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Report:

Background

Polyoxometalates (POMs) are early transition-metal oxide clusters that exhibit various topologies and diverse chemical and electronic properties, leading to applications in catalysis, energy conversion and storage, sensors, molecular electronics, spintronics and medicine.[1,2] However the poor processibility of POMs limit development of POMs-based materials and devices. Introducing the POMs into nanostructured materials such as silica increases the stability of POMs, enabling exploitation of POMs in various applications. Organization of pure POMs into 2D or 3D structures is especially challenging, but the resulting systems could display advanced emergent behaviours. Many methods have been studied to structure POMs, including the use of a structuring agent attached to the POMs by electrostatic interactions,[3,4] or incorporating the POMs into organic matrices by mixing.[5] However electrostatic attachment does not produce a stable chemical bond and limits the types of solvent, which can be used (both POMs and structuring agent need to be dissolved in the same medium). Attaching hydrophobic tails onto the POMs via a covalent bond gives stable species with wider solvent tolerance.[6,7] We have systematically studied the self-assembly of amphiphile POMs in which the headgroups are derivatives of Dawson ions, covalently functionalized with double hydrocarbon tails.[8] In this experiemnt, we have characterized the micelles formed by the mixture of soluble amphiphile POMs and non-ionic surfactants for potential use in templating systems with silica/titania, to obtain an even distribution of the POMs on the surface of nanoporous silica/titania channels.

Results and discussion

In this experiment, we have studied that assembly of a polyoxometalate-headed surfactant (POM-2Cn, n = 12 or 16, see the molecular structure of POM-2C12 in Figure 1A) and a triblock copolymer $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$ (P123, see the molecular structure in Figure 1B). We have used a customerized set-up with a levitator in between the beam and the detector. A droplet of the aqueous solution (12 mM of POM-2Cn and P123 with a mixing ratio at 3:1, 1:1 or 1:3) is put into the levitator where the droplet is levitating in the chamber, and water from the droplet is evaporating at the same time. We applied time-resolved SAXS measurements while the droplet is shrinking to investigate the assembly of two molecules in the solution.

Fig. 1C shows SAXS data from POM-2C_{12}/P123 mixtures with a total concentration of 12 mM in H_2O, which is the starting point of the time-resolved SAXS measurement. SAXS pattern of POM-2C_{12} rich mixture (POM-2C_{12}:P123 = 3:1) is fitted to an elliptical cylinder model with 25.0 ± 0.5 Å radius and 3.4 ± 0.2 axial ratio. Despite the dense POM headgroup, at this mixing ratio there appears to be no distinction between core and shell in the micelle. However, for the P123 rich mixture (POM-2C_{12}:P123 = 1:3), SAXS pattern is fitted into a random

lamellar phase with 11.0 ± 3.5 Å headgroup thickness (close to the size of the POM, ~ 12 Å) and 35.3 ± 0.2 Å tail thickness.
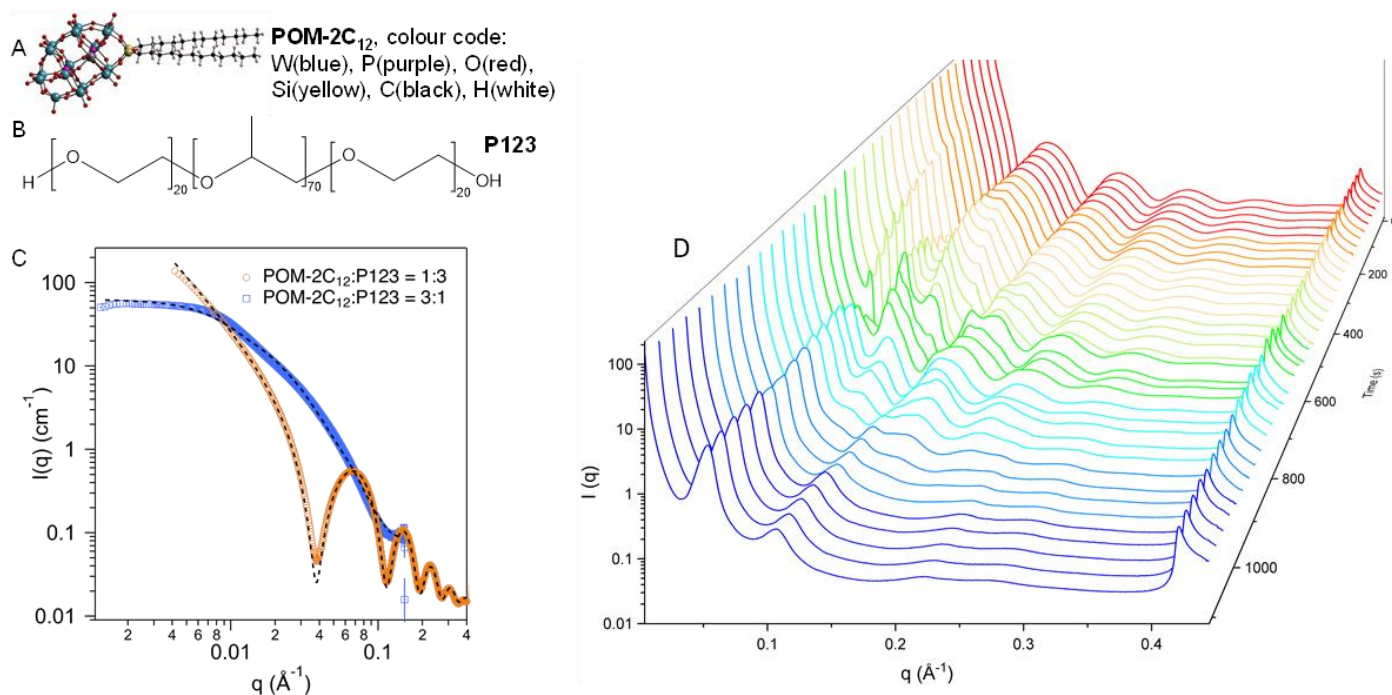

Fig. 1. Molecular structure of (A) P123 and (B) POM-2C$_{12}$, (C) SAXS patterns and the corresponding fit of aqueous solutions with two mixing molar ratios at a total concentration at 12 mM. (D) Time-resolved SAXS data of mixture POM-2Cn and P123 (mixing ratio 1:3).

Time-resolved SAXS patterns for mixture of POM-2C$_{12}$:P123 = 1:3 are plotted in Fig. 1D. At concentrations higher than 20.2 mM (at about 100s in Fig.1D), peaks at around 0.08Å^{-1}, indicating the interactions between the lamellar layers. As the concontration continuously increases, liquid crystal phases form in the droplet. After analyzing the peak positions of the following SAXS pattern at the time between 500 s and 1000 s in Fig. 1D, the phase tranformation follows the track of a cubic phase (mixure of Fm3m space group and Pm3m space group), pure cubic Fm3m phase, a mixture of cubic phase (Fm3m space group) and hexagonal phase, and then ends up as a lamellar phase. These results have indicated the possiblity of forming nanostructure with POM units organized in a specific order in water. These morphologies can be easily transformed to catalytic active ordered materials embedded in a porous material.

Results expected from this beamtime

The analysis of other mixing ratios (1:1 and 1:3) for POM-2C$_{12}$/P123 system and of three mixing ratios for POM-2C$_{16}$/P123 system is still on going. We are expecting an article or two coming out based on the results we collected during this beamtime. And follow-up work based on these results are ongoing; synthesizing mesomorphous POM structures and mesoporous silica/titania containing POMs for further studies of their materials and catalytic properties.

Reference

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