>2</sub>H<sub>5</sub> or CH<sub>3</sub>, R' = aliphatic with various functional groups (aliphatic or cyclic organic groups including N, S, O, etc.)).<sup>60</sup> Studies of sensing and imprinting using PMOs have been reported by several researchers for the removal of organic molecules and metal ions.<sup>61–67</sup>

Riley and co-workers<sup>61</sup> prepared a PMO material with imprinted sites for selective benzene adsorption. They compared their results with those obtained from non-imprinted adsorbents to highlight the importance of the imprinting effect.

Ozin and co-workers<sup>62</sup> prepared molecularly imprinted mesoporous organosilica using a semicovalent imprinting technique. A thermally reversible covalent bond was used to link a 'bisphenol A' imprint molecule to a functional alkoxysilane monomer to generate a covalently bound imprint precursor. This precursor was incorporated into a crosslinked periodic mesoporous silica matrix for the selective removal of bisphenol species from water (Scheme 5).

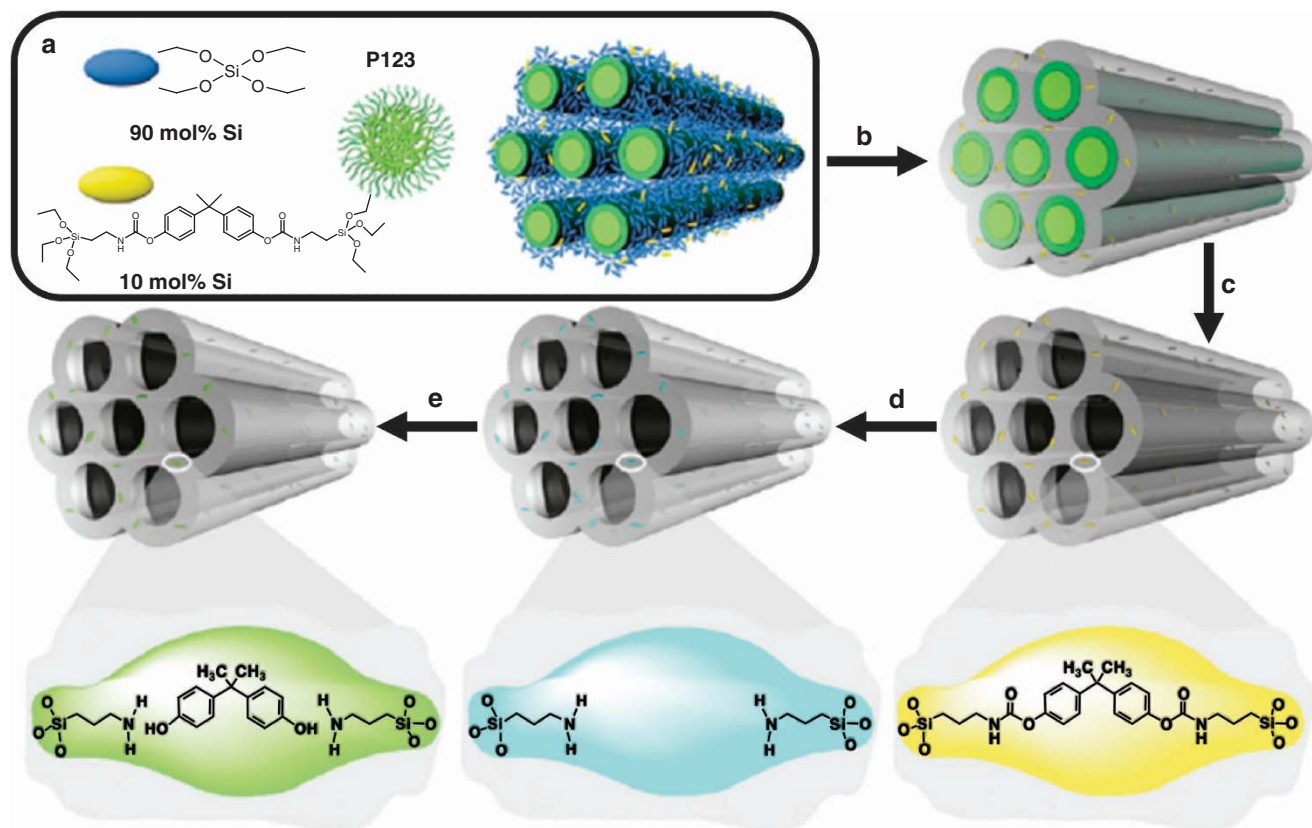
Tang and co-workers<sup>63</sup> prepared highly ordered copper ion-imprinted mesoporous silica by cocondensation using a combination of molecular imprinting technology and traditional

mesoporous materials. Copper ions were used as the template to produce the imprinting site. The recovery of silica remained above 90% after six extraction-stripping cycles.

Recently, Ha and co-workers<sup>23</sup> synthesized a novel ion-imprinted functional ligand derivative bearing PMOs (IIPMO) by a sol–gel process using a chemically synthesized organopolysilane precursor with a metal template (Co<sup>2+</sup>)-imprinted ligand center via a soft-templating approach. The rebinding results revealed the selective efficiency for Co<sup>2+</sup> over other competitive metal ions (Scheme 6).

Kusterbeck and co-workers<sup>64</sup> also prepared a PMO with dimethyl benzene-bridged functional sites for the electrochemical detection of 2,4,6-trinitrotoluene (TNT) molecules using a similar approach. The same research group reported a similar approach with imprinted nanoporous organosilica for the selective adsorption of nitroaromatic targets by the incorporation of diethyl benzene-bridged precursors in the pore walls.<sup>68</sup> The targeted imprinted analog provided recognition of *p*-nitrophenol with high selectivity.

Luka and Polarz<sup>65</sup> designed a PMO material integrated with a pH-sensitive organic dye, methyl yellow, which is a functional molecule that bridged between the alkoxysilane groups in the silica matrix. The resulting materials showed an efficient color-change response driven by pH. Crudden and co-workers<sup>66</sup> designed a PMO film by introducing chemically selective ligands into the envelope of surface-activated fiber-optic cables, which allowed a ppb-level detection limit for Pb(II) ions from aqueous solutions.

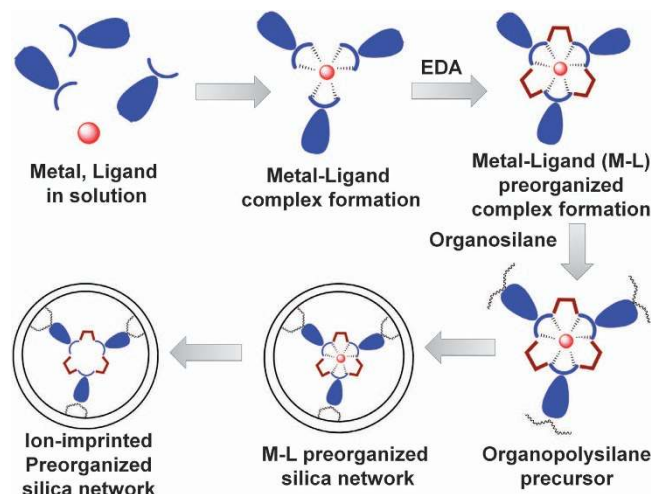


**Scheme 5** Synthesis of molecularly imprinted mesoporous organosilica (MIMO), imprint removal to yield MIMO-ir, and interaction of a target molecule with the imprint site: (a) mixture of tetraethyl orthosilicate (TEOS) and bisphenol A precursor (BPAP) assembles around and between the hexagonal close-packed core-shell micelles of P123 in acidic aqueous media; (b) stirring at room temperature for 24 h followed by quiescent curing at 80 °C for 24 h; (c) P123 template removal by Soxhlet extraction with ethanol for 20 h; (d) thermal cleavage of the imprint by heating in wet dimethyl sulfoxide (DMSO) for 5 h; (e) sequestration of an appropriately sized target bisphenol molecule by hydrogen bonding between phenols and amines (adapted from Ozin and co-workers,<sup>62</sup> Copyright © 2011 American Chemical Society).



### Environmental application including metal ion and pollutant adsorption

Metal ion adsorption is a frequently explored research field because of its importance in practical applications in the water treatment process. This review discusses only representative recently reported works on metal adsorption using PMO adsorbents. Disulfide-bridged PMOs were found to be useful for the efficient adsorption and removal of mercury ions from wastewater.<sup>68</sup> Bhaumik and co-workers<sup>69</sup> reported that a PMO material containing suitable chelating electron donor sites in its framework can be an ideal material for heavy metal ion removal from wastewater.



**Scheme 6** Mechanisms of ion-imprinted functional ligand derivative bearing PMO (IIPMO) network formulation (adapted from Ha and co-workers,<sup>23</sup> Copyright © 2013 Elsevier).

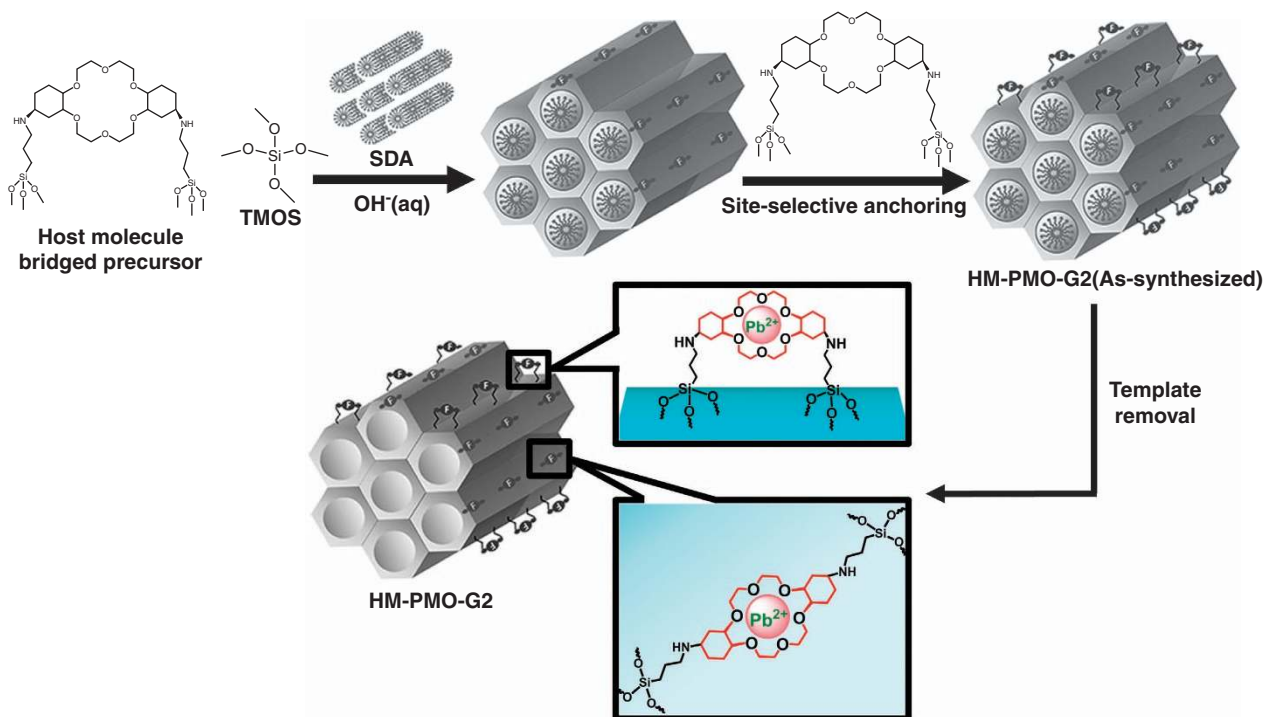
Kao and co-workers<sup>70</sup> reported the direct synthesis of cubic benzene-bridged mesoporous organosilicas with bridged benzene groups in the silica framework and mercapto functionalities as a pendant ligand. This material showed good adsorption efficiency for mercury and silver ions. Nascimento and co-workers<sup>71</sup> prepared benzene-containing PMOs for the adsorption of highly toxic polycyclic aromatic hydrocarbons from aqueous solutions.

Chen and co-workers<sup>22</sup> synthesized macrocyclic-host-functionalized PMO materials for the specific and selective recognition of  $\text{Pb}^{2+}$ . To achieve maximum  $\text{Pb}^{2+}$  adsorption, large moieties were incorporated in the framework walls of the PMO and a large number of macrocyclic host groups were adsorbed onto the external surface (Scheme 7).

A recent study reported a PMO material with imprinting sites for the highly selective recognition of  $\text{Co}^{2+}$  ions; PMO materials with pyridine-bridged organosilane functional moieties and PMO materials with integrated heterocyclic tri-urea-bridged organosilane functional groups for the efficient adsorption of  $\text{Cu}^{2+}$  ion under acidic conditions<sup>72</sup> and selective  $\text{Fe}^{2+}$  adsorption from aqueous solution, respectively,<sup>73</sup> have also been reported.

Fernandes and co-workers<sup>74</sup> prepared amine-functionalized hybrid mesoporous materials with a sol-gel process via the co-condensation of a basic-amine bridged polysilsesquioxane and used the resulting materials as an adsorbent for  $\text{Hg}^{2+}$  ion adsorption.

Sun and co-workers<sup>75</sup> used sulfur-bridged organo-bis-silane functional groups for cadmium and lead removal from aqueous solutions, and Melo and co-workers<sup>76</sup> prepared silica spheres modified with ethylenediaminetetraacetic acid functional groups and examined the detailed adsorption equilibria of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions. Very recently, Wang and co-workers<sup>77</sup> reported the synthesis of bis(rhodamine Schiff-base derivative)-bridged PMOs. Bis(rhodamine Schiff-base derivative)-bridged PMOs displayed strong fluorescence enhancement after chelating with copper ions and could



**Scheme 7** Synthesis and site-selective modification of a PMO functionalized with macrocyclic host groups (adapted from Chen and co-workers,<sup>22</sup> Copyright © 2013 Wiley-VCH Verlag GmbH KGaA, Weinheim, Germany).

be used as a  $\text{Cu}^{2+}$  chemosensor with ultrahigh efficiency that would not be affected by common metal ions.

### Gas separation

Gas separation processes include hydrogen/nitrogen separation in ammonia plants, hydrogen/hydrocarbon separation in petrochemical operations, toxic and irritable gas separation in environmental and industrial discharge, air separation for oxycombustion applications and  $\text{CO}_2$  and water removal from natural gas. Many studies have focused on environmental gas separation applications using ordered mesoporous silicas. Excellent reviews have been published on this subject.<sup>78,79</sup>

Recently, some interesting results have been reported on the adsorption of gases and toxic volatile organic compounds using PMO adsorbents. Two-dimensional hexagonal and three-dimensional cubic benzene-bridged PMOs and the corresponding sulfonated materials have been used successfully for the adsorption of volatile organic compounds.

A range of aromatic functional group-bridged PMOs were successfully used for the adsorption of benzene, toluene and hexane.<sup>80</sup> Jones and co-workers<sup>81</sup> reported the adsorption of other gases, such as sulfur dioxide, cyanogen chloride, ammonia and octane, using ethane-bridged PMO materials (Figure 9).

Okubo and co-workers<sup>82</sup> examined the adsorption of hydrogen gas and its interactions with the bridged organic moieties in materials such as ethylene-, ethane-, phenylene- and biphenylene-bridged PMO materials. This study showed that owing to their ordering, the  $\pi$ -electron containing aromatic phenyl groups in these PMOs adsorbed more hydrogen than the ethane-bridged PMOs. Highly toxic polycyclic hydrocarbons were efficiently removed from aqueous solutions using aromatic benzene-modified PMO materials.<sup>83</sup> Tang and Landskron.<sup>84</sup> reported functionalized amine-bridged PMO materials and examined their effects on  $\text{CO}_2$  adsorption.

### Adsorption of biomolecules

Evaluation of the application of PMOs in the field of biomolecule adsorption involves the immobilization of proteins, enzymes and amino acids. Adsorption studies on proteins, such as cytochrome *c*, serum albumin and hemoglobin, have been carried out by several researchers<sup>23</sup> using PMO materials, including bridged ethane ( $-(\text{CH}_2)_2-$ ) (or ethane functionalized with  $-\text{NH}_2$  or  $-\text{COOH}$ ), benzene ( $-\text{C}_6\text{H}_4-$ ) and biphenyl ( $-(\text{C}_6\text{H}_4)_2-$ ) groups. Adsorption studies have been carried out on enzymes such as lipase, a biocatalyst of great relevance for industrial applications,<sup>85,86</sup> as well as lysozyme, papain, chloroperoxidase and horseradish peroxidase<sup>85–89</sup> using PMO

materials, including bridged ethane (or ethane functionalized with  $-(\text{CH}_2)_3-\text{O}-\text{CH}_2-(\text{CH}_2)_2\text{O}$ ), amine ( $-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_3-$ ), benzene, biphenyl, ethene ( $-\text{CH}=\text{CH}-$ ),  $-(\text{CH}_2)_3-\text{NH}-\text{CO}-\text{NH}-(\text{CH}_2)_3-$ ,  $(\text{CH}_2)_3-\text{NH}-\text{CO}-\text{S}-(\text{CH}_2)_3-$  and  $-(\text{CH}_2)_3-\text{S}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{O}-(\text{CH}_2)_3-$  groups. Ha and co-workers<sup>26,90</sup> reported the adsorption of enzymes (lysozyme and cytochrome *c*) and nicotine using three different types of hollow PMOs produced from bis(3-(trimethoxysilyl)propyl) amine, 1,4-bis(triethoxysilyl)benzene or 4,4'-bis(triethoxysilyl)biphenyl as silica precursors and triblock copolymer as a structure-directing agent via a self-assembly process. The adsorption of benzene- and biphenyl-bridged PMO was faster than that of SBA-15 at a pH near the *pI* of lysozyme because the hydrophobic interactions were dominant.

Chen and co-workers<sup>87</sup> synthesized hierarchical mesoporous SBA-15 and ethane-bridged PMO using poly(acrylic acid) and cetylpyridium chloride as the surfactants, and reported that PMO adsorbed the lysozyme at a higher rate than the silica owing to the bioadsorption facilitated by the more hydrophobic material.

Li and co-workers<sup>88</sup> synthesized bifunctional PMOs with ethane bridging groups in their framework and a range of terminally bonded groups in their pore channels by the cocondensation of 1,2-bis(triethoxysilyl)ethane and 3-glycidoxypolytrimethoxysilane in the presence of triblock copolymer P123 surfactants under acidic conditions and used them as supports for enzyme immobilization. Bifunctional PMOs exhibited higher papain immobilization efficiency and stability than did pure PMOs because of the covalent interactions between the amino groups of papain and the epoxy groups of functionalized PMOs.

Blanco and co-workers<sup>86</sup> compared the use of different mesoporous silica as lipase supports. A slight degree of hydrophobicity (10% methyltriethoxysilane) was introduced in SBA-15 (Me-SBA-15), and more efficient octyltriethoxysilane modification was introduced in amorphous silica (Oct-AS), and compared with PMOs with ethane bridges (ethane-bridged PMO). An analysis of the effects of the hydrophobic nature of the supports along with the porous topology was presented. The enzyme loading, leaching and final activities of the biocatalysts were tested, and they showed promising results for the use of PMO as a support.

Zhu and co-workers<sup>89</sup> reported an increase in enzyme activity through the immobilization of horseradish peroxidase on PMOs. The enzyme activity was improved by 110%, particularly on MI100, which was prepared with a 100% organic silica precursor, compared with the activity of free horseradish peroxidase in solution. In addition, the stability of immobilized horseradish peroxidase to low pH values and to the denaturing agent urea was enhanced.

Fröba and co-workers<sup>91</sup> reported the synthesis of a new, highly ordered divinylaniline-bridged PMO with crystal-like pore walls and the further chemical modification of the amino groups on the inner surface of the product by a peptide formation reaction with a chiral amino acid.

Monduzzi and co-workers<sup>92</sup> compared the behavior of the widely studied SBA-15 mesoporous silica with that of the less investigated ethane-bridged PMO (a PMO whose silicon atoms are connected alternately by  $-\text{Si}-\text{O}-\text{Si}-$  and  $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}-$  groups) regarding the adsorption (pH 7.0 and 9.6) and *in vitro* release (pH 7.4;  $T = 37^\circ\text{C}$ ) of an antimicrobial protein (hen egg white lysozyme). Rather than the structural and textural features, the different chemical compositions of SBA-15 and ethane-bridged PMO appeared to be responsible for the different lysozyme loading and release, as well as for the different stability toward the lixiviating action of the physiological medium (pH 7.4;  $T = 37^\circ\text{C}$ ).

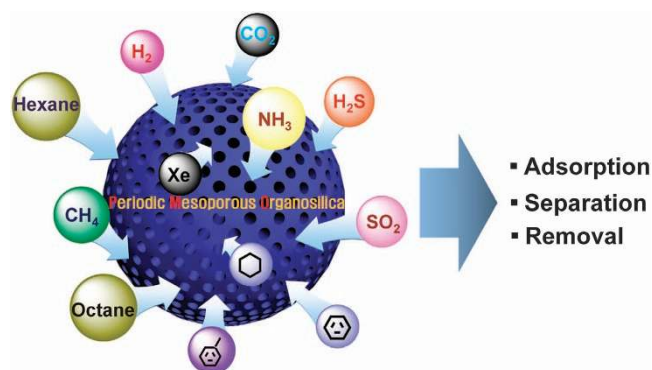


Figure 9 Graphical representation of PMOs as gas absorbents.

In 2011, Hartmann and co-workers<sup>85</sup> reported PMOs with bridged organic moieties (ethane, ethene, benzene) in their framework and large cage-like pores for high-efficiency immobilization of enzymes (Figure 10). Owing to their unique structures and hydrophobic surface properties, the materials showed unprecedentedly high enzyme loading without mass-transfer limitations. Figure 10 presents a schematic diagram of enzyme adsorption by PMOs with a range of organic bridges. The same research group also reported improved activity and stability of lipase immobilized in cage-like large-pore mesoporous organosilica with benzene bridges.<sup>93</sup> The immobilization of lipase as well as the application of these catalysts in hydrolysis and transesterification reactions was examined in detail.

Liu and co-workers<sup>94</sup> proposed a new approach for the large-scale characterization of hydrophobic membrane proteins based on a large-pore PMO, which acts as both an extractor for hydrophobic substrate enrichment and a nanoreactor for efficient *in situ* digestion. To highlight the broad applicability of these materials, they showed the successful identification of complex membrane proteins extracted from mouse liver using this PMO-assisted protocol.

Yu and co-workers<sup>95</sup> reported the enrichment and detection of peptides from biological systems using designed PMO microspheres, suggesting that the PMO microspheres can be used to capture peptides in a range of complex biological systems. Zhu and co-workers<sup>96</sup> synthesized a novel hierarchical PMO monolith using *N,S*-bis[3-(triethoxysilyl)propyl]-carbamoithioic acid to fabricate a highly efficient enzyme immobilizer. Kaliaguine and co-workers<sup>97</sup> examined the adsorption and stability of D-amino acid oxidase and glutaryl-7-amino cephalosporanic acid acylase using two different types of PMOs: PMO-SBA-16 synthesized from 1,2-bis(trimethoxysilyl)ethane (BTME) and 1,4-bis(trimethoxysilyl)benzene. Very high loading ( $68.8 \text{ mg g}^{-1}$  for D-amino acid oxidase,  $51.9 \text{ mg g}^{-1}$  for glutaryl-7-amino cephalosporanic acid acylase), specific enzymatic activities and stabilities were obtained after proper optimization of the mesopore structure and morphology.

### Chromatographic phases

Numerous papers have been published on the synthesis and chromatographic use of highly porous, highly monodisperse mesoporous silicas. The ideal particles should have a size of  $1.5\text{--}5 \mu\text{m}$ .<sup>13,98–103</sup> Some drawbacks in high-performance liquid chromatography (HPLC) columns with mesoporous silicas, such as their hydrolysis

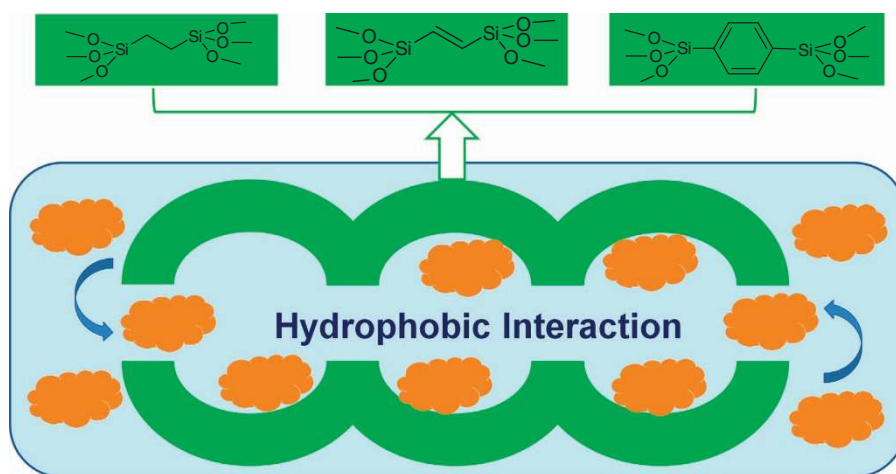
and loss of functionality, can be overcome by using PMOs as packing materials.<sup>13,98–103</sup>

Until now, the use of PMOs as chromatographic phases has been rare. Fröba and co-workers<sup>98</sup> synthesized highly uniform benzene-bridged PMO spheres, based on the Stöber method and using cetyltrimethylammonium chloride (CTAC)/cetyltrimethylammonium bromide (CTAB) as a structure-directing agent under basic conditions for use as a packing material for HPLC.

Li and co-workers<sup>99</sup> prepared a phenyl-functionalized ethane-bridged PMO as a chromatographic packing material by the cocondensation of 1,2-bis(trimethoxysilyl)ethane with phenyl-trimethoxysilane. The resulting column did not show higher retention than commercial columns, but it exhibited a higher base stability. Liang and co-workers<sup>100</sup> reported the synthesis of highly uniform spherical ( $2 \mu\text{m}$ ) particles of benzene-bridged PMOs. Para- and meta-oriented PMOs have their functional groups located inside or sticking out of the pore walls, leading to higher retention. In 2010, Liang and co-workers<sup>101</sup> prepared monodisperse phenylene-bridged organosilica spheres with a tunable particle size ( $3.0\text{--}3.5 \mu\text{m}$ ) and a pore size of  $85 \text{ \AA}$  by cocondensing different proportions of 1,4-bis(trimethoxysilyl)benzene and TEOS. The PMOs were further surface-modified by a C(18) group (octadecyldimethylchlorosilane) and tested in reversed-phase HPLC. The modified phenylene-bridged organosilica stationary phase showed high retention and good chemical stability in the high-pH mobile phase, indicating that the phenylene-bridged organosilica can be used as a packing support for HPLC.<sup>102,103</sup> Spherical particles of a bifunctional ethane-bridged PMO with a chiral trans-(1*R*,2*R*)-diaminocyclohexane and trans-(1*R*,2*R*)-bis-(ureido)-cyclohexane function were used as a ligand-exchange chiral stationary phase in HPLC for the separation of racemic amino acids.

### Electronic devices and low-*k* PMO films

The integration of electroactive organic moieties such as electroactive dye molecules into the porewalls of PMO materials with mesostructural order is an important method for developing a new class of silica hybrid material with large surface area and pore structure for current and future electronic applications. These materials are generally obtained by the incorporation or dense packing of active molecules, such as fullerene  $\text{C}_{60}$ , viologen and dye molecules, with a bridged organosilane precursor that was fixed into the PMO pore walls.<sup>6,104</sup>



**Figure 10** Schematic diagram of the enzyme adsorption for PMOs with various organic bridges (adapted from Hartmann and co-workers,<sup>85</sup> Copyright © 2011 Wiley-VCH Verlag GmbH KGaA, Weinheim, Germany).



The ability of the viologen units in the PMOs to act as electron acceptors from the terminal point was confirmed by the formation of radical cations under thermal activation and photochemical processing. Generally, to prepare electroactive PMOs, the electroactive organosilane precursors are mixed with the pure silica precursors. Therefore, the distribution of electroactive species in the PMO framework is diluted, resulting in a weakening of the electronic coupling between the bridged organic moieties. To enhance the electroactivity of the PMO, it is essential to improve the loading or packing of the active molecules in the PMO silica framework for efficient charge transfer.

Recently, Inagaki and co-workers<sup>19</sup> prepared phenylenevinylene units integrated with a three-arm bridged PMO film, and long-range hole transport was achieved (Figure 11). Because of the presence of three silyl groups, the interaction between the precursor and surfactant micelles increased, and charge hopping between the two-dimensionally expanded  $\pi$ -system was observed. The experimental results revealed the organosilica films to have a hole mobility of  $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This study highlighted the possibility of preparing electrically conductive PMOs by introducing a large conjugated  $\pi$ -system into the framework.

The charge of ion conduction in the mesopores is also useful for developing electroactive hybrid materials. Sulfonated phenyl-bridged PMOs have been efficiently applied as photoconductive hybrid electrolyte membranes for direct methanol fuel cell applications.<sup>105</sup> This PMO material also has a positive effect on reducing the methanol permeability of the composite membranes. PMOs in the confinement of porous anodic alumina membranes were successfully fabricated by Bein and co-workers<sup>106</sup> through a modified evaporation-induced self-assembly process using 1,3,5-tris(styryl)benzene as the silica source. The resulting hierarchical mesoporous composites (PMO/anodic alumina membrane) showed fluorescence in the visible region owing to the strongly interacting phenylenevinylene chromophores in the PMO framework that might offer potential for application in optoelectronic systems.

Overall, the development of new materials greatly endows the PMO field with a novel precursor design and synthesis. Moreover, the development of novel synthetic strategies is necessary for advancing technologies in the semiconductor industry.

Generally, the dielectric constant ( $k$ ) of a material is related to the electron density and polarizability of its constituent atoms/molecules.<sup>107</sup> Materials with a low dielectric constant (low  $k$  values)

are attractive for reducing the dimensions of microelectronic chips to reduce the signal delay and cross-talk from interlayer capacitive coupling.<sup>108</sup>

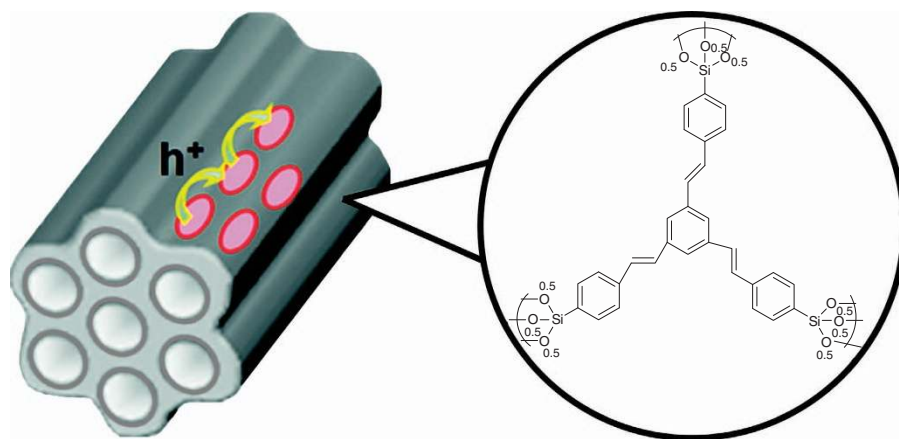
Two approaches are used to achieve low  $k$  values: reducing electron density and avoiding polar bonds. Electron density can be reduced by introducing porosity into materials, and polar bonds can be avoided by introducing hydrophobic molecules, which can reduce water adsorption because water is a highly polar molecule.

PMOs have high porosity that significantly reduces the dielectric constant ( $k_{\text{air}} \approx 1$ ). Furthermore, the organic bridges are less polarizable than the standard low- $k$  material silicon dioxide ( $k = 3.9$ ), resulting in an additional decrease in the dielectric constant.<sup>8</sup>

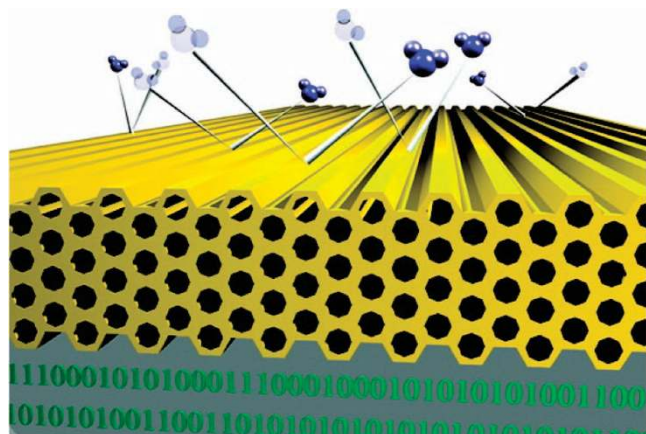
Ozin and co-workers<sup>109</sup> have presented most of the papers related to PMOs as low- $k$  materials. They prepared methane-, ethane-, ethene- and ring-PMO films using cetyltrimethylammonium chloride as a template, and examined their dielectric, mechanical and hydrophobic properties. The  $k$ -values for the films prepared from the cyclohexane derivatives were 2.5 and 2.0 for the samples calcined at 300 °C and 400 °C, respectively.<sup>109</sup>

Van Driessche and co-workers<sup>110</sup> recently reported the chemical stability of ultra-low- $k$  ring-PMO films synthesized using Brij-76 as a surfactant. The improved chemical resistance of the ring-PMOs prepared with Brij-76 was attributed to the presence of carbon bridges that are stable in alkaline media and to the thicker pore walls that can be obtained when using Brij surfactants rather than cetyltrimethylammonium chloride.

Ozin and co-workers<sup>111</sup> developed a new class of PMOs with air pockets in the pore walls, which was achieved by the template-directed spin coating of a polyhedral oligomeric silsesquioxane (POSS) precursor as the silica source. The obtained polyhedral oligomeric silsesquioxane-PMO films exhibited a porosity of 39% and a  $k$ -value of 1.7. Recently, the same group reported the thermally induced gradual hydrophobization, quantitatively monitored by ellipsometric porosimetry, of four prototypical PMOs that were tailored through materials chemistry for use as low- $k$  materials in microprocessors.<sup>112</sup> Figure 12 presents an illustration of a PMO film with low  $k$  and hydrophobic properties coated on a substrate. Ozin and co-workers<sup>112</sup> also fabricated low- $k$  PMO thin films by vacuum-assisted aerosol deposition, which has been a vapor-phase delivery technique favored by the semiconductor industry. The mesostructured films exhibited a good combination of dielectric



**Figure 11** Hole transport in a PMO with a high density of 1,3,5-tris(styryl)benzene bridges (adapted from Inagaki and co-workers,<sup>19</sup> Copyright © 2009 American Chemical Society).



**Figure 12** Illustration of a PMO film with low dielectric constant (low- $k$ ) and hydrophobic properties coated on a substrate (adapted from Ozin and co-workers,<sup>112</sup> Copyright © 2011 American Chemical Society).

and mechanical properties, making them ideal candidates for insulating materials on semiconductor chips.

## SUMMARY AND FUTURE OUTLOOK

This review summarized the most important developments in the field of PMOs since 1999, when they were first described, including the synthesis, features and morphologies of PMO materials. In addition, the main areas of application (that is, catalysis, drug and gene transfer, sensing and imaging, optics, electronic devices, gas sensing, gas adsorption, biomolecule adsorption and chromatographic phases) were reviewed. A wide range of PMOs with various bridges and morphologies have been prepared. However, some aspects remain to be studied. For example, precursors with long and/or flexible bulk bridges led to poorly ordered mesostructures. More challenging is the synthesis of PMOs with molecular-scale periodicity of organic moieties.

The morphology and texture of mesoporous materials are extremely important in many applications. The morphology of materials often controls their function and utility. Among the morphologies of these materials, hollow spheres have attracted considerable attention because of their many potential applications in catalysis, drug delivery systems, microcontainers and other possible functions.

Recently, the synthesis and preparation of organometallic complexes in heterogeneous form has become a popular subject that offers great advantages for green catalysis, given concerns about cost-effectiveness, the recovery and reusability of expensive and/or toxic catalysts and avoidance of product contamination. PMOs with an organometallic complex integrated within the silica pore wall are of great importance in coupling and redox catalytic processes.

Mesoporous materials with a range of organic moieties that can cause particular interactions between guest molecules and functional groups can be used as nanovalves for the controlled release of drugs or useful guest molecules. These features are very important in the biological/biochemical/biomedical fields.

The development of precursors with functional organic bridges, such as chromophores, fluorophores and electroactive species, has significant applicability in the fields of light harvesting, photosensors, etc.

PMOs with a high surface area and particular functional groups are also very useful as excellent adsorbents for heavy metal ions, harmful

organic molecules and pollutant gases in the environment. In addition, they might be replacements for silica as low- $k$  materials.

PMOs are very useful in a variety of applications, and many others can be envisaged for the near future. The current results and the forthcoming advances in PMOs will make them the materials of choice for some high-technology applications in strong competition with other highly porous solids (such as microporous and mesoporous silicas, non-siliceous mesoporous materials and metal-organic compounds).

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