

# Ethylene-bridged Mesoporous Organosilicas with Hexagonal and Cubic Symmetry

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A series of ordered periodic mesoporous organosilicas (PMOs) with cubic and hexagonal symmetries were fabricated by using divalent surfactants  $[\text{CH}_3(\text{CH}_2)_{15}\text{NMe}_2(\text{CH}_2)_3\text{NMe}_3]^{2+} 2\text{Br}^-$  ( $\text{C}_{16-3-1}$ ) or binary surfactant mixtures  $[\text{CH}_3(\text{CH}_2)_{15}\text{NMe}_3]^+ \text{Br}^-$  ( $\text{C}_{16}\text{TABr}$ ) and  $\text{C}_{16-3-1}$  as structure-directing agents (SDAs) and 1,2-bis(triethoxysilyl)ethane (BTEE) as an organosilica source under various basic conditions. The shape/structure of surfactant, molar ratio of binary surfactant mixtures, and base concentration crucially affect the formation of distinct mesophases. Face-centered cubic  $Fm\bar{3}m$  mesoporous organosilicas can be obtained by using various concentrations of divalent surfactant  $\text{C}_{16-3-1}$  or equimolar mixtures of divalent and monocationic surfactants as SDAs under basic conditions. Cubic  $Pm\bar{3}n$  or 2D hexagonal  $p6mm$  mesophases can be synthesized by changing the molar ratio of the binary surfactant mixtures or the amount of the base NaOH. Use of monocationic  $\text{C}_{16}\text{TABr}$  instead of  $\text{C}_{16-3-1}$  as template produced the hexagonal  $p6mm$  mesophase exclusively independent of the amount of the surfactant and the base. In addition, use of trimethylbenzene as expander molecule in the aforementioned binary surfactant template system caused a mesophase transformation from cubic  $Pm\bar{3}n$  to  $p6mm$  symmetry. All samples were characterized by powder X-ray diffraction (PXRD) analysis and  $\text{N}_2$  physisorption. The formation of face-centered cubic  $Fm\bar{3}m$ , primary cubic  $Pm\bar{3}n$ , and hexagonal  $p6mm$  PMOs was also confirmed by transmission electron microscopy (TEM), revealing a good long-range ordering with regular arrays. Moreover, variation of the synthesis parameters resulted in a variety of different PMO morphologies, as ascertained by scanning electron microscopy (SEM). FT-IR and solid-state  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy further revealed that the organic groups were uniformly incorporated into the framework. The various BET surface areas of the PMOs range from 470 to  $780 \text{ m}^2 \text{ g}^{-1}$ , while the pore diameters lie within a 26 to  $30 \text{ \AA}$  range, as derived from  $\text{N}_2$  physisorption.

**Key words:** Organosilicas, Cationic Surfactants, Mesoporous, Mesophase Transformation, Morphology