Robust Core-Shell Supramolecular Assemblies Based on Cationic Vesicles and Ring-Shaped {Mo_{154}} Polyoxomolybdate Nanoclusters: Template-Directed Synthesis and Characterizations

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Abstract: Substantial progress has been made recently in extending the supramolecular assembly of biomimetic structures to vesicle-based sophisticated nanocomposites and mesostructures. We report herein the successful preparation of unilamellar surfactant vesicles coated with a monolayer of ring-shaped {Mo_{154}} polyoxometalate (POM) nanoclusters, $(NH_4)_{28}[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]\cdot\approx 350\,H_2O$, by coulomb attractions using preformed didodecyldimethylammonium bromide (DDAB) surfactant vesicles as templates. The resultant vesicle-templated supramolecular assemblies are *robust* (they do not disintegrate upon dehydration) both at room-temperature ambient and vacuum conditions, as characterized by conventional transmission electron microscopy (TEM) and atomic force microscopy (AFM). The flexibility of the complex soft assemblies was also revealed by AFM measurements. The effect of POM-vesicle coulomb attractions on the dimensions of the templating vesicles was also investigated by using dynamic light scattering (DLS). Although origins of the structure stability of the as-prepared supramolecular assemblies are not clear yet, the nanometer scale cavities and the related properties of macroions of the POM clusters may play an important role in it.

Keywords: molybdenum · nanostructures · polyoxometalate · supramolecular chemistry · template synthesis · vesicles

Introduction

Substantial progress has been made recently in extending the supramolecular assembly of biomimetic structures to vesicle-based sophisticated nanocomposites and mesostructures.[1–5] The interest in such vesicle-based systems lies in the synergy that arises through association of vesicles and the assembled moieties. However, with the exception of polymer-crosslinked vesicles[6] and robust polymer vesicles,[7–8] owing to efficient packing and partly entangled and interdigitated chain structure, all other bare or thinly coated, short-chain, surfactant vesicular superstructures lack structural stability and tend to entirely or partly disintegrate upon dehydration. These structures can be protected and only integrally visualized by cryoelectron microscope[2–5] and/or negative staining.[9–10] To our knowledge, room-temperature robust, surfactant vesicle-based supramolecular assemblies with a monolayer coating of fine nanoclusters have hardly been reported to date. The challenge has been to develop chemical or physical strategies to stabilize and visualize these fragile systems. We report here a counterintuitive synthesis route to room-temperature *robust* "core-shell" supramolecular assemblies based on didodecyldimethylammonium bromide (DDAB) cationic surfactant vesicles and ring-shaped {Mo_{154}} polyoxometalate (POM) nanoclusters.

Intermediate between the colloidal and molecular ranges, the polyoxometalates (POMs) has recently received increasing attention.[11] Their involvement in hybrid organic–inorganic materials is of great interest, and attention was recently paid to the rational design of POM multicomponent materials with well-defined supramolecular architectures. An impressive approach towards this goal is exploited by Kurth et al.[12] based on modifying the POM surface with surfactants, yielding discrete surfactant-encapsulated clusters (SECs). Recently, Polarz et al.[13] reported that under one-pot conditions, the complexation of aqueous solution of POMs with surfactants results in the organization of POM nanoclusters into a liquid-crystalline-like alignment with long-range order through their shape and amphiphilicity. However, to the best of our knowledge, no work is presented in the literature in which unilamellar surfactant vesicles are used as templates for the electrostatic deposition of POM nanoclusters from solution to produce novel core-shell supramolecular assemblies.

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In this article, we report the successful preparation of unilamellar surfactant vesicles coated by a monolayer of ring-shaped {Mo_{154}} POM clusters by coulomb attractions using preformed DDAB vesicles as templates. Generally, the formation of the core-shell supramolecular assemblies occurs in two steps: formation of unilamellar vesicles from surfactant with subsequent generation of the POM shell upon mixing the aqueous solution of POM with preformed vesicle solution. The resultant vesicle-templated supramolecular assemblies are *robust* (i.e., they do not disintegrate upon dehydration) both at room-temperature ambient and vacuum conditions, as characterized by conventional transmission electron microscopy (TEM) and atomic force microscopy (AFM). The flexibility of the complex soft assemblies was also revealed by AFM measurements. The effect of POM-vesicle coulomb attractions on the dimensions of the templating vesicles was also investigated by using dynamic light scattering (DLS). Although the origins of the structure stability of the as-prepared supramolecular assemblies are not clear yet, both the nanometer scale cavities and the related properties of macroions of the {Mo_{154}} POM clusters may play an important role in it.

Results and Discussion

DDAB vesicle-templated electrostatic assembly of the ring-shaped {MO_{154}} POM nanocluters: A water-soluble big wheel, $(NH_4)_{28}[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]\cdot\approx 350\,H_2O$, was prepared completely according to the preparation method of Müller et al.[14] Figure 1A shows a typical transmission electron micrography (TEM) image of the as-prepared {Mo_{154}} POM nanoclusters.

The {Mo_{154}} POM nanoclusters with uniform size in the range of 3.5–4.0 nm are well dispersed due to strong coulomb repulsion between the huge anions. It should be pointed out that the presence of crystallographically discrete or linked ring-shaped POM anions are dependent on synthetic methods, and the ring-shaped feature of the huge anions would be more clearly discriminated by TEM in a uniform material than in an amorphous material.[14c,d] An optical enlarged TEM image (Figure 1B) reveals most of the nanoclusters as a blurred ring-shaped feature with inner diameter (nanocavity) about 2 nm. In this case, the center portion (nanocavity) of most individual clusters was lighter than its edge (ring), indicating the formation of a ring-type nanostructures. The thickness of the ring, on the order of about 1.0 nm, was revealed by additional atomic force microscopy (AFM) characterization of the nanoclusters on mica surface

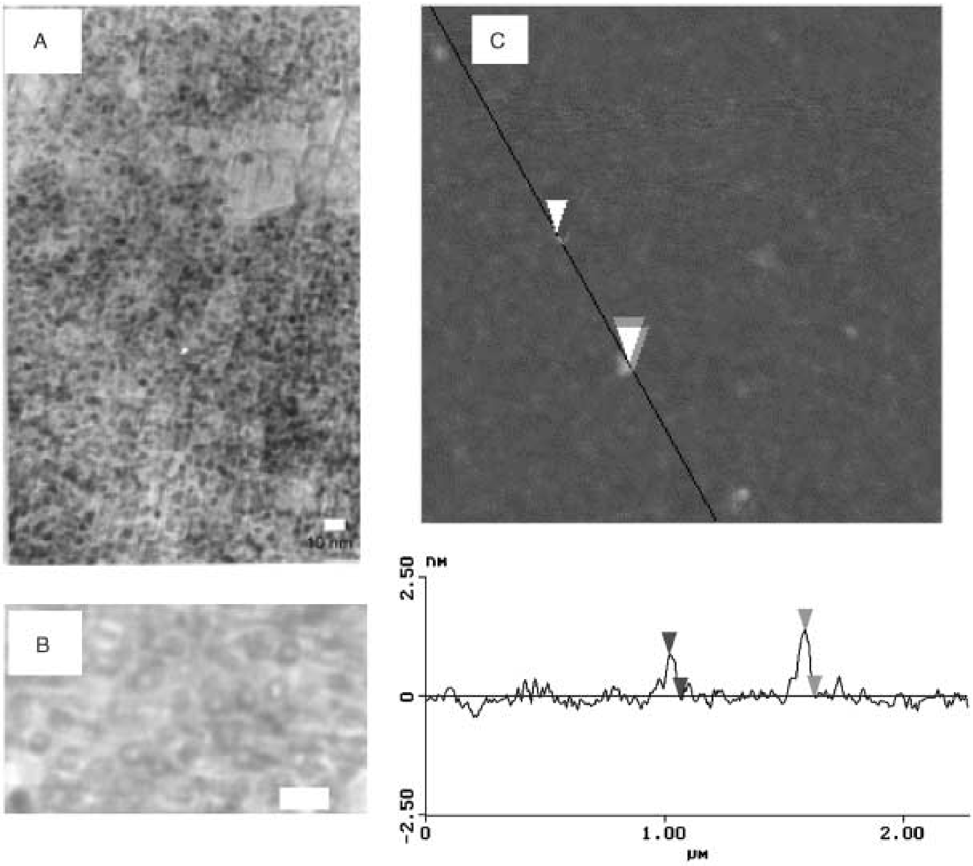

Figure 1. A) TEM image of ring-shaped {Mo_{154}} POM nanoclusters and B) an optical enlarged TEM image showing blurred ring-shaped nature of the POM nanoclusters: bar = 10 nm. C) Contact mode AFM image of pure {Mo_{154}} POM nanocluster submonolayer on mica surface. The line scan shows that the thickness of the POM nanoclusters is ~1 nm.

(Figure 1C). The blurred TEM image is a reflection of poor electron contrast due to the thinness in nature (~1.0 nm) of the fine POM clusters. The exact shape and size of the nanoclusters are available from single-crystal X-ray analysis of the POM clusters.[14a] Although the synthesis procedure given in reference1 [14] is known to yield crystalline material that contains impurities of smaller polyoxomolybdate clusters (<5% in our case, as revealed by TEM in Figure 1A), the dominant species is the ring-shaped $\{Mo_{154}\}$ nanocluster.

Unilamellar surfactant vesicles were prepared by first dissolution of didodecyldimethylammonium bromide (DDAB), a cationic, double-chained amphiphile, in chloroform. After evaporation of the volatile solvent in a stream of pure N_2 and overnight dessication, the amphiphile was hydrated in 1 mM aqueous NaCl solution and sonicated at 40 °C to obtain a homogeneous suspension. Above the critical micelle concentrations (cmc), DDAB alone self-assembles into bilayer vesicles.[15] It should be pointed out that the size of DDAB vesicles varies in the range of tens to hundreds of nanometers and is highly dependent on DDAB concentration and preparation approaches.[16] The as-prepared unilamellar DDAB vesicles (1 mg mL^{-1}) here, with a mean diameter of ~77 nm, were detected by dynamic light scattering (DLS) experiments (see Figure 5 later). The as-prepared DDAB cationic vesicles were then used as supramolecular templates for further surface self-assembly of the negatively charged $\{Mo_{154}\}$ POM nanoclusters. Coulomb attractions cause the adsorption of the POM nanoclusters onto the vesicle surfaces. Although the electrostatic adsorption tactics has been used to synthesize discrete surfactant-encapsulated POM clusters (SECs)[12] and even three-dimensional organized structures,[13] the vesicle-templated surfactant/POM core-shell supramolecular system has not been reported to date.

In a typical preparation, 10 µL of freshly prepared DDAB vesicle suspension (1 mg mL^{-1}) was injected into an aqueous $\{Mo_{154}\}$ POM nanocluster suspension (1 mL, 5 µM) under sonication at 40 °C. After sonicating for about 20 min, the solution was then kept at 4 °C overnight. In the synthesis, the ratio of molar concentration of the POM nanoclusters to that of DDAB is about 1:4. This ratio was chosen to ensure that the surface area of the DDAB vesicles is fully covered by the POM nanoclusters. Samples for TEM characterization were prepared by placing a droplet of solution on a carbon-coated copper grid and letting it air-dry, without additional staining. Figure 2A and 2B shows representative conventional TEM images of the resultant vesicle/POM core-shell supramolecular assemblies, with sizes in the range of 80–100 nm. The size of the POM-covered DDAB vesicles is very similar to and slightly larger than the size of the original DDAB vesicles. It is reasonable, since there is only one layer of the POM nanoclusters and the fact that POM–DDAB interactions exist. The thin darker edges (circular rings) indicate the vesicular nature and thin POM coating of the assemblies. Contrast in the TEM image is generated by the variation of the projection of the electron beam, which is normal to the image in these figures, through the vesicular assembly. The projection through the edges of the vesicular assembly is greater than through the central part. As the width of the dark rim (~2–3 nm) of the vesicular assembly is wider than the actual thickness of the POM coating, because of the curvature of the vesicular assembly,[17] the thickness of the POM coating is essentially on monolayer level. An image taken with higher magnification (Figure 2C) shows more clearly the monolayer nature (dictated by interfacial electrostatic interactions) of the POM coating and the well-arranged domain sub-structure, and reveals the size and even blurred ring-shaped feature of most of the $\{Mo_{154}\}$ POM nanocluster building blocks. Tilting the specimens in the electron microscope further confirmed that the supramolecular assemblies are spherical in shape. Taking into account the dense monolayer coverage of the POM nanoclusters on the DDAB vesicle (80–100 nm in diameter) surface, each assembly contains about 1000–2000 $\{Mo_{154}\}$ POM nanoclusters and possesses few vacancy defects.

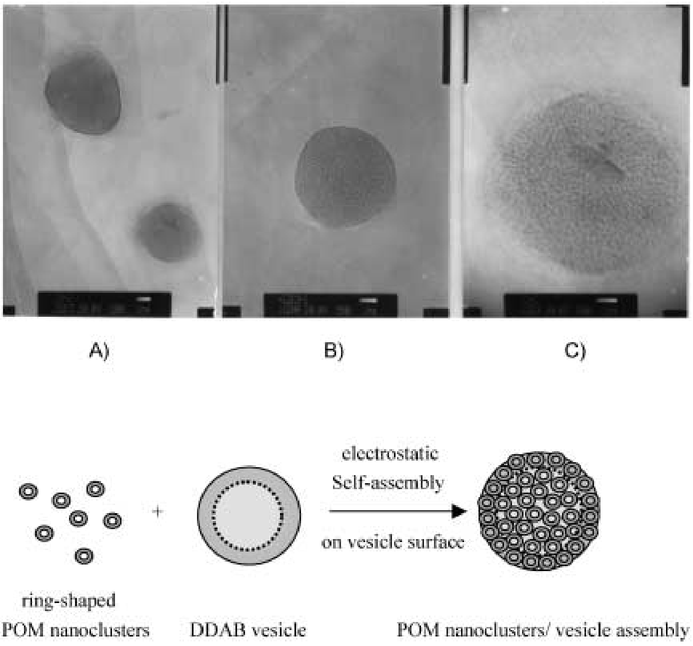

Figure 2. Representative conventional TEM images of as-prepared $\{Mo_{154}\}$ POM nanocluster monolayer-covered DDAB vesicles supramolecular assemblies: A) bar = 20 nm; B) bar = 10 nm. C) An enlarged TEM image showing the monolayer nature, uniform size and even the ring-shaped feature of the POM nanoclusters: bar = 10 nm. At the bottom is a schematic representation of electrostatic self-assembly of ring-shaped POM nanoclusters on the cationic DDAB vesicle surface.

To obtain more information about the shape of the as-prepared supramolecular assemblies we examined them with atomic force microscopy (AFM). The three-dimensional morphology nature of the supramolecular assemblies was further confirmed by AFM experiments. Figure 3 shows a typical AFM image of an as-prepared supramolecular assembly. The horizontal size of the assemblies is about 50 nm larger than that observed by TEM, due to the tip-sample interactions and tip convolution effect. Interestingly, the vertical dimension of the assemblies is typically 18 nm, much smaller than the horizontal size and larger than the thickness of otherwise burst and flattened multilayer structures, indicating that the supramolecular assemblies are flexible

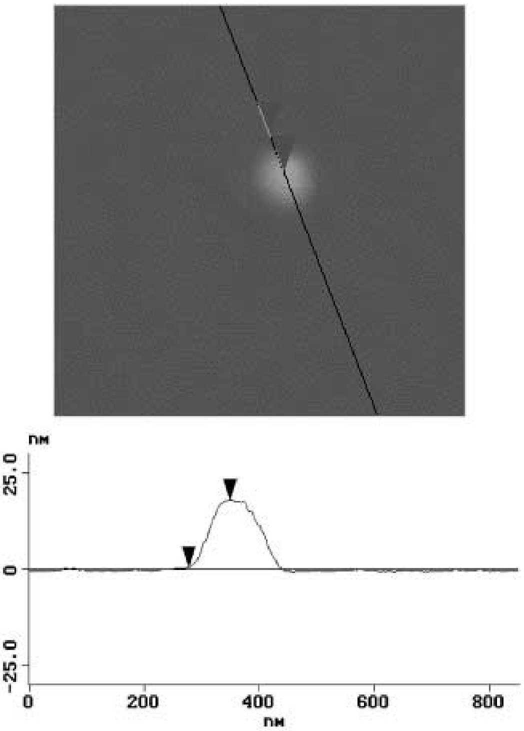

Figure 3. Contact mode AFM image and line scan analysis of an as-prepared vesicle/POM supramolecular assembly on mica surface.

(deformed) and still intact (robust!) under the tip-sample interactions. The AFM image shows that the profile is flat with an extended plateau in the middle, as expected for vesicular structure in AFM. It is very interesting and astonishing that under the contact of the AFM tip, the POM monolayer-coated DDAB vesicles are still robust (not disintegrate) and flexible so that they severely deform, that is, the horizontal size is enlarged and the vertical height reduced as revealed by AFM. The conventional TEM and AFM characterizations revealed that the as-prepared vesicle/POM core-shell supramolecular assemblies are robust both under vacuum and ambient conditions, even under contact interaction of the AFM tip.

It should be pointed out that most of the known POM giant anions themselves tend to form vesicle structures in different polar solvents, including water.[18,19] For example, Müller et al.[18] recently reported that another similar $\{Mo_{154}\}$ POM giant anion, with only slightly different ligands, tends to aggregate into vesicle structures in non-aqueous media such as methanol and acetone. Liu[19] also revealed that the self-association of POM-based giant molecules in solution has unusual behavior with respect to common inorganic ions. These POM giant molecules need days or months to reach an equilibrium state. Moreover, it is known that the $\{Mo_{154}\}$ POM anions also form 80–90 nm size vesicles in solution.[18] However, all these vesicle structures were observed only in solution state, and no robust vesicle structure of these POM giant anions has been observed in solid form, especially in a high-vacuum environment. It is known that those POM vesicle structures *burst* upon switching the scanning electronic microscope (SEM) from the environmental to the high vacuum mode.[18] However, the strong coincidence in vesicular size of both cases made us wonder whether the vesicle-templated assemblies here were actually just pure POM vesicles. To address this issue, we repeated conventional TEM and AFM studies on a pure POM aqueous solution (template-free) that was prepared ~2 months ahead. However, no three-dimensional vesicular structures were observed, both by conventional TEM and AFM. The results are similar to those of a pure POM aqueous solution prepared ~2–3 days ahead, as shown in Figure 1. It is therefore confirmed that the vesicular structures in the solid state, observed here by conventional TEM and AFM, were not formed from pure $\{Mo_{154}\}$ POM giant anions, even if it is possible that they would form in solution state, and that the DDAB surfactant vesicles do play a template role in vesicle formation of the POM nanoclusters.

The results were reproducible and the assemblies showed durable structure stability, indicating that the as-prepared supramolecular assemblies were robust relative to the native DDAB vesicles. These "petrified" DDAB vesicles cover in a $\{Mo_{154}\}$ POM nanocluster monolayer are stable to dehydration and can be visualized by using AFM and conventional TEM without additional staining. In a control experiment, the DDAB vesicles (1 mg mL^{-1}) alone disintegrated completely upon dehydration and as a consequence become "invisible" in TEM, as shown in Figure 4A, in which individual vesicles collapsed and the amphiphile organized to form

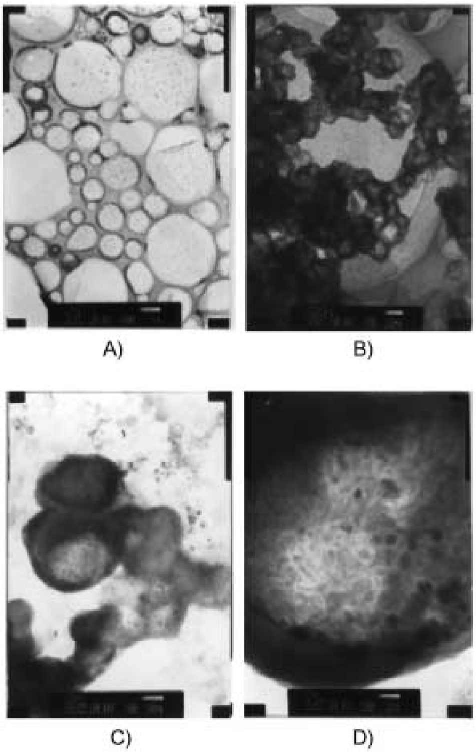

Figure 4. A) A representative conventional TEM image of disintegrated, and then reorganized mesostructures of the DDAB vesicles alone: bar = 1 μm. B) A conventional TEM image of three-dimensional aggregated vesicles/POMs core-shell supramolecular assemblies: bar = 100 nm. C) and D): Typical conventional TEM images of as-prepared vesicles/POM nanoclusters supramolecular assemblies without sonication: C) bar = 100 nm; D) bar = 20 nm.

multilayered and flattened pattern with opal-like vacancy. Although templated shells of electrostaticly multilayered polyelectrolytes[20] show robustness that has lead to hollowed structures, to the best of our knowledge, *robust* surfactant vesicle-based core-shell structures with only electrostaticly monolayered shells have never been reported. Although the origins of the structure stability of the supramolecular assemblies and the exact chemical composition of the POM nanoclusters (due to the low stability of the molybdenum blue-ring clusters) are still unknown, we presume that both the ring-shaped feature, that is, the nano-cavities, and the related properties of the macroions of the POM giant anions, might play a key role in the system. The water nanostructures outside the wheels (i.e., between the adjacent $\{Mo_{154}\}$, formed due to the small inter-POM distance) may also play an important role. In control experiments, the preparation of similar core-shell supramolecular assemblies failed when we used other commercially available polyoxometalate anions or citrate-stabilized fine gold nanoparticles (2–4 nm in diameter) instead of the ring-shaped $\{Mo_{154}\}$ POM nanoclusters, which further confirms our assumption.

The free individual supramolecular assemblies are governed by the concentrations of the vesicles and the POM nanoclusters. For example, adding more vesicles (25 μL) to an aliquot of a suspension of POM nanoclusters (1 mL, 5 μM) caused the vesicles to aggregate, as revealed by conventional TEM (Figure 4B). Most of the vesicles were present in the large three-dimensional aggregates and few free vesicles were seen in this case. The aggregates in which the adjacent vesicles tethered together by sharing part of the POM nanoclusters, due to their proximity, are still robust and did not break up. As more vesicles and less POM nanoparticles were used, the vesicle surface is not covered well by the POM nanoclusters, and the shape and size of the vesicles are severely affected by the electrostatic interactions with POM nanoparticles and possible reorganization of the vesicles.

It was also found that sonication is very important to obtain structurally well-defined unilamellar vesicles/POM supramolecular assemblies. Long-time incubation of vesicle suspension and without sonication during preparation lead to the formation of uni- and multilamellar vesicles that ranged from 80 to 400 nm in diameter, and with an ill-defined POM nanocluster coating. Compared with those prepared under sonication, the complex vesicles are not stable enough and tend to partly disintegrate, as revealed by conventional TEM images (Figure 4C and 4D). These facts provide more evidence of our "templating" model, because the size of the pure POM vesicles in solutions usually does not have evident size variation.[18,19]

Dynamic light scattering: Dynamic light scattering (DLS) investigations were employed to determine the hydrodynamic diameter of the DDAB surfactant vesicles. In this article, we also used DLS to examine the effect of POM–vesicle coulomb attractions on the dimensions of the templating vesicles. In a typical preparation, a DDAB vesicle suspension (1 mg mL^{-1}, 10 μL) was injected into an aqueous suspension of $\{Mo_{154}\}$ POM (5 μM, 1 mL) under sonication at 40 °C for approximately 20 min. To our surprise, the vesicles remain in the dispersion when the POM giant ions were added, as revealed by DLS data (Figure 5). Thus the process here is an ion-exchange process. As expected, the coulomb attractions between the cationic head groups of the DDAB surfactant and the anionic $\{Mo_{154}\}$ POM clusters do have effect on the curvature of the resultant supramolecular structures and therefore the size of the vesicles. As shown in Figure 5, the mean diameter of the unilamellar DDAB vesicles (1 mg mL^{-1}) were expanded from ~77 nm to ~94 nm. The size of the as-prepared supramolecular assemblies is in good agreement with that observed by conventional TEM.

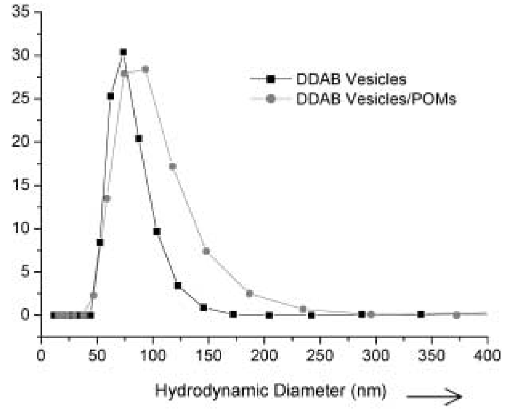

Figure 5. DLS study on a DDAB vesicle aqueous solution before and after addition of the $\{Mo_{154}\}$ POM nanoclusters.

POM-protected intermediate fusion structure of DDAB vesicles: The development of the cellular membrane was a defining advance in the evolution of life,[21] and nobody will dispute the important of the process of vesicle formation.[22] Scientists have long struggled to understand how bilayers, which seem to be thermodynamically designed to maintain their integrity, can be coerced to fuse and merge with one another. The primary experimental difficulty in studying this process has been the unstable and highly transient nature of intermediate fusion structures.[21] Very recently, Yang and Huang[23] show how membrane fusion intermediates can be stabilized, and present an important new experimental tool for studying the fusion process, namely, a stable lattice of lipid fusion structures. Herein, we found, surprisingly, that the simple procedure developed here can also stabilize (or "freeze") intermediate fusion structures of this system well and presents an important experimental approach for studying the fusion process. Figure 6A shows a conventional TEM image of an interesting intermediate fusion structure of several vesicles with a channel form. The enlarged TEM images (Figure 6B and 6C) show more clear the presence of fusion pore and kidney-like conduit characters of the fused vesicles, as well as the well-arranged POM monolayer lattice with different domain orientations and the blurred ring-shaped nature of the POM nanocluster building blocks.

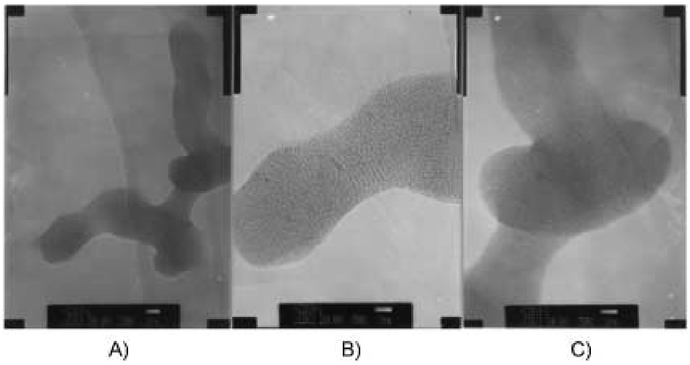

Figure 6. A) A conventional TEM image of an interesting intermediate fusion structure of several vesicles with a channel: bar = 20 nm; B) and C): Enlarged TEM images showing more clearly the presence of fusion pore and kidney-like conduit characters of the fused vesicles, and the well-arranged monolayer lattice and the ring-shaped nature of the POM nanoclusters: bar = 10 nm.

Conclusion

We report here that the ring-shaped {Mo_{154}} POM nanoclusters can electrostaticly self-assemble onto the preformed cationic DDAB vesicle surfaces and form room-temperature *robust*, three-dimensional core-shell supramolecular assemblies both at ambient and vacuum conditions, as characterized by conventional transmission electron microscopy (TEM) and atomic force microscopy (AFM). The flexibility of the complex soft assemblies was also revealed by AFM measurements. The effect of POM–vesicle coulomb attractions on the dimensions of the templating vesicles was also investigated by using dynamic light scattering (DLS). The template effect of the DDAB vesicles was confirmed by control TEM experiments of the pure POM nanoclusters and by DLS experiments.

Although origins of the structure stability of the as-prepared supramolecular assemblies and the exact chemical composition of the POM nanoclusters are not clear yet and need further investigations, the nanometer scale cavities of the POM clusters may confine water[24] in them (nonvolatile at room temperature)[25,26] and the water nanostructures inside and outside the wheels might play an important role.

Experimental Section

Materials: All chemicals were obtained from Aldrich and used without further purification. The ring-shaped {Mo_{154}} POM compound, $(NH_4)_{28}[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]\cdot\approx350\,H_2O$, was synthesized according to the preparation method of Müller et al.[14] The crystal structure of the POM compound was reported in the literature.[14] The water used was distilled twice and purified with the Millipore Milli-Q system.

Sample preparation: Unilamellar surfactant vesicles were prepared first by dissolution of didodecyldimethylammonium bromide (DDAB) in chloroform. After evaporation of the volatile solvent in a stream of pure N_2 and overnight desiccation, the amphiphile was hydrated in 1 mM aqueous NaCl and sonicated at 40 °C to obtain an homogeneous suspension. The as-prepared DDAB (1 mg mL^{-1}) cationic vesicles were then used as supramolecular templates for further surface self-assembly of the negatively-charged {Mo_{154}} POM nanoclusters. In a typical preparation, a freshly prepared DDAB vesicle suspension (1 mg mL^{-1}, 10 μL) was injected into an aqueous suspension of {Mo_{154}} POM nanoclusters (1 mL 5 μM) under sonication at 40 °C. After sonicating for about 20 min, the solution was then kept at 4 °C overnight.

Characterization: Samples for transmission electron micrographs (TEM) were prepared by placing a drop of solution onto a carbon-coated copper grid. Samples were examined with a JEOL 2010 TEM operated at 200 KV. Surface images were also acquired in contact-mode atomic force microscopy (AFM) under ambient condition (Nanoscope IIIa; Digital Instruments Inc.). Samples for AFM characterizations were prepared by placing a drop of solution onto a fresh mica surface and letting it air-dry. Dynamic light scattering (DLS) investigations were routinely employed to determine the hydrodynamic radius of the samples. The DLS experiments were performed on a commercial ZETASIZER 1000 HAS (MALVERN Instruments, UK) with laser wavelength $\lambda = 633.0$ nm. The refraction index of water was 1.33, and the refraction index of the DDAB and POM used were both set to be 1.42.

Acknowledgment

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[26] The volume of the nanocavity of a ring-shaped POM nanoparticle, $V \approx \pi r^2 d$, in which r and d are the inner diameter and thickness of the cavity, respectively, is about 3×10^{-24} L, which can accommodate ~100 H_2O. Taking other H_2O ligands into consideration that are arranged around the ring's plane with thickness of several molecular layers, the amount of the H_2O reaches about 300–400, which corresponds with the reported value ($\approx 350\,H_2O$).

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