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Mesoporous Materials

Ecodesign of Ordered Mesoporous Materials Obtained with Switchable Micellar Assemblies**

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The synthesis of long-range ordered nanoscale structured materials and ordered mesoporous materials (OMMs) was strongly developed in the past 15 years, owing to the exploitation of the amphiphilic properties of some lyotropic molecules[1–4] that also behave as structure-directing agents (SDA). The success of these materials is due to their easy shaping (into powders, thin films, and monoliths), the wide chemical compositions of the inorganic frameworks, and, after removal of the SDA, the high specific surface areas as well as the controlled pore size distribution and geometry.[5] Easy surface modification also contributed to their success. These features have made them very interesting materials for applications in adsorption, catalysis and sensing or as host materials for drugs.[6]

In spite of several hundred recent reports that emphasize the fascinating potential of OMMs, their implementation on a large scale remains limited. The first and main reason is the production cost of the porous materials associated with the syntheses developed to date. It was recently shown in the final report of an EU-funded project[7] that over 80% of the final cost of OMMs comes from the energy demand associated with the calcination step of the structure-directing agent (SDA) to expose porosity, which also destroys the SDA. For this reason, washing in organic solvents (methanol or ethanol)[8] and very seldom in water at reflux has become an interesting alternative route. Nevertheless, the efficiency of the process depends on the SDA used.[9,10] Alternative physical methods (use of ozone, CO_2 extraction) have been proposed,[11–13] but the required equipment and effort overwhelms the real benefits. In all cases, a multistep approach from the synthesis of the material to the creation of open porosity is always followed.

A question arises: is there any strategy allowing a one-pot process for both synthesis of structured material and pore formation? This task is challenging, and the first report in which such an idea was considered appeared only recently in the field of microporous zeolite materials.[14] In this study, covalent bonds of the single-molecule SDA were chemically broken, yielding two separate smaller entities, which could then be released from the microporous structure. Recycling of the SDA after re-formation of the broken bonds was shown to be successful. Supramolecular assemblies held together by π–π interactions were also used as SDA for the synthesis of Linde type A zeolites, but the recovery of the SDA was impossible.[15] To obtain mesoporous materials, authors generally try to develop new ways of structuring solids,[14,15] but in the reported studies,[16–19] low-cost sustainable methods are hardly proposed. Moreover, there are environmental concerns over the realization of these methods, for example when hot HCl solution is used.[14]

For the first time, we now propose an ecologically minded design for preparing ordered mesoporous materials: a one-pot process in water at room temperature and a mild pH value for structuring inorganic materials and creating porosity by means of smart micellar assemblies of water-soluble block copolymers. Micellization of hydrophilic block copolymers and, more specifically, double-hydrophilic block copolymers (DHBCs)[20–29] can in fact be easily triggered in water by changing simple physicochemical parameters, such as the pH value, temperature, or ionic strength of the solution. Furthermore, micellization can be reversible in the same aqueous synthesis batch, leading to the possible disassembly of the structuring agent. The latter process leads to porosity formation in the material, and it makes the building units of the SDA available for further synthesis runs. Thus, this process allows SDA recycling in water under sustainable conditions owing to the nontoxic nature of initial components (e.g. polysaccharides) and solvent (water) and to the low-energy interactions (electrostatic, van der Waals) involved in the reversible micellar assembly process. The present energy- and atom-saving methodology that we propose is shown schematically in Figure 1.

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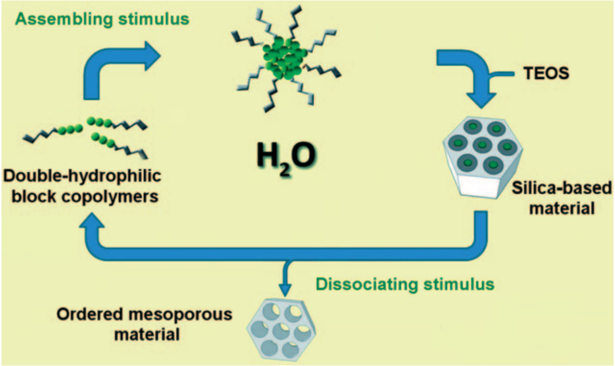

Figure 1. Strategy for structuring silica using induced micelles of water-soluble block copolymers. Porosity is created at room temperature, while the structuring agent is recycled in aqueous solution. TEOS = tetraethoxysilane.

Hence, the present report proposes three main innovations: 1) Ordered nanostructured materials can be prepared using smart micellar aggregates of stimuli-responsive DHBCs as new structuring agents. 2) The SDA can be driven out of the OMM by a simple washing step in water at room temperature at a well-chosen nearly neutral pH value, thus creating porosity. 3) On the basis of the two first points, a continuous one-pot process can be developed, which allows synthesis of a nanostructured material, washing to yield the corresponding mesoporous material, and recycling of the SDA to prepare a new porous solid within the same batch.

The feasibility of our strategy is demonstrated by structuring silica at room temperature using reversible pH-responsive micellar aggregates. As a proof of concept, we prepared mesostructured silica-based materials by templating with micelles of poly(ethylene oxide)-*block*-poly(methacrylic acid) (PEO-*b*-PMAA) or poly(ethylene oxide)-*block*-poly(acrylic acid) (PEO-*b*-PAA) and an oligochitosan lactate (OCL) as a co-micellization agent. Block copolymers are now easily available at the bench scale thanks to the development of various controlled radical polymerization methods, some of which have been developed on an industrial scale.[30–32] Micellization of the present polyelectrolyte/neutral DHBCs is induced by electrostatic complexation of the oppositely charged macroion. Herein, double-hydrophilic polyacid/neutral block copolymers[20–22] are used in the presence of a weak polybase. Formation of an electrostatic complex between the two oppositely charged polyions leads to the formation of core–corona aggregates with a water-insoluble complex core and a water-soluble corona. Formation of the micellar aggregates can be driven by the pH value, since the charges of the polyacid and polybase blocks are pH-dependent. Micellization of DHBCs,[20,21,23–25] and more specifically formation of polyion complex (PIC) micelles,[26–29] has been extensively studied. Mixtures of PEO-*b*-PMAA or PEO-*b*-PAA block copolymers and OCL lead to PIC micelles with an electrostatic complex core and a PEO corona. Because the switchable assembly/disassembly of DHBCs only involves weak interactions, such as electrostatic interactions, the energy demand for disassembly is quite low in comparison with breaking covalent bonds. When a silica precursor, such as tetraethoxysilane (TEOS), is added to the PIC micelle solution, a nanostructured solid is obtained after hydrolysis and condensation of the silicon alkoxide.

The formation of micellar objects between OCL and the water-soluble block copolymer as a function of the pH value was monitored by dynamic light scattering (DLS). The measurement of the scattered light intensity of the DHBC/OCL mixture indicated formation of micellar aggregates at pH 4.5–7. Results are shown in Figure 2 for the PEO-*b*-PAA/OCL system (with an amine/carboxylic acid molar ratio of 1). For pH 4.5–7, well-defined micelles are formed, and their intensity-averaged hydrodynamic diameter equals 25 nm. Increasing the pH value above 7.5 (by adding a NaOH solution) leads to a strong decrease of the scattered intensity, which reveals the dissociation of the micelles; this effect is due to the neutralization of the amine functions of the homopolymer polybase.

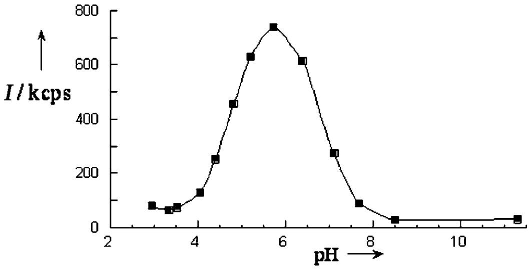

Figure 2. Variation of the scattered light intensity of the PEO-*b*-PAA/OCL suspension as a function of the pH value, revealing the formation of micellar aggregates between pH 4.5 and 6.5 and the polymer disassembly outside of this pH domain.

In detail, the synthesis of the hybrid material proceeds as follows: first, the DHBC and the polyamine are dissolved in an aqueous solution, then TEOS is added, and the pH value is decreased to pH 2 for TEOS hydrolysis, which is completed within 15 min. The hybrid material is then synthesized at room temperature by increasing the pH value of the mixture to pH 4.5–6.5 (by adding a NaOH solution). After 24 h, a precipitate is recovered; it can be either filtered out and washed ex situ in water for 48 h at 25 °C and pH 8 (at which micelle dissociation occurs for the OCL/DHBC system) or left in the synthesis medium, the pH value of which is then raised in situ to above pH 8 for micelle disassembly and polymer template removal. The solid is then recovered and allowed to dry at 60 °C overnight. In both cases, leftover solutions, expected to contain the SDA-forming polymers, are tested for new material synthesis under the same conditions.

The possibility of structuring silica with PIC micelles is shown in Figure 3. TEM images together with Fourier transforms of the structures are presented. Mesostructured hybrid silica-based samples are obtained in all cases. Micelle morphology and arrangement vary from cylindrical micelles arranged in a two-dimensional hexagonal structure to lamellar structures. In the PEO-*b*-PMAA/OCL (pH 4.5, Figure 3 a) system, cylindrical micelles of 5 nm are arranged in a hexagonal pattern with a *d* spacing of 12 nm. When the synthesis pH value is adjusted to pH 6.5, the micellar aggregates change shape and adopt a lamellar morphology

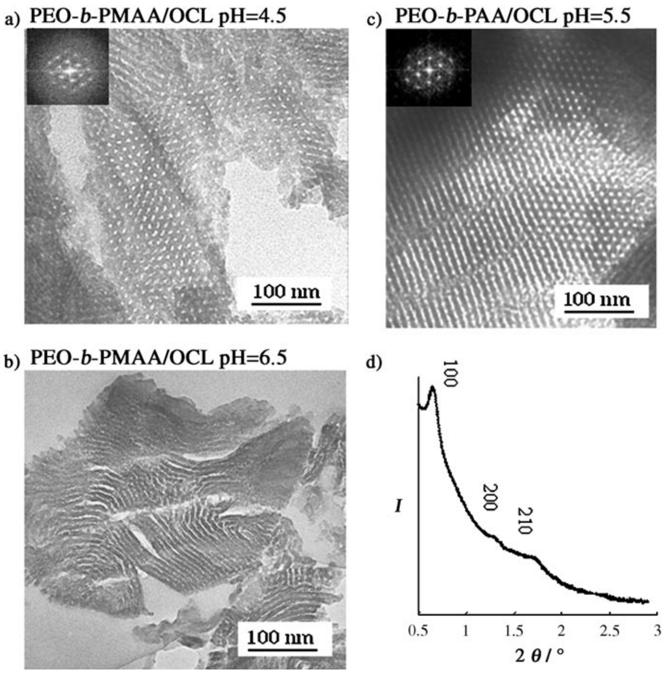

Figure 3. Transmission electron microscopy (TEM) images of structured silica obtained with the PEO-*b*-PMAA/OCL complex at a) pH 4.5 and b) pH 6.5 and c) with the PEO-*b*-PAA/OCL complex at pH 5.5. Insets in (a) and (c) are Fourier transforms of TEM images. d) SAXS pattern of the as-synthesized material prepared with micelles of PEO-*b*-PAA and OCL at pH 5.5.

(Figure 3b); the lamellae thickness is about 6 nm. When the synthesis was carried out with PEO-*b*-PAA/OCL at pH 5.5, a well-ordered two-dimensional hexagonal structure of cylindrical micelles is obtained (Figure 3c); Figure 3d shows the small-angle X-ray scattering (SAXS) pattern of the material with the three diffraction peaks ascribed to the (100), (200), and (210) planes of the hexagonal structure. The correlation distance is calculated to be 13.5 nm. These data show that complex micelles of DHBCs and oppositely charged polyelectrolytes can direct the formation of nanostructured silica in a well-chosen range of pH values. On the contrary, any attempt to obtain silica OMMs in the absence of either the DHBC or the polyelectrolyte component was unsuccessful. Importantly, the pH value during the synthesis has a great influence on the structure of the silica-based material. Changing the synthesis pH value from 4.5 to 6.5 allows tuning the material structure and changing from cylindrical to lamellar micelles. A key result of this study is evidence of PIC micelles with various morphologies: cylindrical and lamellar PIC micelles are present in the hybrid silica-containing material. The behavior of DHBC–polyamine micelles had been thoroughly investigated in dilute aqueous solution at various pH values, at different ionic strengths, and in the absence of silica precursors: under these conditions, only spherical PIC micelles had been detected. The demonstration of the existence of different morphologies for the present PIC micelles is interesting for various applications, and to our knowledge, well-defined cylinders and lamellae had never been observed for electrostatic polyion complex micelles.

As the micelles consist of a polyion complex core surrounded by a PEO corona, formation of the mesostructured silica-based material must be the result of hydrogen bonding between ethylene oxide units and silanols of the silica network under formation. The structuring process may then be similar to that occurring in the case of non-ionic PEO-based surfactants such as pluronics in the synthesis of SBA15-type materials.[4] PIC micelles have the same interface with the solvent and with silica precursors as conventional PEO-based surfactant micelles, which allows precipitation of silica/micelle mesophases and further implies that PIC micelles do not dissociate under the material synthesis conditions. Finally, it is known that the driving force for PIC micelle core formation is the decrease of the total electrostatic free energy of the system, which includes the mixing entropy gain from the release of polymer counterions in solution, whereas in classical amphiphilic systems, hydrophobic interactions drive the formation of the micelle core. The properties of these attractive interactions and their response to the physicochemical characteristics of the medium are exploited for driving the dissociation of the micelles inside the material.

The ex situ washing step of the mesostructured hybrid material in aqueous solution at pH 8 is efficient for forming porosity, as shown by the N_2 adsorption/desorption isotherms presented in Figure 4 in the case of the PEO-*b*-PAA/OCL–silica system. Isotherms of the material washed in water at pH 8 show a hysteresis loop in the range $0.6 < P/P_0 < 0.9$, as expected for mesoporous materials, and the final apparent BET surface area is $250\,m^2\,g^{-1}$. The pore size distribution is centered at 8.5 nm, as determined from the desorption isotherm. This average pore size is smaller than the hydrodynamic diameter D_h of the micelle (25 nm), which is expected, since D_h includes the core size (PAA/OCL complex) and the size of the large and hydrated POE corona in a good solvent. The efficiency of the removal of the organic structuring agent in the washed sample is quantified by comparing its thermogravimetry analysis to that of the as-synthesized sample. As a preliminary result, a single washing step at pH 8 allows recovery of about 62% of organic matter in the case of the PEO-*b*-PAA/OCL system. For the sake of

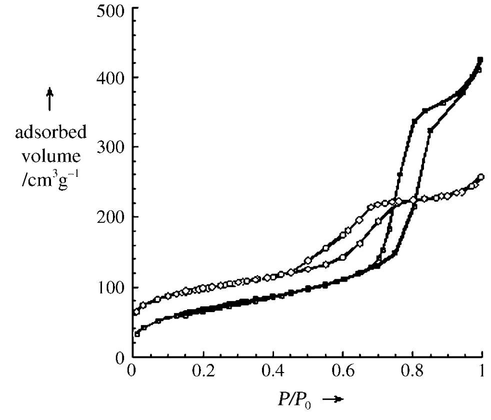

Figure 4. N_2 adsorption/desorption isotherms of ordered mesoporous materials prepared with the PEO-*b*-PAA/OCL system (synthesis at pH 5.5): Material washed ex situ in an aqueous solution at pH 8 (■) and corresponding material calcined at 893 K without washing (○).

comparison, textural properties were also examined on an unwashed PEO-*b*-PAA/OCL sample for which the porosity was created by a classical calcination step at 823 K (Figure 4): a BET surface area of 340 $m^2 g^{-1}$ was obtained, with a mean pore size of 5.5 nm. When varying the polymer characteristics, specific N_2 adsorbed volumes range from 0.3 to 0.6 $mL g^{-1}$, while BET specific surface areas vary between 110 and 740 $m^2 g^{-1}$. Porosity characteristics are given in the Supporting Information for different porous materials obtained either by washing at room temperature or by calcination (Figure S1 in the Supporting Information).

Finally, the third new feature is the possibility of a continuous one-pot synthesis with recycling of the SDA and preparation of new material. Figure 5 illustrates this concept for materials synthesized at pH 4.5 with PEO-*b*-PMAA and OCL polymers. It is shown that it is possible to perform multiple in situ synthesis runs. First, sample S1 was synthesized at pH 4.5. It was separated by filtration, without any washing step, and recovered. The leftover supernatant solution was directly reused for a new synthesis step by addition of TEOS, and it gave new material, S1R. On the other hand, the same synthesis of material S1 was performed again, but this time the pH value of the synthesis medium was increased up to pH 8 after powder precipitation to yield the washed material S1w, which was then separated and collected. The leftover solution was reused for a new similar synthesis procedure by adding fresh TEOS, yielding the material S1wR after synthesis and washing.

TEM images with respective Fourier transforms and SAXS patterns show that mesostructured silica was obtained for both S1 and S1w samples, as expected, presenting an ordered micellar arrangement with intermicellar distances of $d = 11.6$ and 13.4 nm, respectively. Interestingly, S1R, which is prepared by using the supernatant solution of the unwashed S1 sample, does not exhibit any nanostructure (see Figure S2 in the Supporting Information). In contrast, in the case of S1wR, a mesostructure is clearly identified, and a long-range intermicellar correlation distance of 12.3 nm is obtained. There is no change in the ordering degree of the second material, prepared from recycled polymers, compared to the first material, provided that the second synthesis is run under the same synthesis conditions. Consequently, the washing step at pH 8 of sample S1 leading to S1w indeed disassembles the micellar objects and releases PEO-*b*-PMAA and OCL, which are then able to act as templates again; they allow a new synthesis of mesoporous material to occur after reassembly of the SDA constituents at the desired pH value.

^{29}Si magic-angle spinning (MAS) NMR experiments (Figure S3, Supporting Information) on as-synthesized sample S1 show about 42% fully condensed silica sites $Si(OSi)_4$ (Q_4, $\delta = -110$ ppm), corresponding to an overall silica condensation degree of 0.83. In situ treatment at pH 8 leads to an increase of the fraction of Q_4 sites up to 65% (in S1w and in S1wR), which increases the degree of silica condensation to 0.90. Hence, washing at pH 8 is interesting for two reasons. Firstly, the degree of condensation is comparable to materials usually obtained after a hydrothermal treatment at 100°C, which is usually used to strengthen the silica network. Secondly, no calcination step is needed to create porosity. In both cases, the savings in energy and matter can be significant.

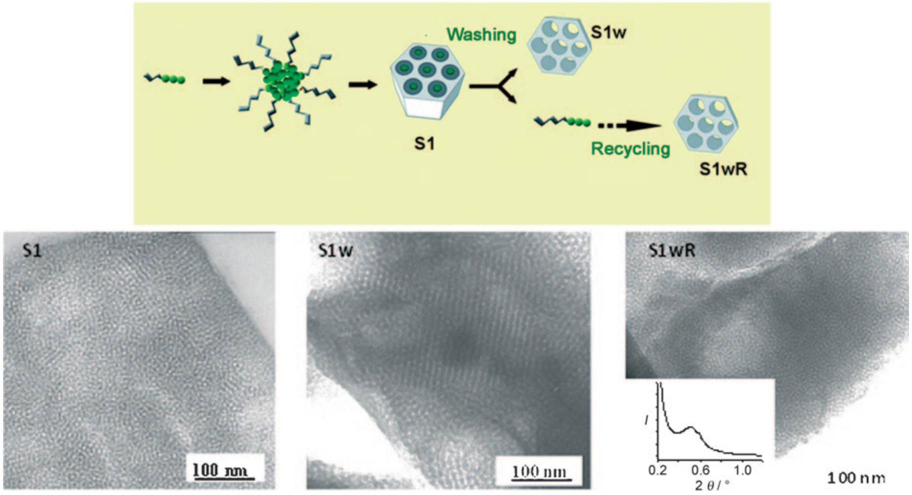

Figure 5. TEM images and SAXS curves of as-synthesized sample S1, washed sample S1w, and washed sample S1wR (prepared from recycled polymer) obtained with the PEO-*b*-PMAA/OCL complex system. S1 was obtained at pH 4.5, while powders S1w and S1wR were obtained after in situ treatment at pH 8.

In conclusion, we describe herein an innovative strategy to prepare mesoporous materials at room temperature in aqueous medium using induced and reversible micelle formation of DHBCs as structuring agents. The new templates are formed by an induced micellization process in water, which can be triggered back and forth by adjusting the pH value of the aqueous medium. This reversibility makes it possible to dissociate the template and remove it from the inorganic network under mild conditions and to recycle it for subsequent syntheses. By using polyion complex micelles between a weak polybase and a polyacid–poly(ethylene oxide) DHBC, different well-ordered mesostructures can be obtained by tuning the physicochemical parameters (pH value, temperature) and by changing the composition of the system. Specific surface areas of the mesoporous materials obtained by room-temperature washing vary from 70 to 500 $m^2 g^{-1}$, depending on the synthesis conditions. Finally, we have opened the way to an in situ multiple-templating process of silica in water, without the use of organic solvents. Treating the material in the aqueous synthesis medium at mildly basic pH values firstly enhances the degree of silica condensation and secondly allows recycling of the templating agent, which is re-used in the same reaction medium to perform a new synthesis run. The strategy presented herein was developed using macroion electrostatic complex micelles for which the micellization process was triggered by changing the pH value, but it can be extended to other triggers. At present, we are testing the silica structuring and SDA recycling processes with micelles of DHBC whose formation in water is induced by a change of either ionic strength or temperature. In the latter case, the number of viable synthesis cycles can be increased. Finally, the approach can also be extended to various other metal oxide based materials.

Experimental Section

Preparation of mesoporous materials: The employed DHBC was poly(ethylene oxide)-*b*-poly(methacrylic acid) (PEO-*b*-PMAA, $M_{\mathrm{PEO}} = 5000\,\mathrm{g\,mol^{-1}}$; $M_{\mathrm{PMAA}} = 2100\,\mathrm{g\,mol^{-1}}$) from Polymer Source, while the polyamine is oligochitosan lactate (OCL, Aldrich) with $M < 5000\,\mathrm{g\,mol^{-1}}$. Silica precursor is tetraethoxysilane (TEOS, Aldrich). Typical synthesis molar ratios are TEOS/PEO-*b*-PMAA/H_2O/OCL = 1:0.0086:370:0.11 with the value for OCL corresponding to an oligochitosan lactate unit ($C_{12}H_{24}O_9N_2$, $C_3H_5O_3$). The synthesis procedure was adapted from that of pluronic P123 templated silica synthesized at neutral pH values.[33] Typically, OCL (8.0×10^{-2} g) is mixed with PEO-*b*-PMAA (8.8×10^{-2} g) in deionized water (9.5 g) at $T = 25$ °C. The equilibrium pH value is about pH 4.3, and it is reached immediately. TEOS (0.319 mL) is then added to the stirred solution. An emulsion forms, and the pH value of the solution is lowered to about pH 2. When TEOS hydrolysis is completed (after about 15 min under vigorous stirring), the pH value of the solution is brought to pH 4.5–6.5. A precipitate is observed after 20 min, and the solution is stirred for 24 h at 25 °C. In general, the as-synthesized sample is filtered and placed in an oven overnight at $T = 60$ °C. After synthesis, the powder is treated by raising solution pH value to pH 8 for 48 h at 25 °C to remove the structuring agent. This treatment can take place after powder filtration or in situ in the synthesis batch, just after the synthesis step. The treated material is finally filtered and dried at 60 °C overnight. TEOS can then be added again to the leftover solution obtained after washing, if a second synthesis cycle is desired.

Synthesis conditions of silica-based materials structured with micelles containing PEO-*b*-PAA are very similar to those with PEO-*b*-PMAA polymers, but the washing step is somewhat different. These experiments are described in the Supporting Information.

Study of micelle formation as a function of pH value by DLS: A solution of copolymer was mixed with a solution of oligochitosane. The pH value of the mixture was adjusted to pH 2. The mixture was then titrated by adding small amounts of a 0.5 M NaOH solution. The pH value was thus progressively increased up to a final value close to pH 11.5. DLS measurements were performed on all the mixtures at varying pH values after each addition of base and after vigorous stirring during five minutes.

Characterization: Dynamic light scattering measurements were carried out with an Autosizer 4800 instrument (Malvern, U.K.) with a 50 mW laser source operating at 532 nm. Scattered light intensities were collected together with hydrodynamic diameters and polydispersity indexes (PDI) of the micellar colloids. Hydrodynamic diameters were obtained from measured diffusion coefficients using the Stokes–Einstein equation. The solid mesostructures were studied by SAXS and TEM. SAXS measurements were performed in transmission configuration using a turning copper anode (4 kW) as X-ray source with a multilayer focusing Osmic monochromator giving high flux (10^8 photons $\mathrm{s^{-1}}$); punctual collimation was employed. An image plate 2D detector was used. TEM images were collected on a JEOL 1200 EX II microscope on microtomed samples. Thermogravimetric analysis was performed in air on a TG-DSC 111 Setaram instrument; the temperature was raised at 10 °C $\mathrm{min^{-1}}$ up to 1000 °C. N_2 adsorption/desorption experiments were performed on a Micromeritics Asap 2010 instrument. Solid-state ^{29}Si MAS NMR experiments were performed on a Bruker Avance spectrometer ($B_0 = 9.4$ T) using a 4 mm zirconia rotor.

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