Layered Assemblies

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Onionlike Hybrid Assemblies Based on Surfactant-Encapsulated Polyoxometalates**

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The incorporation of functional units into amphiphilic molecules can lead to final assemblies with particular properties,[1] and in this context diverse units including oligo(*p*-phenylene vinylene),[2a] thiophene,[2b] fullerene,[2c] and even metal ions have been employed to fabricate functional amphiphiles.[2d] However, instances of large inorganic clusters, especially polyoxometalates, have rarely been reported, although they have been proved promising inorganic building blocks.[3] The exception is several examples of absorption of individual polyoxometalates on preformed cationic micelles[4a] or vesicles.[4b] Illuminated by the precedents of designing and utilizing functional amphiphiles, the direct use of polyoxometalate-containing amphiphiles can rationally provide a simpler way to construct polyoxometalate-based self-assemblies, in which the functions of polyoxometalates may be better developed.

Recently, to tailor the compatibility of polyoxometalates with organic materials and biological tissues, cationic surfactants have been applied to improve the surface properties of these clusters.[5] The resulting surfactant-encapsulated complexes (SECs) are compatible with organic matrixes and have been successfully incorporated into polymeric and liquid-crystalline materials,[6] while the basic physical and chemical properties of the polyoxometalates are retained. Meanwhile, the coexistence of hydrophobic alkyl chains and hydrophilic clusters in SECs gives them an amphiphilic character, which results in interesting self-assembly of SECs into honeycomb films under a moist airflow,[7] just like the case of amphiphilic copolymers.[8] Furthermore, this amphiphilic character is also exhibited in a solution environment, and an unusual vesicular assembly of $(DODA)_4H[Eu(H_2O)_2SiW_{11}O_{39}]$ (DODA = dimethyldioctadecylammonium) has been observed by us lately.[7] This finding suggests the feasibility of utilizing SECs as polyoxometalate-containing amphiphiles to construct regular assemblies from solution, and it is also helpful to comprehend the catalyzing reactions of polyoxometalates in organic media. However, the origin of the assembly process and whether it is a general behavior of SECs in solution are both ambiguous. Herein, we try to elucidate the universality and possible mechanism of SEC self-assembly and the path to stabilize the morphology of the assemblies.

It has been reported that a weak Eu–O_d (O_d: terminal oxygen atom) bond exists between adjacent $[Eu(H_2O)_2SiW_{11}O_{39}]^{5-}$ clusters in the crystalline state.[9] To exclude the possible influence of this interaction on the assembly of $(DODA)_4H[Eu(H_2O)_2SiW_{11}O_{39}]$, here we select $(DODA)_4SiW_{12}O_{40}$ as the object for investigation, as the $DODA^+$ and $SiW_{12}O_{40}{}^{4-}$ contained in the complex are the common surfactant and polyoxometalate, respectively. Similar to the previous report, a rapid assembling of $(DODA)_4SiW_{12}O_{40}$ in chloroform is also observed, and dynamic light scattering (DLS) measurements indicate that assemblies ranging in size from 100 to 300 nm are formed in a very short time (0.5 min) after the sample is dissolved. The self-assembly process can occur in almost all the common organic solvents, such as chloroform, toluene, tetrahydrofuran, dimethylformamide, and even in a mixed solvent of chloroform and methanol. The corresponding DLS results are shown in the Supporting Information.

Optical microscopy and scanning electron microscopy (SEM) measurements demonstrate that the assemblies have a spherical shape (Figure 1 a and Supporting Information), and

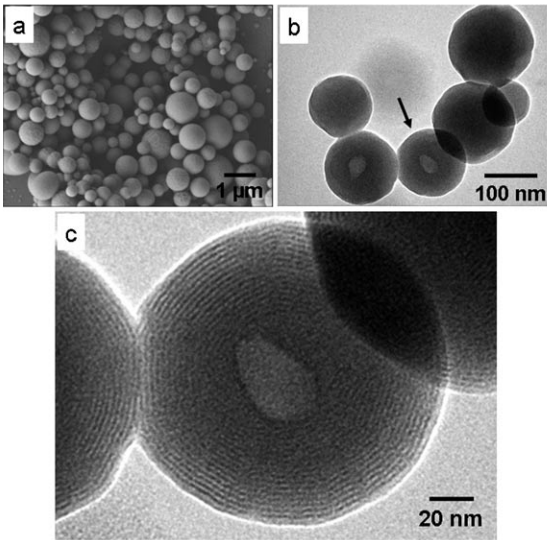

Figure 1. a) SEM and b) TEM images of $(DODA)_4SiW_{12}O_{40}$ assemblies from a mixed solvent (chloroform/methanol = 4:1), and c) magnified image of the local region in (b) indicated by an arrow.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

X-ray energy-dispersive spectroscopy (EDS) coupled with SEM shows that both tungsten and carbon elements exist throughout the assemblies (Supporting Information), which are contributed by $SiW_{12}O_{40}^{4-}$ and $DODA^+$, respectively. In pure chloroform, the assemblies are unstable and always fuse into layers during solvent evaporation. Interestingly, the addition of methanol can improve their stability, and very firm spheres are thus obtained from an optimized mixed solvent (volume ratio of chloroform/methanol = 4:1), which can maintain the spherical shape quite stably even when free of solvent (see Figure 1 a). As a result of the high tungsten content, the electron beam cannot penetrate large spherical assemblies efficiently, whereas the precise structure of relatively small spheres can be observed clearly by transmission electron microscopy (TEM; see Figure 2 b and c). The spherical assemblies are onionlike and exhibit ordinal circular multilamellas, with a layer spacing estimated at about 3.0 nm.

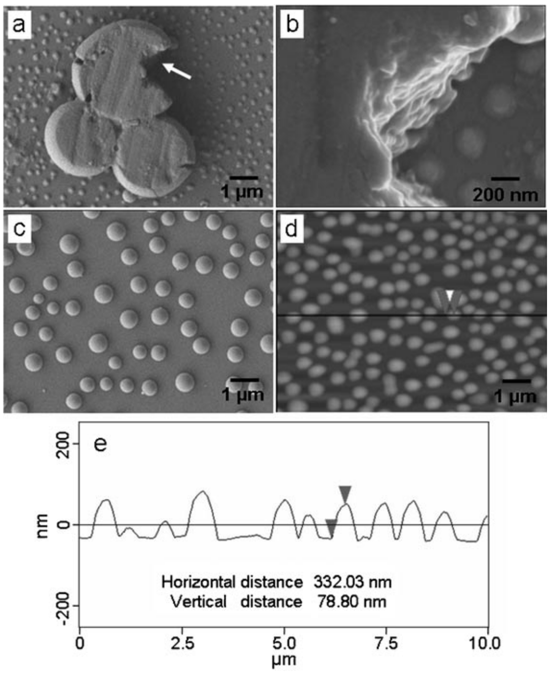

Figure 2. a) SEM image of giant $(DODA)_4SiW_{12}O_{40}$ spherical assemblies. b) Magnified image of the rough edge of the broken sphere in (a) indicated by an arrow. c) SEM image, d) AFM height image, and e) section analysis of the flat spherical assemblies on mica. All the assemblies were obtained from the mixed-solvent solution (volume ratio of chloroform/methanol = 4:1).

Meanwhile, X-ray diffraction (XRD) of the dry spheres also shows a lamellar pattern with a spacing of about 3.1 nm (see Supporting Information), which is consistent with the TEM result and also supports the formation of a new composite between DODA and $H_4SiW_{12}O_{40}$. The static contact angle of a film of the assemblies is larger than 120°, which suggests that the external surfaces of the spherical assemblies are composed of hydrophobic alkyl chains of $DODA^+$. We thus speculate that these spherical assemblies are in an inverted-vesicle-like structure, similar to the inverted vesicles formed by Ru-based metallosurfactants in toluene solution that were reported recently.[10] In such a mode, the nonpolar alkyl chains of $DODA^+$ face the weakly polar solvent and the polar $SiW_{12}O_{40}^{4-}$ clusters are separated from the solvent, which is polarity-suited and energetically favorable. Therefore, we believe that the dark circular stripes with light sides in the onionlike spheres are the $SiW_{12}O_{40}^{4-}$ layers each shielded by two $DODA^+$ layers.

The multilamellar SEC spheres are morphologically similar to the onion phase of conventional surfactant vesicles,[11] and empty spaces are found in the central part of some spheres, also like the hollow vesicles formed by organic amphiphiles. The SEC spheres reveal a certain fastness and toughness, because they contain both inorganic clusters and organic alkyl chains. In the case of pressing and rubbing of these assemblies, some giant spheres become staved, as seen in the cross section (Figure 2 a, b), which probably arises from the fracturing of the multilamellar structure. During the loss of solvent molecules, some spheres become flat, especially those that fall directly on the substrate (Figure 2 c). Atomic force microscopy (AFM) images show that their horizontal sizes are much larger than the corresponding vertical heights by almost eight to ten times (see Figure 2 e).

For conventional vesicles prepared by synthetic surfactants or lipids, the phase transitions of the alkyl chains from gel to liquid-crystalline state take place during the heating process.[12] Here, a similar phase transition also occurs for $(DODA)_4SiW_{12}O_{40}$ spherical assemblies, and the transition temperatures (T_c) rely on the solvent polarity. In pure chloroform, the alkyl chains of DODA in $(DODA)_4SiW_{12}O_{40}$ are relatively flexible as a result of their good solubility and tend to be disordered; thus, the corresponding T_c value is relatively low (at 3.3 °C). The addition of methanol can enhance the rigidity and the hydrophobic interaction between alkyl chains, and thus a higher energy is required to break the stacking interaction upon heating. Consequently, the T_c gradually rises with the increasing content of methanol, up to 6.2 and 10.2 °C when the volume ratios of chloroform to methanol are 8:1 and 4:1, respectively. Moreover, the calculated ΔH value of $(DODA)_4SiW_{12}O_{40}$ assemblies is about 10.7 $kcal\,mol^{-1}$, consistent with the ΔH value of pure DODA vesicles.[13] This result implies that the $DODA^+$ chains in the assemblies do indeed undergo an essential phase transition from a gel to liquid-crystalline state.

Details of the phase transitions are analyzed by temperature-dependent ^1H NMR measurements (Figure 3). At temperatures below T_c, the NMR signals of $(DODA)_4SiW_{12}O_{40}$ in $CDCl_3$ solution are very weak, and only the proton signals of the outer part of $DODA^+$ chains can be observed. This finding suggests that most of the $DODA^+$ chains are in a restricted state, except that a few terminal groups are fluid in the solvent. Upon increasing the temperature, the thermal movement of alkyl chains becomes more active, and the mobility of these chains is thus enhanced. As a result, the intensity of the proton signals of $DODA^+$ gradually becomes stronger. Once the temperature reaches T_c, a sharp enhancement of proton signals appears and the characteristic chemical shifts of the protons near the head group of $DODA^+$ become clear. This result shows the typical character of well-fluid alkyl chains,

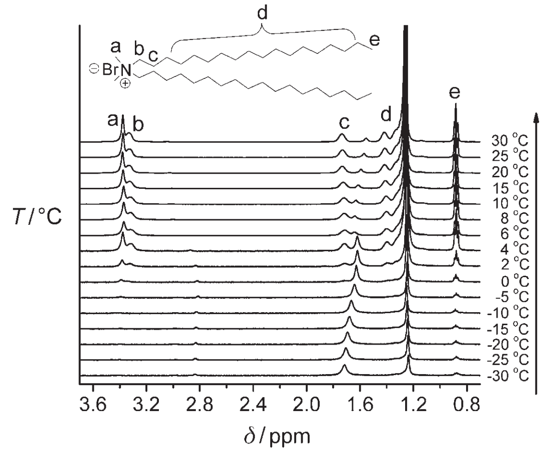

Figure 3. Temperature-dependent ^{1}H NMR spectra of $(DODA)_4SiW_{12}O_{40}$ in $CDCl_3$ (2×10^{-3} mol L^{-1}) during the heating process.

and indicates the transition of $DODA^+$ chains from compact gel stacking into a relaxed liquid-crystalline state.

To pursue the driving force and mechanism of formation of these onionlike assemblies, we further investigated the possible change in structure of $(DODA)_4SiW_{12}O_{40}$ during its assembly process. According to the accepted model, $SiW_{12}O_{40}{}^{4-}$ can be understood as a $SiO_4{}^{4-}$ unit encapsulated by a neutral $W_{12}O_{36}$ cage.[14] So, in $(DODA)_4SiW_{12}O_{40}$, $DODA^+$ is reasonably thought to be electrostatically drawn by the central $SiO_4{}^{4-}$, but separated by the $W_{12}O_{36}$ cage. Such a model provides the possibility for $DODA^+$ to rearrange on the $SiW_{12}O_{40}{}^{4-}$ surface, as the electrostatic interaction is not fixed at a certain site but is equilibrated in the whole potential field. This speculation could be further verified by spreading $(DODA)_4SiW_{12}O_{40}$ onto an air/water interface. Based on the surface pressure–area isotherm, the condensed molecular area per complex is deduced to be 2.52 nm^2, much larger than the total area of two $DODA^+$ cations, for the lateral area of one DODA molecule has been reported to be 0.57 nm^2 in its crystalline state.[15] On the other hand, this value just fits the area of four $DODA^+$ ions, which suggests that the four $DODA^+$ cations around one $SiW_{12}O_{40}{}^{4-}$ anion have mostly rearranged above the cluster at the air/water interface and depart from the aqueous subphase driven by the hydrophobicity force (see Figure 4). Such an uneven distribution of $DODA^+$ at the air/water interface has already been observed for another SEC, $(DODA)_{16}AsW_{30}Cu_4O_{112}$, in our previous study. The two surfaces of the $(DODA)_{16}AsW_{30}Cu_4O_{112}$ Langmuir–Blodgett monolayer film above and below the air/water interface were affirmed to be asymmetric, in terms of different frictional force, by scanning force microscopy.[5b] Thus, from either a theoretical or experimental aspect, the rearrangement of $DODA^+$ cations on the $SiW_{12}O_{40}{}^{4-}$ surface is feasible, which is directly related to the final formation of $(DODA)_4SiW_{12}O_{40}$ spherical assemblies. Moreover, the recent report that pure polyoxometalate can form vesicles in aqueous solution[16] also supports the notion that these clusters can keep their curved layers, even in the surfactant bilayers. Therefore, we believe that $DODA^+$ alkyl chains capped on $SiW_{12}O_{40}{}^{4-}$ clusters reorganize under the driving force of solvent polarity, thus inducing $(DODA)_4SiW_{12}O_{40}$ to form inverted-vesicle-like assemblies.

To confirm the universality of such assembly in SEC solutions, two other ammonium surfactants with different alkyl chain lengths and chain numbers, dimethyldidodecylammonium bromide and tetraheptylammonium bromide, were also employed to encapsulate $H_4SiW_{12}O_{40}$. Meanwhile, by keeping DODA constant as the surfactant, we encapsulated two other polyoxometalates with different charges and topological shapes, $Na_9EuW_{10}O_{36}$ and $K_{13}Eu(SiW_{11}O_{39})_2$, respectively. Similar phenomena were found in all these SEC solutions of chloroform. The corresponding structural schemes of the surfactants and polyoxometalates, together with the DLS data, are shown in the Supporting Information.

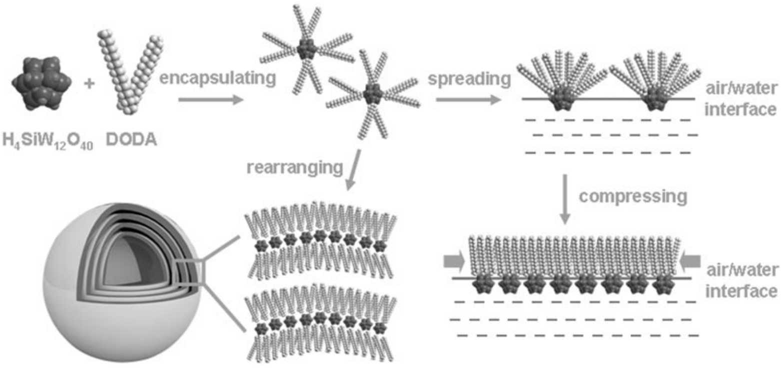

Figure 4. Assembly mechanism of $(DODA)_4SiW_{12}O_{40}$ under different conditions, including initial formation by encapsulation, inverted-vesicle assembly in organic solvent, and rearrangement at the air/water interface.

In conclusion, we found that SECs have the general tendency to assemble into spherical aggregates in organic solvents, which is attributed to the rearrangement of surfactants on the exterior of the polyoxometalate. By controlling the solvent polarity, stable assemblies of $(DODA)_4SiW_{12}O_{40}$ have been obtained as onionlike spheres. These spherical assemblies possess the ordinal circular multilamellar structure, and each fundamental layer has a sandwich structure in which alkyl chains shield the outside while clusters are located inside. Such an onionlike structure can provide a similar microenvironment to vesicles, which makes these spherical assemblies suitable carriers to perform the catalytic[17a] and pharmacological[17b] functions of polyoxometalates.

Experimental Section

The surfactants and $H_4SiW_{12}O_{40}$ were purchased as commercial products. $Na_9EuW_{10}O_{36}$ and $K_{13}Eu(SiW_{11}O_{39})_2$ were synthesized according to published procedures.[18] All the SECs were prepared by following the previous procedures.[5b] For example, for the synthesis of $(DODA)_4SiW_{12}O_{40}$, a solution of DODA in chloroform was dropped into an aqueous solution of $H_4SiW_{12}O_{40}$ under stirring, and the molar ratio of DODA to $H_4SiW_{12}O_{40}$ was controlled at 3.8:1. The organic phase was separated, and $(DODA)_4SiW_{12}O_{40}$ was obtained by evaporating the chloroform to dryness. Then the product was placed in a vacuum desiccator until the weight remained constant. Other SECs were obtained in the same way, and the fundamental characterization of all SECs can be found in the Supporting Information. All the SEC solutions were prepared at room temperature.

Optical photographs were obtained on an Olympus BX51 optical microscope. SEM images were acquired with a JEOL FESEM 6700F electron microscope, and TEM images were obtained with a Hitachi H 8100 electron microscope. AFM images were obtained in the tapping mode with a commercial digital instrument, Nanoscope III, and Dimension 3000TM. DLS was measured on a DAWN EOS enhanced optical system (Wyatt Technology Corporation). ^1H NMR spectra were recorded on a Bruker Ultrashield 500 MHz spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204 apparatus.

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