Self-assembly of a Surfactant-encapsulated Polyoxometalate Mediated by Coordination of Metal Ions

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The introduction of functional 4-(4-pyridylvinylene)phenyl group into surfactant encapsulated polyoxometalate complex (SEC) can form a terminal-group-modified organic/inorganic hybrid complex, SEC-1. This complex, which acts as basic building blocks, can aggregate into size controlled nanoensembles mediated by the addition and coordination of metal ions ($ZnCl_2$) in organic phase.

Organic/inorganic hybrid material based on coordination interactions is a fascinating research area and has attracted much attention because of their specific properties originating from a synergy between organic and inorganic parts.[1] Self-assembled coordination polymers from transition-metal ions and bridging ligands exhibit a number of interesting properties including redox behavior, anion exchange, gas adsorption, etc.[2] Recently, efforts have been focused on the preparation of a coordination polymer at nanoscale.[3] Considering further exploiting the potential of this field, more building blocks with functional properties (e.g. clusters) should be introduced.

Polyoxometalates (POMs) are fascinating inorganic polyanions due to their accurate structures, chemical and electronic versatility, and have been applied in the fields of catalysis, magnetism, luminescence, energy storage, and biomedicine.[4] Some recent progresses in POM surface chemistry find that positively charged surfactants can replace the counter ions of POMs, resulting in surfactant-encapsulated clusters (SECs) with a core–shell structure and a well-defined composition.[5,6] The discrete SECs are proved to be potential supramolecular building blocks for further functional assembly construction.[7] However, it is still a challenge to obtain size- and structure-stabilized SEC assemblies through a convenient way, in view of the requirement for the component miniaturization and the precise control of the organized architecture. Here, we report a new organic/inorganic hybrid nanoensembles based on coordination interaction with SEC as a supramolecular building block. A dual functional surfactant, 10-[4-(4-pyridylvinylene)phenyl]decyloxyldodecyldimethylammonium bromide ($PyC_{10}C_{12}N$) (Figure 1, it is prepared according to literature[7b,8]), with an ammonium head group capable of encapsulating the POM and a stilbazole group capable of coordinating to metal ions, was utilized to achieve our goal.

The encapsulation of $K_{15}[Eu(BW_{11}O_{39})_2]$ (POM-1) by equal molar ratio of $PyC_{10}C_{12}N$ and didodecyldimethylammonium bromide (DDDA) was carried out following a reported procedure.[5–7] In order to demonstrate the successful complexation of SEC-1, elemental analysis, ^1H NMR, thermogravimetric analysis (TGA), and IR measurements are performed, indicating one POM-1 cluster with fifteen negative charges is averagely encapsulated by six $PyC_{10}C_{12}N$ and six DDDA cations. The rest three protons have not been completely replaced due to the limited surface area of POM-1 (Figure 1).[6b,14]

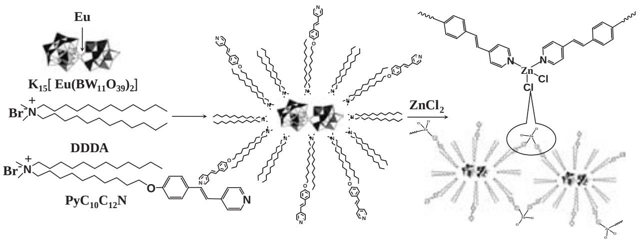

Figure 1. The schematic route for the preparation of SEC-1 and the following nanoensemble formation through $ZnCl_2$ coordination.

$ZnCl_2$ solution (CH_3OH/CH_2Cl_2, 1:1 v/v) was dropped into SEC-1 solution (CH_3OH/CH_2Cl_2, 1:1 v/v, 6.61×10^{-6} mol/L) at different molar ratio to the terminal pyridyl (Py) group of SEC-1 under ultrasonication at room temperature. The coordinating interaction between the external Py of SEC-1 and $ZnCl_2$ has been confirmed by confocal Raman spectra. The pyridyl-ring breath mode of SEC-1 is shifted from 987 to 1029 cm^{-1} after adding $ZnCl_2$, which is the indication of the coordination interaction.[9a] In addition, two bands at 1603 and 1587 cm^{-1} due to in-plane pyridyl-ring stretching modes turn into a single band at 1595 cm^{-1}.[9] The coordination interaction can be further proved by the white precipitates produced by mixing concentrated $ZnCl_2$ and SEC-1 solution.

The formation of the coordinated polymer was characterized by UV–vis spectra, dynamic light scattering (DLS) and TEM. Figure 2a shows the UV–vis spectral changes when $ZnCl_2$ is gradually added to the SEC-1 solution. As the absorption bands of POM-1 locate below 300 nm,[10] the band at 328 nm is assigned to the absorption of stilbazole group, which can be further confirmed by comparing it with the spectrum of neat $PyC_{10}C_{12}N$ surfactant. This band position is independent on the concentration of pure SEC-1 solution, indicating no obvious π–π interac-

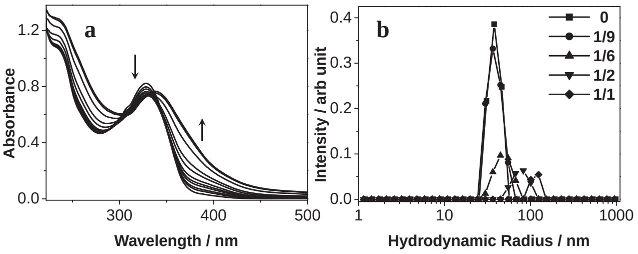

Figure 2. (a) The UV–vis spectra of the SEC-1 solution before and after the addition of different amount of $ZnCl_2$. (b) DLS plots of the R_h of the SEC-1 nanoensembles formed at different molar ratio of $ZnCl_2$/Py.

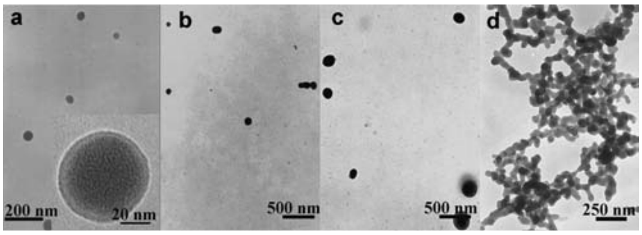

Figure 3. TEM images of SEC-1 nanoensembles formed at different molar ratio of $ZnCl_2$/Py: (a) 1/6, (b) 1/2, and (c) 1/1. Inset of (a): high magnification TEM image of a single SEC-1 nanosphere. (d) TEM images of the SEC-1 nanoensembles formed at $ZnCl_2$/Py molar ratio of 1/6, while the concentration of SEC-1 is increased to 2-fold.

tion between stilbazole groups. After adding $ZnCl_2$, the changes in the absorption spectra (Figure 2a) can be ascribed to the coordination interaction between pyridyl group and $ZnCl_2$[11] along with the light scattering effect as a consequence of the zinc-directed assembling of many hundreds of small SEC-1 clusters.[12] Resembling the fact that some SECs form vesicles in chloroform solution,[7a,13] pure SEC-1 also exists in the aggregated state with a hydrodynamic radius (R_h) of about 30 nm. The introduction of small amount of $ZnCl_2$ ($ZnCl_2$/Py in 1/9) shows no obvious influence. As can be seen from Figure 2b, however, the scattered intensity of the aggregate decrease remarkably whereas the size of the aggregate changes little when the molar ratio reaches 1/6. The quick decreasing of the intensity should be derived from the solidification of the nanoensembles propelled by zinc coordination because the number (proportional to the scattered intensity[13b]) of solid nanoensembles is less than that of hollow vesicles when they exhibit similar R_h.

Further TEM study on the nanoensembles prepared under different conditions illustrates that, at SEC-1 concentration of 6.61×10^{-6} mol/L and $ZnCl_2$/Py molar ratio of 1/6, well dispersed nanospheres with an average size of 65 nm, which can distribute over a large area, were observed (Figure 3a). Below this ratio, we only observe featureless structures. High magnification TEM image (Figure 3a inset) indicates that the nanosphere is composed of many evenly dispersed individual SEC-1s and the diameter of one SEC-1 is estimated to be 3 nm (including POM-1 diameter of 1 nm and double surfactant length of 2 nm).[6b] Increasing $ZnCl_2$/Py molar ratio from 1/6 to 1/1, nanospheres with larger mean diameter were observed (Figures 3b and 3c). Furthermore, we studied the nanospheres prepared at different SEC-1 concentration while $ZnCl_2$/Py molar ratio is held constant at 1/6. 2-Fold concentration gave product containing closely packed nanoparticles (Figure 3d). Further increasing the concentration to 4-fold or higher, white precipitate was produced. In addition, because varying the molar ratio of $PyC_{10}C_{12}N$/DDDA, the species of POM and metal ions will influence the number of the coordination sites, the shape and size of the basic building block and the coordination strength, respectively, the size and shape of the nanoensembles will also be influenced accordingly.[1c]

In contrast to the interaction between SEC-1 and zinc ions, when $PyC_{10}C_{12}N$ was replaced by surfactant without coordination group under encapsulation to POM-1 such as only DDDA, no nanospheres were observed after the addition of $ZnCl_2$. Moreover, mixing concentrated DDDA encapsulated POM-1 and $ZnCl_2$ solution cannot produce precipitate as well. These results further demonstrate that the formation of such nanospheres is due to the coordination-induced assembly from $PyC_{10}C_{12}N$ and $ZnCl_2$. A plausible formation process is briefly presented as follows: When SEC-1s and $ZnCl_2$ are mixed together, two Py groups from two different SEC-1s can coordinate to one Zn^{2+}, resulting in zinc-bridged structure, and the other Py groups contained in the as-formed structure can further capture other Zn^{2+} by coordination interactions along different directions and nanoensembles were finally formed.

In summary, we demonstrated that SEC can be used as a supramolecular building block to fabricate organic/inorganic nanoensembles based on coordination interaction with properly selected dual functional surfactant. This approach may be extended to the preparation of the hybrid with other metal ions and with other clusters. As a novel system in the inorganic/organic hybrid nanomaterial, it may exhibit new properties that arise from the synergy between each component, e.g. luminescence, which is currently under investigation.

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