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Controllable vesicular structure and reversal of a surfactant-encapsulated polyoxometalate complex†

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An organic–inorganic complex, surfactant-encapsulated polyoxometalate $(DDDA)_9EuW_{10}O_{36}$, demonstrates reversible self-assembly behavior in organic solvents and water. This hybrid complex can spontaneously organize into inverse vesicles by simply dispersing it in an organic solvent. Interestingly, by dissolving the water-insoluble complex in a water-miscible organic solvent such as ethanol and subsequently addition of water, it could be transferred into aqueous solution and the inverse vesicles in the organic solvent transformed into a regular bilayer structure in water. The vesicular aggregate, which had a regular structure, was studied by dynamic light scattering and transmission electron microscopy, as well as X-ray diffraction. The structural transformation was proved by zeta potential analysis and X-ray photoelectron spectroscopy, and the process was followed by ^{1}H NMR. These results provide the first example of aggregation behavior in this kind of complex, which is different from that exhibited by well known amphiphilic molecules with polar and non-polar ends, in water. Moreover, the reverse process, from a regular bilayer to inverse vesicles, can be conveniently carried out by simply extracting the complex from water into the organic phase. The results described may provide new opportunities in performing catalytic and biomimetic functions of polyoxometalates.

Introduction

Organic–inorganic hybrid complexes with precisely defined chemical compositions have attracted much attention over recent years due to the integration of the specific properties of both organic and inorganic components.[1] From the supramolecular point of view, an efficient approach to fabricate these hybrids is to incorporate inorganic functional units into organic matrices through certain intermolecular interactions.[2] Of the diverse inorganic materials, polyoxometalates (POMs) are representative of this group, having discrete metal-oxide clusters with sizes from about one to several nanometers, and their architectures not only exhibit a wide variety of topologies and compositions, but also lead to chemical, physical, and electronic versatility.[3–6] Meanwhile, due to their structural uniformity and abundant functional properties, POMs have been proved to be promising inorganic building blocks.[7] Recently, in order to incorporate POMs into various organized systems and tailor their assembly in organic materials and biological tissues, cationic surfactants have been employed to improve their surface properties while retaining their basic physical and chemical characteristics.[7–9] The resultant surfactant-encapsulated polyoxometalate (SEP) complexes, based on electrostatic interactions,

have become remarkable organic–inorganic hybrid building blocks due to their perfection both in chemical structure and geometric morphology, although such an idea has been extensively utilized in homogenous catalysis for many years.[8]

Although much research related to the functional applications of these complexes has been carried out, the state in which they exist in solution is still not always clear.[10a] In a recent report, SEP complexes have been proved to form inverse onion-like vesicular self-assemblies in organic solvents due to their amphiphilicity and ability to rearrange.[10b] This result provides an insight that allows us to understand the catalytic properties of this type of complex in organic media. However, if SEPs could be transferred into an aqueous system, the organic part would provide a hydrophobic microenvironment for POM-based microreactors, which could be beneficial to the catalysis of lipophilic substrates in water, as in the case of certain POM-containing assemblies.[11,12]

Organic–inorganic hybrid complexes that form core-shell particles can also be amphiphilic, undergoing reorganization under certain conditions, such as at the air–water interface or in organic solutions, *etc*.[8c,13,14] The hybrid complex represents a new kind of building block, different from the well-known small amphiphilic molecules with polar and non-polar ends and polymers in general, and therefore, it is useful to explore the aggregation and organization of this kind of amphiphilic building block in different media.

In this paper, we report the onion-like aggregates of a SEP both in organic solvent and in water, discussing in particular the reorganization of the complex. An interesting transformation between an inverse bilayer to a normal bilayer was discovered, and its mechanism deduced. The results are interesting for the following reasons. Firstly, although the aggregation of many amphiphiles has been thoroughly investigated, the aggregation of amphiphilic complexes, especially those with similar structures to the SEPs we have used here, has never been well evaluated in water. Secondly, not all the complexes that are similar to the present case show the same results; for example, complexes with a lower ratio of organic component or with larger inorganic cores have been confirmed to have more complicated behaviors. The present complex, as a special kind of building block, exhibits its own unique characteristics in solution. Thirdly, the present results are not only interesting with regard to the aggregation and structure reversal behavior, but also because of the novelty of the aggregation structure, because it provides a more precise and consistent aggregation model for the further functionalization. We believe that the present investigation provides a general understanding into such complexes in aqueous solution, and may provide a useful perspective on the catalytic and pharmacological application of POMs.

Experimental

Materials

The surfactant didodecyldimethylammonium bromide (DDDA • Br, 99%) was purchased from Acros Organics and used without further purification. Chloroform was distilled over CaH_2 prior to use. Ethanol (99%) and deionized water were used throughout the preparation and characterization. The polyoxometalate, $Na_9EuW_{10}O_{36} \cdot 32H_2O$ (POM-1), was synthesized as a crystalline material according to published procedures.[15]

Preparation of surfactant-encapsulated polyoxometalate

The sample complex was prepared by the following procedure. A solution of DDDA • Br dissolved in chloroform (1.0 mg mL^{-1}) was added dropwise into an aqueous solution of POM-1 (1.0 mg mL^{-1}) with stirring at room temperature. Considering the requirement for complete replacement of the sodium cations in POM-1, the initial molar ratio of DDDA • Br to POM-1 was controlled at 8:1. After 2 h of stirring, the organic phase was separated and washed with deionized water three times, leaving the inorganic salt, sodium bromide, in the aqueous solution. Then the complex $(DDDA)_9EuW_{10}O_{36}$ (SEP-1) was obtained by evaporating the

solvent to dryness. Finally, the product was dried in a vacuum desiccator until the weight remained constant. IR (KBr, cm^{-1}): ν = 3544 ν_{as}(O – H), 2921 $\nu_{as}(CH_2)$, 2852 $\nu_s(CH_2)$, 1467 $\delta(CH_2)$, 943 δ(W – O_d), 865 ν_{as}(W – O_b – W), 845, 786 and 721 ν_s(W – O_c – W). ^{1}H NMR (500 MHz; $CDCl_3$; TMS): δ (ppm) = 0.88 (t, J = 7.0 Hz, 6H, CH_3), 1.25 (m, 36H, CH_2), 1.65 (br, 4H, CH_2), 3.29 (br, 6H, N-CH_3), 3.44 (br, 4H, N-CH_2). Anal. Calc. (%) for SEP-1 ($C_{234}H_{504}N_9O_{36}EuW_{10}$, M = 6010.91): C 46.20, H 8.48, N 2.07; Found (%): C 46.70, H 8.55, N 1.88. The first stage of weight loss in the thermogravimetric curve (TGA) of SEP-1 (temperature range: 40 to 180 ° C) matches the amount of the crystalline water (1.34%), and the calculated number of water molecules per molecule of SEP-1 is about 4. Combining the TGA and elemental analysis, SEP-1 should correspond to the formula $(DDDA)_9EuW_{10}O_{36}$ • $4H_2O$.

Preparation of SEP-1 aqueous solution

1.0 mg of SEP-1 solid powder was dissolved in 1.0 mL of ethanol, and to the solution 10.0 mL of distilled water was added dropwise at room temperature. After 24 h of continuous stirring, the ethanol evaporated almost completely, leaving an aqueous solution of SEP-1 for structural characterization.

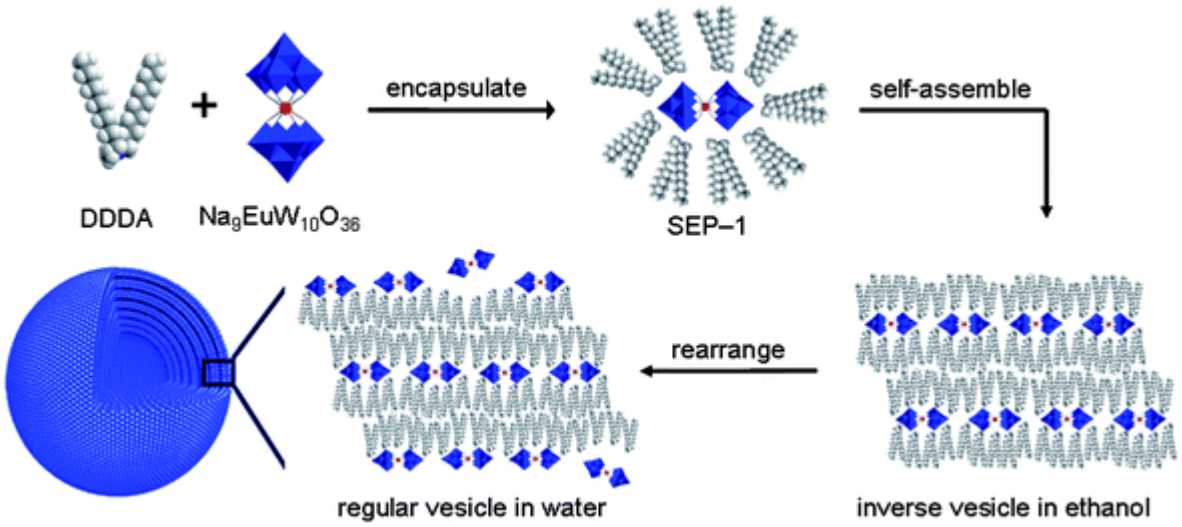
Measurements

FT-IR spectra were carried out on a Bruker Vertex 80v FT-IR spectrometer equipped with a DTGS detector (32 scans) with a resolution of 4 cm^{-1} on a KBr pellet. ^{1}H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. For ^{1}H NMR spectra performed using different volume ratios of CD_3OD/D_2O solutions, the samples were left for more than 12 h prior to the NMR scans and sodium 2,2,3,3-d_4-3-(trimethylsilyl)propionate (TSP) was used as the internal reference. X-ray photoelectron spectroscopy (XPS) spectra were acquired on an ESCALAB-250 spectrometer with a monochromic X-ray source (Al Kα line, 1486.6 eV) and the charging shift was corrected by the binding energy of C1s at 284.6 eV. X-ray diffraction (XRD) data were recorded on a Rigaku X-ray diffractometer using Cu Kα radiation at a wavelength of 1.542 Å. Elemental analysis was performed on a Flash EA1112 from ThermoQuest Italia S.P.A. Scanning electron microscope (SEM) images were acquired on a JEOL FESEM 6700F electron microscope, and transmission electron microscopic (TEM) images were carried out on a Hitachi H8100 electron microscope. High-resolution images were obtained with a JEOL 3010 high-resolution TEM operating at 300 kV. Dynamic light scattering (DLS) was carried out on a DAWN Enhanced Optical System (DAWN EOS, Wyatt Technology Corporation). Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204 apparatus. Zeta potential measurements were operated on a Nano-ZS instrument, model ZEN 3600 (Malvern Instruments). At least 5 measurements of each sample were carried out to check the reproducibility. TGA was performed on a Perkin-Elmer7 series thermal analysis system in a N_2 flow with a heating rate of 10 ° C min^{-1}.

Results and discussion

In contrast to the case that the complexes encapsulated with more hydrophobic surfactants can only form organized aggregates in organic solvents, to increase the solubility of the complex in aqueous solution, we selected a surfactant with dodecyls (DDDA • Br) to encapsulate POM-1 ($Na_9EuW_{10}O_{36}$) to give the SEP-1 complex, $(DDDA)_9EuW_{10}O_{36}$, as shown in Scheme 1. The complex was fully characterized by IR, elemental analysis, TGA, and ^{1}H NMR, which were in good agreement with the expected structure. Typically, as presented in Fig. 1, the chemical shifts of the protons nearest to the N atom (H_a, H_b and H_c) in SEP-1 in $CDCl_3$ move upfield noticeably, while those of the other groups (H_d, H_e) remained unchanged. The peak shifting and

broadening of these protons clearly indicates that the head groups of DDDAs combine with POM-1 electrostatically.[7e,23b] We chose a POM with nine negative charges with luminescent and catalytic properties,[16] which could be employed for further functionalization of the aggregates in subsequent investigations. Although SEP-1 is still difficult to dissolve in water directly because of its hydrophobic shell, it is amphiphilic,[8c] and is similar in this respect to amphiphilic copolymers.[17] Therefore, we dissolved the sample in a water-miscible organic solvent first, and then transferred the sample complex into aqueous solution by the addition of water and the evaporation of the organic solvent.[18] We also tried direct addition of the complex into water followed by sonication and heating. Although aggregates similar to those prepared through solution transfer were found when we analysed these solutions, the results were not typical or consistent, due to the poorer dispersion of the solid SEP-1 in aqueous solution.



Scheme 1 Schematic representation of preparation of SEP-1 complex, its aggregation, and the reversal of aggregation structure.

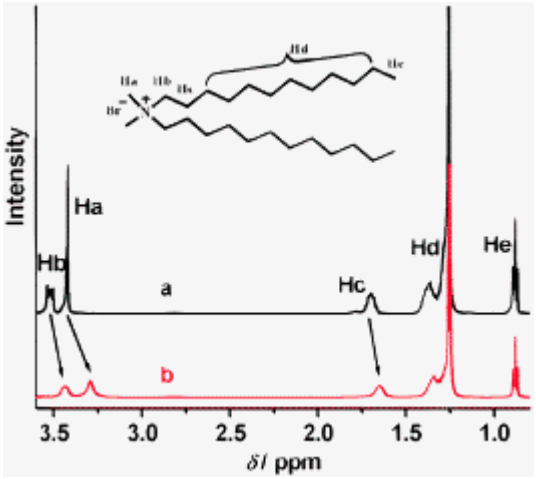


Fig. 1 ^{1}H NMR spectra of (a) pure DDDA • Br and (b) SEP-1 in $CDCl_3$.

Due to the hydrophobicity of the complex, the highest concentration is only *ca.* 1.0 mg mL^{-1} in water, and the aqueous solution displays obvious Tyndall scattering – a general feature of vesicles of this size.[19] DLS measurements indicate the aggregates have a hydrodynamic radius (R_h) centered at 58.8 nm (Fig. 2a). From repeated experiments, we find that the aggregates of SEP-1 are quite stable because both the scattering intensity and R_h change little even upon

standing at room temperature for more than five months (see Fig. S1†). SEM measurements carried out by casting the sample solution onto a silicon wafer demonstrate the good dispersion of the complex in water, and show that the aggregates have an average diameter of 85 nm (Fig. 3a). The size given by SEM is smaller than the result of DLS, but this is understandable due to the drying-induced shrinkage. Most of the aggregates are spherical, but there are some large elongated aggregates, which obviously result from the accumulation of isolated spheres during solvent evaporation.

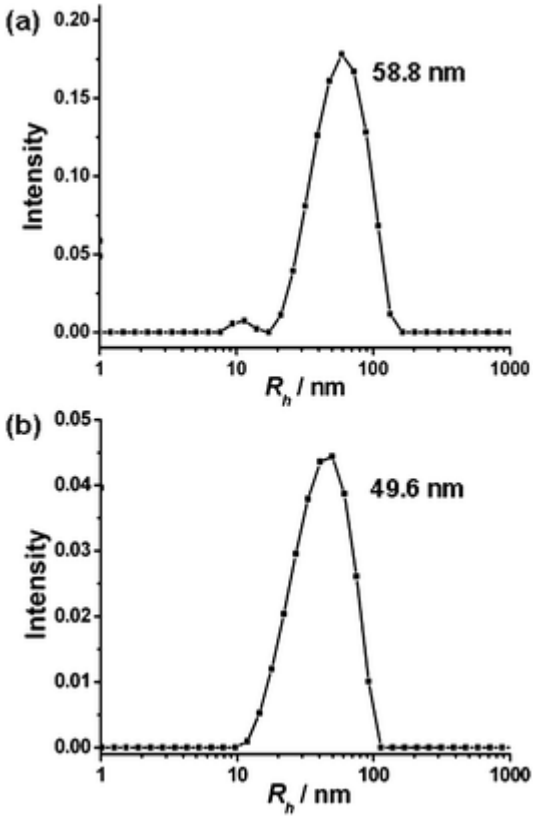


Fig. 2 DLS plots of SEP-1 in (a) 0.1 mg mL^{-1} aqueous solution and (b) 0.1 mg mL^{-1} ethanol solution.

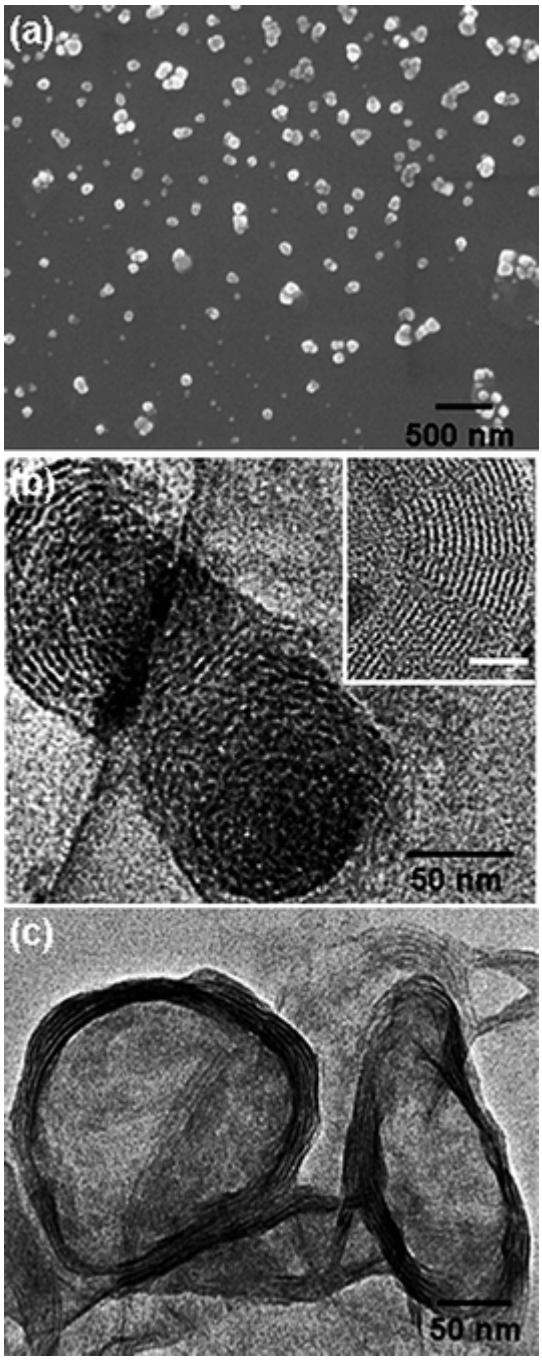


Fig. 3 (a) SEM and (b) TEM images (inset: locally amplified HRTEM; scale bar 20 nm) of SEP-1 aggregates in water; and (c) TEM image of SEP-1 in ethanol.

For conventional vesicles prepared by synthetic surfactants or lipids, the phase transition from gel to a liquid-crystalline state takes place during the heating process.[20] Here, a similar phase transition also occurs for the aggregates of SEP-1 complex in aqueous solution, as shown by the DSC curve (Fig. 4). Moreover, the calculated enthalpy change (ΔH) is about 24.20 kJ mol^{-1}, which corresponds to 1.22 kJ mol^{-1} per methylene group (CH_2) in one SEP-1 complex, in perfect agreement with the value of 1.2 kJ mol^{-1} estimated from the vesicular aggregates of dioctadecyldimethylammonium bromide, a homologue of DDDA • Br.[21] This result means that the DDDA components of SEP-1 are indeed in an ordered aggregation state and undergo a phase transition from gel to liquid-crystalline state. In addition, the transition temperature estimated from DSC curve is 12.6 ° C, close to but less than the value of 15.8 ° C for pure DDDA • Br.[20b] As confirmed in the following discussion, the decrease of phase transition

temperature is reasonable if the distortion of the bilayer structure induced by the incorporation of POMs that have similar size to DDDA is considered.

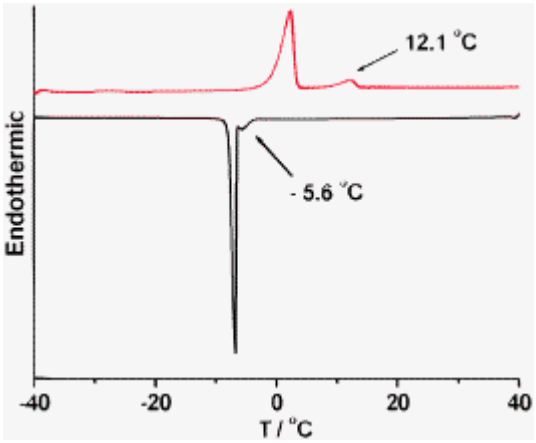


Fig. 4 DSC thermograms of SEP-1 in aqueous solution under heating (top) and cooling (bottom) runs. The distinct sharp peaks are attributable to the melting and freezing of water, respectively.

To identify the aggregated structure of SEP-1 assemblies in aqueous solution, TEM was employed by spreading the sample solution onto a copper grid covered with carbon film. Because of the high content of tungsten in the POMs, the electron beam does not easily penetrate the normal-sized spherical aggregates. Fortunately, the precise aggregation structure was observed clearly for the smaller spheres (Fig. 3b and Fig. S2†). An onion-like inner structure with a layer spacing of *ca.* 2.8 nm was found in these spherical aggregations, very similar to previous results obtained in organic solution.[10b] From the high-resolution TEM image, the multilayered structure could be ascertained authentically (Fig. 3b, inset).

XRD measurement was carried out to further confirm the vesicular structure by casting the sample solution onto a silicon wafer as we did for the SEM measurement. The multi-level diffractions also demonstrate the layered structure (Fig. 5), indicating the well-ordered aggregation. The *ca.* 2.74 nm layer spacing according to the Bragg equation is in perfect agreement with the layer thickness estimated from TEM. For the oviform POM-1, the long axis is 1.43 nm and the short axis is 0.80 nm, based on its single-crystal structure (see ESI†).[15] On the other hand, pure DDDA • Br has been proved to form vesicular structures in aqueous solution and possesses a bilayer spacing of 1.95 nm, according to our measurement (Fig. S3†) and the literature.[22] Therefore, we can propose a layered structural model for SEP-1 aggregates; that is, a DDDA bilayer and a single layer of POM-1 lying along its long axis, as concluded from the structural model of cast SEP films.[23a] Thus, the estimated layer spacing of 2.75 nm (0.80 nm + 1.95 nm) is perfectly consistent with the measured layer spacing.

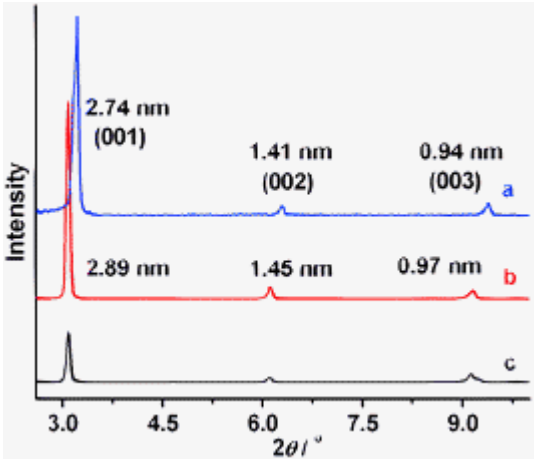


Fig. 5 X-ray diffraction patterns of dry SEP-1 films prepared through casting of an (a) aqueous, (b) chloroform and (c) ethanol solution on a silicon wafer.

However, compared with similar complexes,[10b] SEP-1 can also self-organize into onion-like vesicular aggregates with an inverse bilayer structure in organic solution. DLS reveals the aggregation in ethanol and chloroform (Fig. 2b); XRD spectra exhibit a layered structure with a slightly larger spacing (2.89 nm) (Fig. 5b and 5c), which is attributed to the weaker packing force in organic solvent than in water; TEM illustrates an evident vesicular structure (Fig. 3c and Fig. S4†). Considering the fact that the present vesicular aggregates in water were prepared from phase transfer of the vesicular aggregates from an organic solvent, extra evidence must be provided to prove the structural difference between the aggregates in water and in organic media because the two cases should have the same ideal layer spacing.

Normally, the inverse bilayer model with the POM located at the middle of the sandwich structure that exists in organic solution is thermodynamically unstable in water due to the unfavorable interfacial energy. However, owing to the compatibility and stability of SEP-1 aggregates both in the organic phase and in water, there must be a structural transformation during the change of solvents.

We employed zeta potential measurements to monitor the alteration of the surface potential of SEP-1, as normally used in colloidal systems.[24] If the real aggregated structure in water is similar to that in chloroform and ethanol, the surface potential should be zero or slightly negative based on a non-ionized surface for inverse vesicular aggregates. Interestingly, as shown in Fig. 6a, the measured potential is +48.6 mV, which is quite positive, implying that the aggregation structure in water is different from that in the organic phase. Considering the partial ionization of POM-1 from the surface of SEP-1 aggregates and the hydration in water, it is reasonable that it leaves behind a relatively positive surface of the DDDA quarternary ammonium head. In this case, the vesicular aggregates with a regular bilayer structure become more hydrophilic and keep their thermodynamic stability. We also compared the zeta potential of SEP-1 with pure DDDA • Br aqueous solution at the same molar concentration of DDDA. The smaller surface potential for the complex just matches the weak ionization and the strong interaction between DDDA and POM-1. Due to the strong hydrophobic interaction, the aggregates of the complex in water have a shorter bilayer structure, as revealed by XRD measurements (Fig. 5a).

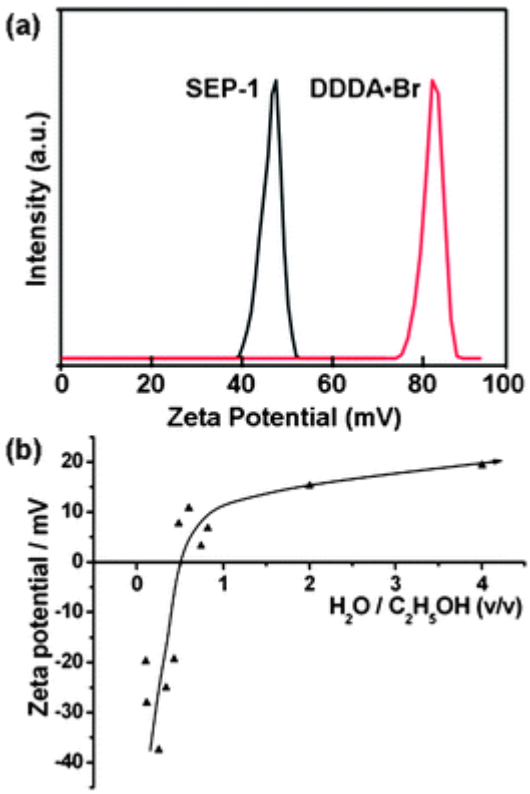


Fig. 6 (a) Zeta potential of SEP-1 and DDDA • Br in aqueous solution and (b) plot of zeta potential of SEP-1 aggregates *versus* the volume ratio of H_2O/C_2H_5OH (increasing from left to right: 0.1, 0.12, 0.25, 0.33, 0.43, 0.48, 0.60, 0.74, 0.82, 2.0, 4.0).

XPS was further used to characterize the proposed bilayer structure and the microenvironment of both components in these aggregates. In comparison with O1s appearing at 529.7 eV for pure POM-1, the O1s for SEP-1 in chloroform and ethanol is at 532.0 eV, *i.e.* an obvious shift, indicative of the change of microenvironments of POM-1 clusters (Fig. 7). This result provides an effective means of detecting the bilayer structure in water. As the SEP-1 aggregates prepared by casting an aqueous solution on a silicon wafer display two O1s peaks that are identical to those of pure POM-1 and SEP-1 in organic phases, respectively, we conclude that both bare and encapsulated POM-1s exist in the aqueous aggregates. In addition, from the comparison of O1s peak areas, we know that there are fewer bare or free POMs in the aqueous SEP-1 aggregates than the encapsulated POMs, which supports again the notion that some POM-1 clusters are exposed on the surface of the aggregates when transferring SEP-1 into water. It should be noted that only in the case of the regular bilayer structure can partial POM-1 clusters exist in an incompletely covered state while still being absorbed on the surface of DDDA bilayer, while most of POM-1s are inside the aggregates. The surface elemental ratios of the aggregates prepared from different media provide further confirmation of the surface structure. With the same casting amount, the ratios of nitrogen to tungsten atoms (N/W) and carbon to tungsten atoms (C/W) for the aggregates prepared in organic solvents and water depend on the elemental composition within the detection depth range of XPS. From the integration of peak areas in XPS spectra (Table 1), the lower values of N/W and C/W in the aggregates obtained from water than from organic solvents indicate that more bare POM-1 clusters are on the top surface of the aqueous vesicular aggregates.

Table 1 Elemental ratios in dry SEP-1 aggregates prepared from different solutions at 1.0 mg mL^{-1}

	Elemental ratio	
Solvent	N/W	C/W
$CHCl_3$	1.53	43.63
C_2H_5OH	1.27	43.63
H_2O	0.16	6.53

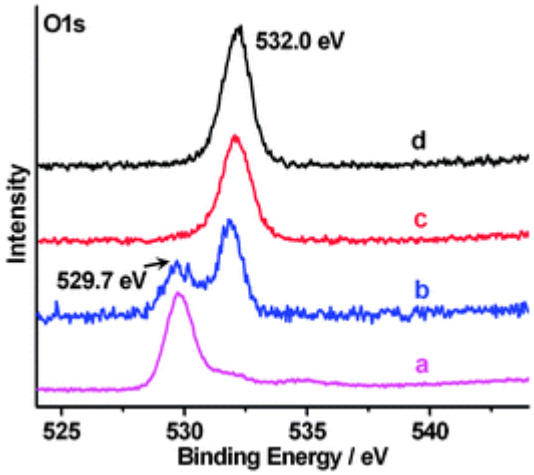


Fig. 7 XPS spectra of (a) pure POM-1 powder, and films of SEP-1 aggregates cast from (b) water, (c) ethanol and (d) chloroform solution.

This analysis supports the structural and morphological model for the aggregation of SEP-1 in aqueous solution, namely, the DDDAs adopt a regular bilayer form with POM-1 clusters covering it as the counterions, as shown in Scheme 1. Because SEP-1 exists in an inverse onion-like vesicular aggregation in organic solution, one key issue relating to the structural transformation during the dispersion of SEP-1 ethanol solution into water should be identified.

A series of ^1H NMR spectra of SEP-1 under the same concentration but in mixed deuterated solvents with different volume ratios of D_2O/CD_3OD were recorded (Fig. 8a) to examine the structural conversion process. Because the protons of methyl and methylene groups bound to the quaternary ammonium hydrophilic head are sensitive to the environment of the solution, their chemical shifts can be used as a probe to detect the alternation of aggregated structures of SEP-1. When the strong electrostatic interaction occurs between DDDA and POM-1 the chemical shifts move upfield.[23] With increasing D_2O content, the chemical shifts of $-N^+-CH_3$ and $-N^+-CH_2$ move downfield gradually, finally approaching the position for pure DDDA • Br in pure D_2O (Fig. S5†). A distinct transformation point, estimated from the plot shown in Fig. 8b, emerges at a D_2O/CD_3OD volume ratio of *ca.* 0.4, indicating that the structural transformation takes place at that point.

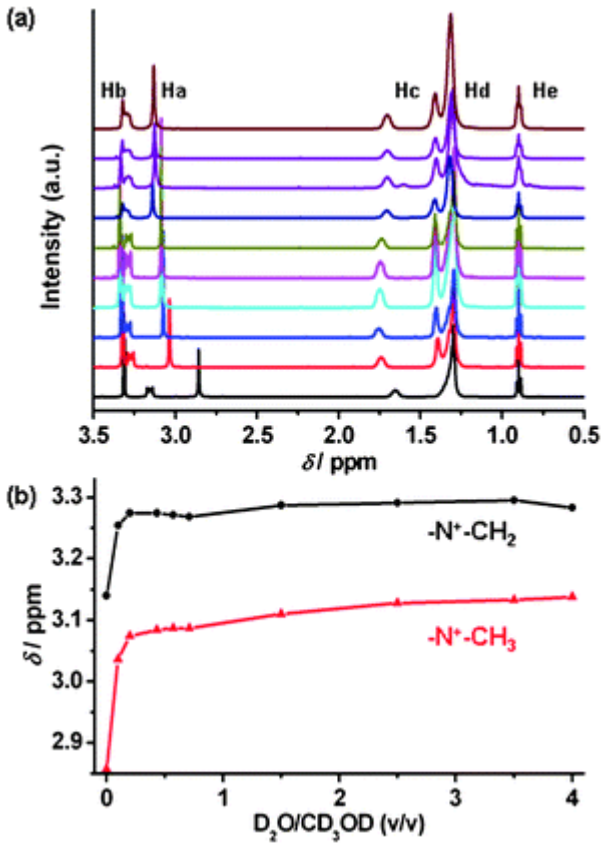


Fig. 8 (a) ^{1}H NMR spectra of SEP-1 in a mixed solvent with a D_2O/CD_3OD volume ratio of: 0, 0.1, 0.2, 0.43, 0.57, 0.71, 1.5, 2.5, 3.5, 4.0 (increasing from bottom to top), with TSP as an internal reference; (b) plots of ^{1}H chemical shifts of $-N^+-CH_2$ and $-N^+-CH_3$ *versus* the volume ratio of D_2O/CD_3OD.

The structural transformation of SEP-1 vesicular assemblies can also be observed from the zeta potential analysis by gradually increasing the volume ratio of water to ethanol, as shown in Fig. 6b. The increase of surface potential represents the change of surface chemical composition and we find that the zeta potential undergoes a quick change from zero to negative, and then passes through zero to become positive with increasing water content. The turning point obtained in the zeta potential plot *versus* the volume ratio of water/ethanol emerges at around 0.5, in accordance with the transformation point observed in the ^{1}H NMR spectra. These results prove the structural reversal of the complex aggregates at a critical solvent polarity. More interestingly, SEP-1 aggregates can be easily transferred back into the organic phase by extraction with chloroform. Because of the strong electrostatic interaction between DDDA and POM-1 components, the chemical structure and the composition of SEP-1 are retained during the transformation process, as indicated by their consistent fluorescence spectra (Fig. S6 and S7 †). Thus, after such a cycle, we again obtain the inverse vesicles of SEP-1.

Conclusion

In conclusion, we have successfully introduced an amphiphilic POM-based hybrid complex into aqueous solution. The complex, as a building block, exhibits reorganization properties and forms regular vesicular aggregates in water, in contrast to the inverse vesicular aggregates in organic phases. We believe that the hydrophobic microenvironment will make these spherical aggregates suitable carriers to perform catalytic and biological functions. In preparing the regular vesicles of SEP-1 by solvent transfer, we found a novel phenomenon, namely that there

was an structure reversal from inverse vesicles to normal onion-like vesicles with increasing water content in the solution. The turning point for the reversal between the two bilayers can be found by adjusting the ratio of water and ethanol in a controlled fashion. Significantly, this inversion process can be conveniently carried out by simply extracting the SEP-1 from water into organic phase.

Acknowledgements

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Footnote

† Electronic supplementary information (ESI) available: DLS and XRD of DDDA • Br aqueous solution, PL and additional TEM images. CCDC reference number 727463. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b912011d

Controllable vesicular structure and reversal of a surfactant-encapsulated polyoxometalate complex

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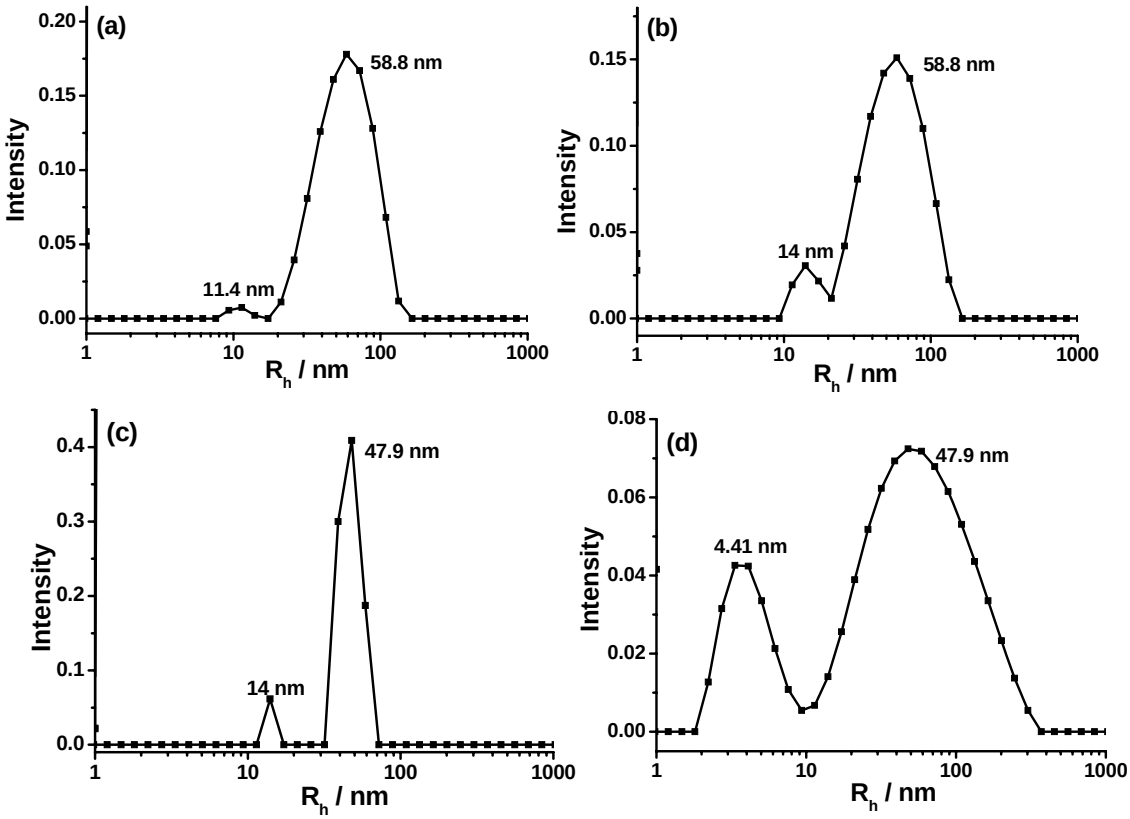
Supporting Information



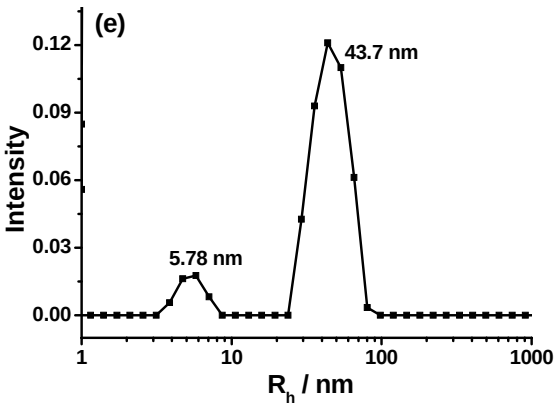


Figure S1. DLS results of SEP–1 aqueous solution with different concentrations and preparation time: (a) 0.1 mg mL^{-1}, (b) 0.1 mg mL^{-1} prepared at another day, (c) 0.1 mg mL^{-1} stored at RT for more than 5 months, (d) 0.5 mg mL^{-1}, (e) 1.0 mg mL^{-1}.

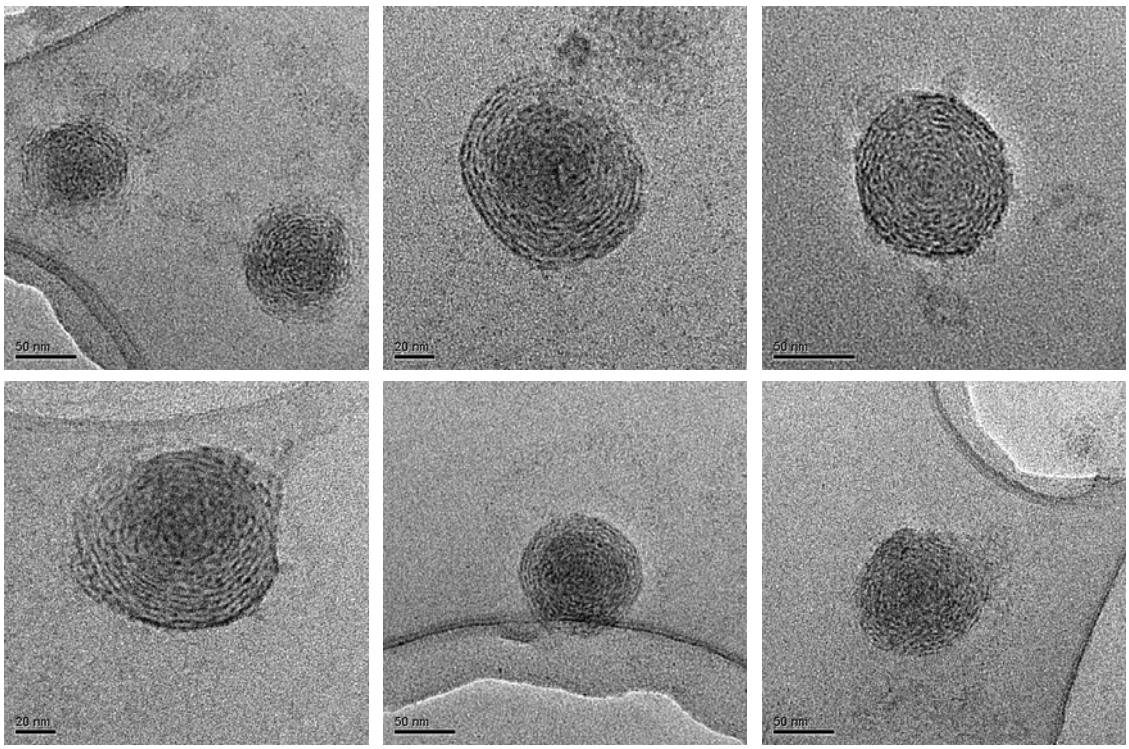


Figure S2. More TEM images of SEP–1 aggregates in aqueous solution.

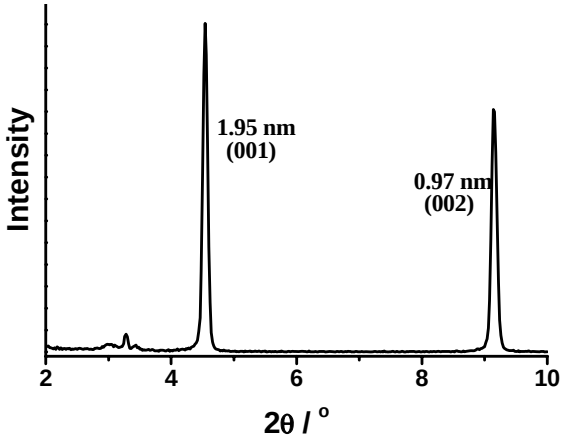


Figure S3. XRD pattern of DDDA·Br vesicle in water.

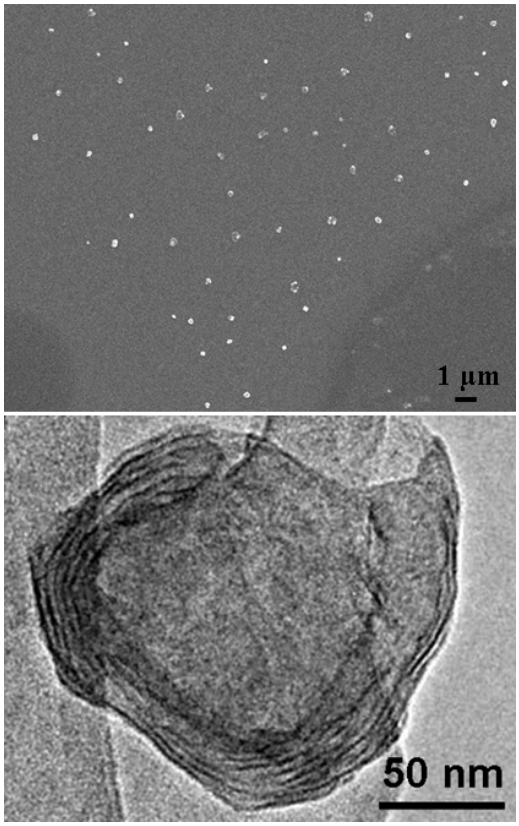


Figure S4. SEM and HRTEM image of SEP–1 in 1.0 mg mL^{-1} of ethanol solution.

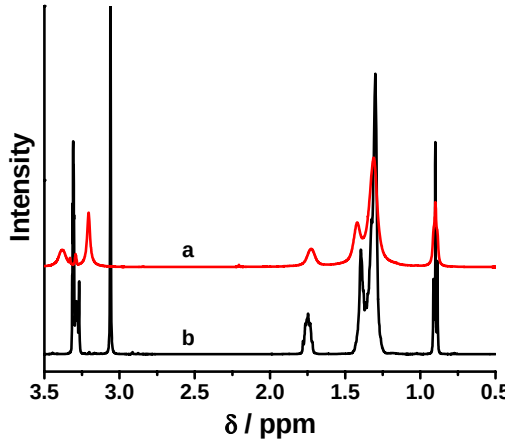


Figure S5. ^{1}H NMR spectra of DDDA·Br in (a) D_2O and (b) CD_3OD.

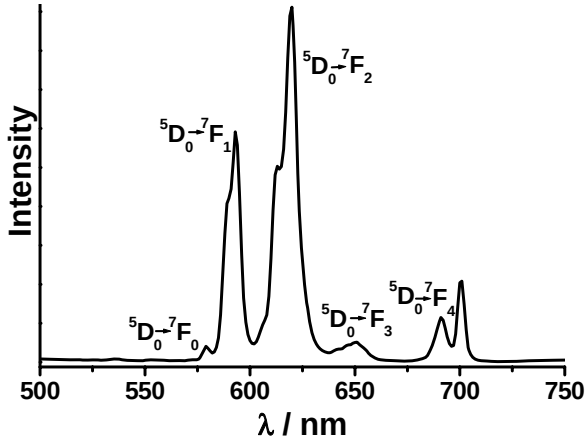


Figure S6. Fluorescent spectrum of SEP–1 aqueous solution (excited at 289 nm).

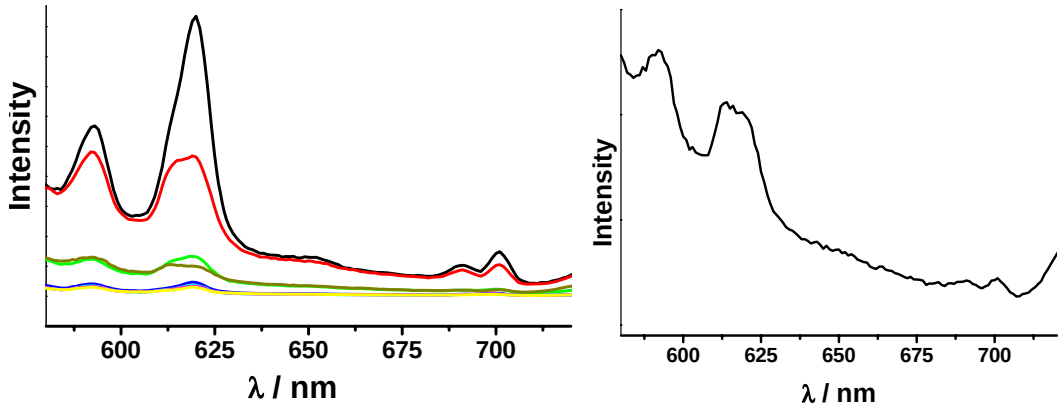


Figure S7. Fluorescent spectra of SEP–1 solution (a) from top to down are aqueous solution after different time of extracting with $CHCl_3$ and (b) $CHCl_3$ solution after extracting.