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## COMMUNICATION

# Organic/inorganic hybrids formed by polyoxometalate-based surfactants with cationic polyelectrolytes and block copolymers

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**Electrostatic self-assembly of an Anderson-based surfactant with polyelectrolytes and block copolymers lead to the formation of polyoxometalate-based polyelectrolyte-surfactant and block ionomer complexes, respectively. Furthermore, vesicular aggregates form in the solutions of the block ionomer complexes.**

Polyoxometalates (POMs) are discrete polyanionic metal-oxide clusters with a great diversity of shapes, compositions, and functions.[1] They are prepared through the connection of $\{MO_x\}$ polyhedra (usually, $M = V^{IV,V}$, $Mo^{VI}$, or $W^{VI}$) and are clearly hydrophilic. Recently, the covalent linkage of POMs with hydrophobic tails has resulted in the formation of POM-based surfactants.[2,3] Similar to the conventional surfactants, these POM-based surfactants can form Langmuir and Langmuir-Blodgett films on surfaces[2a-d] and nanosized aggregates with morphologies of micelles[2e-g] and vesicles[2h,i,3] in solution. They also demonstrate lyotropic liquid crystalline,[2e,f] emulsified and catalytic properties.[2e,g]

On the other hand, electrostatic combination of surfactants with oppositely equimolar charged polyelectrolytes leads to the formation of polyelectrolyte-surfactant complexes (PSCs). They show unique supramolecular nanostructures such as lamella, rodlike, and column and intriguing functions such as low surface energy, optoelectronic and electrochemical devices, drug and gene delivery.[4,5] To date, the investigation of water-insoluble PSCs has been concentrated on the modification of polyelectrolytes such as conventional synthetic polyelectrolytes with flexible chains or rigid rods,[4a,b,d,e] charged synthetic polypeptides[4c] and biomolecules (DNA or RNA).[5] Basically, the surfactants have only conventional charged heads, such as ammonium, pyridinium, phosphate, acetate, or sulfate ions.[4,5]

In a similar way, the complexation of block ionomers with oppositely charged surfactants results in the formation of block ionomer complexes (BICs).[6] The water-insoluble PSCs formed

by ionic segments and oppositely charged surfactants are stabilized by neutral blocks, leading to the formation of micelles and vesicles in
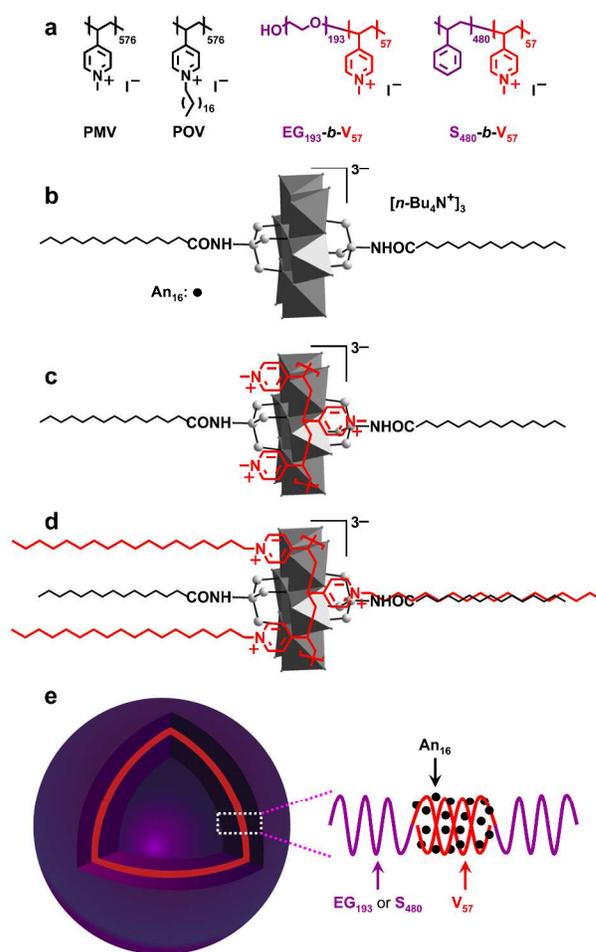
**Fig. 1** Structural formulae of polyelectrolytes (PMV and POV, a), block ionomers ($EG_{193}$-$b$-$V_{57}$ and $S_{480}$-$b$-$V_{57}$, a), and POM-based surfactant ($An_{16}$, b). Structural formulae of POM-based PSCs (PMV-$An_{16}$, c) and (POV-$An_{16}$, d). (e) Schematic drawing of vesicular nanostructures fabricated through electrostatic self-assembly of $An_{16}$ with $EG_{193}$-$b$-$V_{57}$ and $S_{480}$-$b$-$V_{57}$ in solution.

solution. These micelle-like aggregates have potential applications in the fields of drug delivery and template synthesis. These collective progresses have provided further impetus for us to investigate POM-based PSCs and BICs through the electrostatic self-assembly of POM-based surfactants with cationic polymer species.

Grafting of alkyl chains onto the both sides of Mn-Anderson clusters forms a kind of POM-based surfactants. They can form both regular and reverse vesicles in aqueous media and organic solvents, respectively. Recently, we[7] and other[8] reported the preparation of POM-based polymeric composites and their self-assembly into micelles and vesicles in solutions. Herein, we report the preparation and characterization of POM-based PSCs by combining $[n$-$Bu_4N]_3[MnMo_6O_{18}\{(OCH_2)_3CNHCO(CH_2)_{14}CH_3\}_2]$ ($An_{16}$) with poly($N$-alkyl-4-vinylpyridinium iodide) (alkyl = methyl, PMV and octadecyl, POV), respectively (Fig. 1a-d). And by the electrostatic combination of An-16 with poly(ethylene glycol-$b$-$N$-methyl-4-vinylpyridinium iodide) ($EG_{193}$-$b$-$V_{57}$) and poly(styrene-$b$-$N$-methyl-4-vinylpyridinium iodide) ($S_{480}$-$b$-$V_{57}$), the regular and reverse POM-based vesicles were achieved in both aqueous media and organic solvents, respectively (Fig. 1a and e).
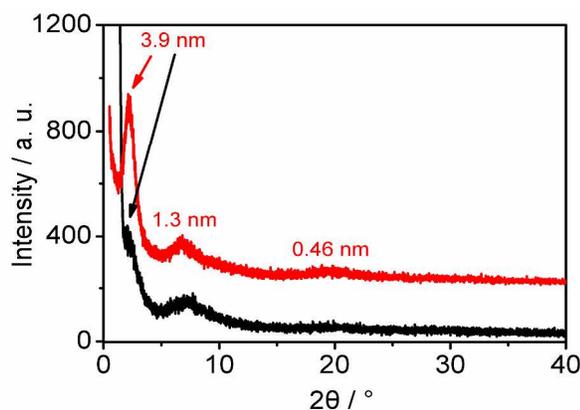


**Fig. 2** Powder XRD of PMV-$An_{16}$ (black line) and POV-$An_{16}$ (red line).

The polyelectrolyte solutions of PMV (water) and POV (tetrahydrofuran) were dropwise added into the orange solution of $An_{16}$ in an acetonitrile/water mixed solvent containing 50 v% acetonitrile with vigorous stirring, leading to orange precipitates of POM-based PSCs, PMV-$An_{16}$ and POV-$An_{16}$, respectively. The charge ratios between the POM-based surfactant and polyelectrolytes were controlled at 1:1. The constitution of the complexes was first ascertained by infrared (IR) spectra (Fig. S1). The bands characteristic of the $An_{16}$ anion appeared at 1670, 942, 922, and 666 $cm^{-1}$.[3] The bands at 1640 and 1467 $cm^{-1}$ associated with pyridinium rings were observed. These data showed the presence of both PMV/POV and $An_{16}$ in the POM-based PSCs. In contrast, one of characteristic bands for $n$-$Bu_4N^+$ at 2873 $cm^{-1}$ disappeared totally. The bands at 2924 and 2853

$cm^{-1}$ are assigned to $CH_2$ antisymmetric and symmetric stretching modes of hydrocarbon chains of both PMV-$An_{16}$ and POV-$An_{16}$. As well documented previously,[9] the frequencies of the $CH_2$ stretching bands are the diagnostic conformation of a hydrocarbon chain. The low frequencies (2918 and 2848 $cm^{-1}$) of the bands mean a highly ordered alkyl chain, while their high-energy shifts (2927 and 2856 $cm^{-1}$) are indicative of the increase in conformational disorder, i.e. gauche conformers, in the hydrocarbon chain. The fact that the $CH_2$ stretching bands appeared at 2924 and 2953 $cm^{-1}$ in the IR spectra suggests that the alkyl chains in the POM-based hybrids have a disordered conformation with many gauche conformers. The elemental analyses confirmed the ratios of 3:1 between the repeating units of polyelectrolytes and $An_{16}$ in both hybrids, consistent with their charge ratios. The thermogravimetric analysis (TGA) curves showed both PMV-$An_{16}$ and POV-$An_{16}$ were stable up to about 250 °C, which agreed well with that of $An_{16}$ (Fig. S2).[3a] Their first stages of both PMV and POM from room temperature to 250 °C corresponded to the loss of the residual water molecules (3.2 % and 3.5 %) and the calculated numbers of the water molecules were about 4 and 5, respectively. These TGA data are consistent with the results of the elemental analyses of the hybrids based on the accuracy of the measurements. All the lines of evidence showed a successful complexation of $An_{16}$ with both PMV and POV, forming POM-based PSCs, PMV-$An_{16}$ and POV-$An_{16}$, respectively.
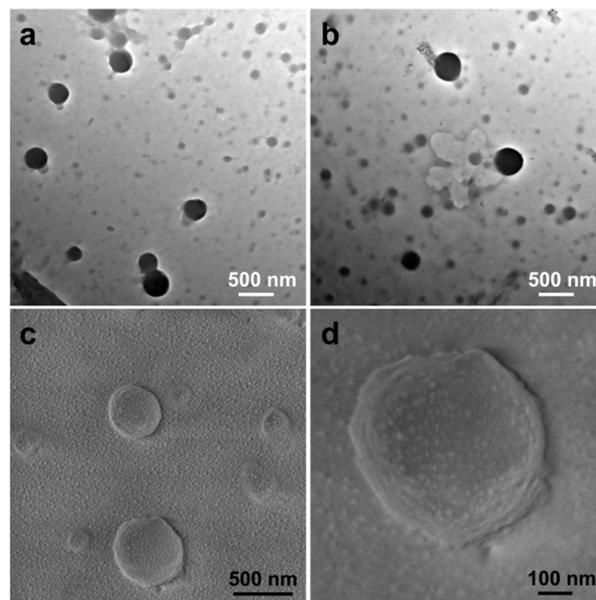


**Fig. 3** TEM (a and b) and SEM images (c and d) of BIC-1 as drop-cast from its stock solution (0.4 mM/L).

The hybrids were further characterized by using powder X-ray diffraction (XRD). The X-ray diffraction pattern of POV-$An_{16}$ (Fig. 2) shows three Bragg diffraction peaks at 2.27°, 6.82°, and 19.35°, corresponding to the spacings of 3.9, 1.3, and 0.46 nm, respectively. The spacing of 0.46 nm was assigned to the lateral packing of alkyl chains in POV-$An_{16}$, suggesting the alkyl chains had a liquid-like conformation.[4,10] This result was consistent with

the IR spectra. The former two spacings were attributed to (001) and (003) Brag peaks of a lamellar structure with a layer distance of 3.9 nm. However, we cannot observe the even-order Bragg peaks such as (002) and (004), indicating that the organization of POV-An$_{16}$ was different from the solid structures of usual PSCs. Similarly, the absence of the even-order Bragg peaks were also observed in the XRD patterns of behenic acid/CdS and behenic acid/PbS Q-particle hybrid films.[11] Such situation may be due to the presence of positional disorder along a direction normal to the bilayer. The hydrophilic {MnMo$_6$O$_{24}$} cluster of An$_{16}$ has a plate-like structure with dimensions of ~ 0.9 × 0.9 × 0.3 nm$^3$ according to the crystal structure.[3] And thus POVs are proposed to align along its plane as shown in Fig. 1d. Assuming a fully-extended conformation, the repeated unit of POV-An$_{16}$ have a length of 2.9 nm. Considering the thickness of planar {MnMo$_6$O$_{24}$} cluster with the length of the repeated unit of POV, the total layer spacing was estimated to be 5.8 nm, which was much larger than the measured value by the powder XRD. As discussed above, both the IR bands at 2924 and 2953 cm$^{-1}$ and the XRD spacing at 0.46 nm suggested that the alkyl chains of POV-An$_{16}$ were highly disordered and thus in the liquid-like state. Therefore, the much shorter spacing was due to the highly disordered alkyl chains in POV-An$_{16}$. Similarly, the shortened spacing was also observed in the temperature dependent XRD of a Langmuir-Blodgett film fabricated by a branched polymer, where the alkyl chains was in the state of conformational disorder at high temperature.[12] PMV-An$_{16}$ showed a similar XRD pattern with that of POV-An$_{16}$, suggesting a liquid-like conformation of the alkyl chains and a lamellar structure with a positional disorder (Fig. 1c and 2). The scanning electron microscopy (SEM) images revealed that the powder of POV-An$_{16}$ was rod-like aggregates, while the piece-like aggregates were observed in the case of PMV-An$_{16}$ (Fig. S3). These aggregates were in the micrometeric range.

Both PMV-An$_{16}$ and POV-An$_{16}$ were insoluble in any solvents, which was presumably due to the ionic linkage between the polyelectrolytes and An$_{16}$. Such insoluble hybrids could be used as an ionic core to fabricate micelle-like nanoassemblies, in which the ionic hybrids can be stabilized by neutral blocks, poly(ethylene glycol) and polystyrene in solution. With these results in mind, we further studied the self-assembled behaviors of the POM-based surfactant with oppositely charged block polymers, where POM-based BICs formed. To this end, we prepared the stock solutions of the EG$_{193}$-b-V$_{57}$/An$_{16}$ hybrid in water (BIC-1) and the S$_{480}$-b-V$_{57}$/An$_{16}$ hybrid in toluene (BIC-2) by mixing the block copolymers, EG$_{193}$-b-V$_{57}$ and S$_{480}$-b-V$_{57}$ with An$_{16}$ as described in the footnote part.[‡] The concentrations of cationic monomers were controlled at 0.4 mM/L. These two solutions were subjected to dynamic light scattering (DLS), TEM, and SEM measurements. The DLS plot of BIC-1 offered two modes with $D_h$s of 159 and 574 nm (Fig. S4), indicating the formation of supramolecular aggregates by the electrostatic self-assembly of EG$_{193}$-b-V$_{57}$ and An$_{16}$. In the DLS measurements, much stronger signal intensity can be obtained from large particles than small particles.[13] That is to say, a small number of large particles can even scatter incident light more strongly than

many more small particles. It was therefore estimated that the number of the supramolecular aggregate with a $D_h$ of 159 nm was much more than that with a $D_h$ of 574 nm. Such estimation was further supported by TEM and SEM images. Consequently, the stock solution of BIC-1 was further cast onto a carbon-coated copper grid for both TEM and SEM observations. The resulting TEM images revealed that vesicular nanostructures formed in the stock solution of BIC-1 with a typical feature of the higher transmission in the center than around the peripheral ring (Fig. 3a and b). The vesicular nanostructures were further confirmed by the SEM images, in which the collapsed vesicles were clearly observed (Fig. 3c and d). In these TEM and SEM images, the large size vesicles clearly coexisted with those vesicles with the much smaller size. The large vesicles occupied an average diameter of 450 nm, while the average diameter of the smaller vesicles was estimated to be 135 nm. Their occurrence probabilities were estimated to be 5% and 95%, respectively. Such coexistence and occurrence probabilities were totally consistent with the DLS results. In the DLS plot of the stock solution of BIC-2, two signals were recognized with $D_h$s of 41 and 445 nm (Fig. S4). Accordingly, the electrostatic self-assembly of S$_{480}$-b-V$_{57}$ with An$_{16}$ also resulted in the formation of supramolecular aggregates. In the corresponding SEM images, the collapsed vesicles were also observed (Fig. 4). BIC-1 and BIC-2 formed regular and reverse vesicles in water and toluene, in which the ionic cores were stabilized by poly(ethylene glycol) and polystyrene, respectively (Fig. 1e).
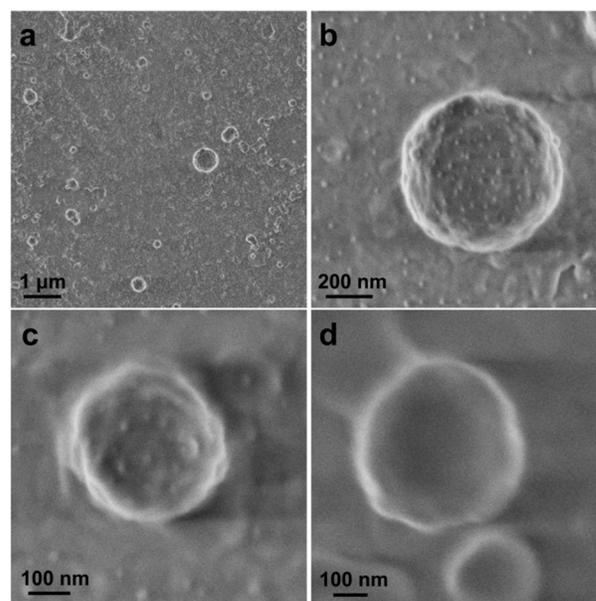


Fig. 4 SEM images of BIC-2 as drop-cast from its stock solution (0.4 mM/L).

In summary, we have prepared and characterized POM-based PSCs by combining the Anderson-based surfactant, An$_{16}$, with the cationic polyelectrolytes, PMV and POV, respectively. Furthermore, the electrostatic combination of An$_{16}$ with EG$_{193}$-b-V$_{57}$ and S$_{480}$-b-V$_{57}$ leads to the formation of POM-based BICs with the regular and reverse vesicles in aqueous media and organic solvents, respectively. The successful fabrication of the

POM-based PSCs and BICs will open a new avenue to developing novel POM-based functional hybrid materials.

## Notes and references

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‡ **Preparation of the Stock Solution of the EG$_{193}$-*b*-V$_{57}$/An$_{16}$ Hybrid.** A solution of An$_{16}$ in CH$_3$CN was obtained with a concentration of 6.68 mmol/L. EG$_{193}$-*b*-V$_{57}$ was dissolved in water with a cationic monomer concentration of 0.4 mmol/L. The An$_{16}$ solution (80 μL) was dropwise added into a 2 mL aqueous solution of EG$_{193}$-*b*-V$_{57}$ with vigorous stirring, where their final charge ratio was controlled at 1:1. The resulting mixture was further stirred for 1 h for complete electrostatic self-assembly. This stock solution was named as BIC-1.

**Preparation of the Stock Solution of the S$_{480}$-*b*-V$_{57}$/An$_{16}$ Hybrid.** Both An$_{16}$ and S$_{480}$-*b*-V$_{57}$ were respectively dissolved into *N,N*-dimethylformamide (DMF) with concentrations of 10.67 and 32 mM. Similarly, the latter concentration is for the monomeric cation in S$_{480}$-*b*-V$_{57}$. The DMF solution of An$_{16}$ (100 μL) was mixed with a 100 μL DMF solution of S$_{480}$-*b*-V$_{57}$ with vigorous stirring. Their charge ratio was also controlled at 1:3. The resulting solution (100 μL) was further injected into 4 mL toluene with vigorous stirring for 1 h for complete ionic exchange. Similarly, this stock solution was named as BIC-2 with a final concentration of 0.4 mM/L for the cationic monomer.

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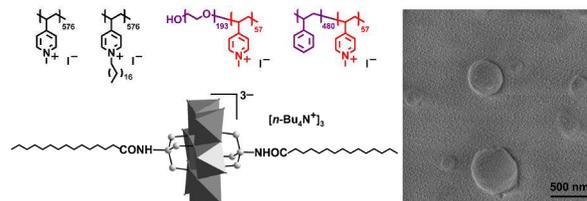
Graphical Abstract

Organic/inorganic hybrids formed by polyoxometalate-based surfactants with cationic polyelectrolytes and block copolymers

**Chunxia Tan, Nijuan Liu, Bingran Yu, Cheng Zhang, Weifeng Bu,* Xiuli Liu and Yu-Fei Song***

Polyoxometalate-based polyelectrolyte-surfactant complexes and vesicles were fabricated by electrostatic self-assembly of an Anderson-based surfactant with polyelectrolytes and block copolymers, respectively.