

A Case of Adaptive Self-Assembly

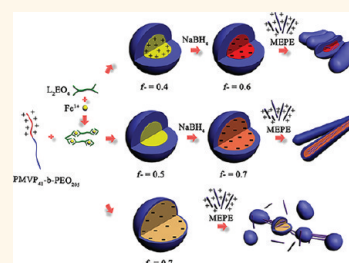
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Metal coordination polymers represent a class of fascinating supramolecular structures that features both metal and polymeric properties.^{1,2} Since the formation of this type of structure can be realized upon simple mixing of one solution containing metal ions and another containing bis or poly ligands, it allows facile fabrication of polymers of various types and structures containing metal elements, without complicated polymer synthesis procedures.^{3,4} The presence of coordination bonds renders these systems reversible and responsive to appropriate stimuli,⁵ making them suitable for fabrication of smart materials.^{6–8} For instance, Rowan *et al.* showed that self-healing materials can be obtained by casting a film from a coordination polymer solution;^{6,7} upon choosing proper ligands and metal ions, the coordination polymers may also display fluorescent properties.^{4,9} At higher concentrations, these coordination polymers may easily form hydrogels with flow and gelling behavior that respond to temperature changes.^{10,11}

Apart from gels and films obtained from pure “coordination polymers”, co-assembly of these species with other components is also an attractive way to formulate materials that possess the advantages of coordination polymers. Kurth *et al.* found that the coordination polymer formed by Fe²⁺ and bis-terpyridine ligands (so-called metallosupramolecular coordination polyelectrolytes, MEPE) may co-assemble with amphiphilic dialkyl phosphoric acid esters to form thin films at the air/water interface,¹² as well as liquid crystalline structures¹³ in solution that show magnetic properties. More interestingly, the co-assembled films and liquid crystals show a spin crossover phenomenon upon raising the temperature, which is caused by distortion of the coordinating field^{12–14} induced by a phase transition in the coat of dialkyl phosphoric acid esters. These results demonstrate that co-assembly

ABSTRACT We report in this paper direct observation of redox-induced uptake of a charged species in micelles with a complex coacervate core, using a system consisting of negatively charged iron-coordination polymers and positively charged-*b*-neutral block co-polyelectrolytes. Neutral, charge-balanced micelles are first prepared by stoichiometric



mixing of the oppositely charged components. Upon a redox stimulus, the micelles develop excess charges, which (as proposed in our previous work) most likely lead to sequestration of oppositely charged species, as the charge balance has to be restored. In this work we verify this prediction by using a rigid, rod-like iron coordination polymer, namely, the positively charged MEPE, as the species to be taken up. After uptake of this rigid cargo, the morphology of the micelles was found to transform from spheres to banana-shaped bundles and fibers, which clearly indicate the uptake of MEPE in the micellar core. Our result proves that the redox stimulus indeed induces excess charges in the core, which forces the self-assembled particles to change both composition and shape. As an interesting example of “adaptive self-assembly”, our findings also pave the way to novel redox-triggered uptake and release systems.

KEYWORDS: electrostatic micelles · uptake · coordination polymers · redox

of coordination polymers is indeed a way to fabricate interesting functional materials.

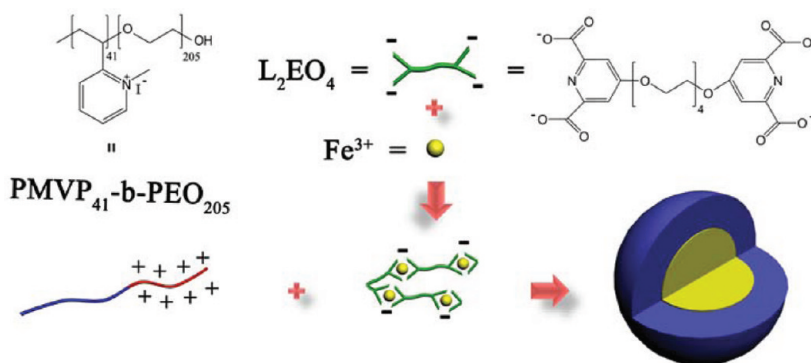
Since the coordination center of a coordination polymer normally possesses charges, it is easy to further co-assemble the coordination polymers with other components *via* electrostatic interaction. Simple methods are to fabricate thin films *via* the layer-by-layer technique^{15,16} or to form complex coacervate core micelles,¹⁷ as illustrated in Scheme 1 (C3 micelles, C3Ms; or polyion complex micelles, PIC). We recently demonstrated that upon formation of C3Ms, coordination polymers are clearly taken up in the micellar core, as they lead to high electron densities in the core, which allow direct observation of the micelles under transmission electron microscopy (TEM) without any staining.^{18–20} More interestingly, the micelles may display different functionalities, such as fluorescence,²¹

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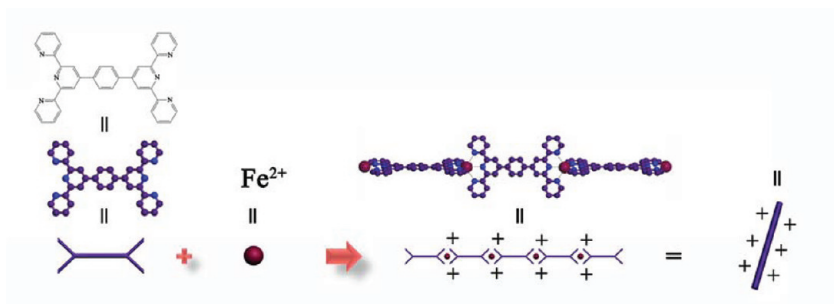
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Scheme 1. Preparation of Fe(III) Micelles



Scheme 2. Preparation of MEPE

magnetic resonance imaging (MRI) contrast,²² and redox-responsive properties²² with appropriate metal ions. Specifically, the redox responsiveness is no doubt very attractive since it allows fabrication of smart materials. Because the charge density of every coordination center changes when it undergoes a redox reaction, the originally charge-balanced micelles will develop a net charge (in the form of a change in the number of mobile countercharges in the core) so that they can take up oppositely charged species from their neighborhood. We have proposed this hypothesis in our previous work²² without direct experimental proof, since the system that we studied was subjected to two major limitations: (1) the small size of the micellar core (10–15 nm)¹⁷ leads to the fact that the “cargo” normally carried in the core of this system are molecules that can hardly be observed under TEM due to the high electron contrast of the micellar core; (2) spectroscopy, such as UV–vis and fluorescence, is also not suited to characterize the *in situ* condition after uptake, since strong dilution is needed to attain the proper concentration for measurement, and this may trigger disassembling of the micelles. We therefore attempted to find an alternative “payload”, such that it would trigger changes of the micelles that can be directly visualized under TEM, in order to verify the uptake process. The rigid MEPE coordination polymer frequently used by Kurth *et al.*, which is assembled from Fe²⁺ and bis-terpyridine ligands (demonstrated in Scheme 2), would seem to fulfill this requirement, since this species forms

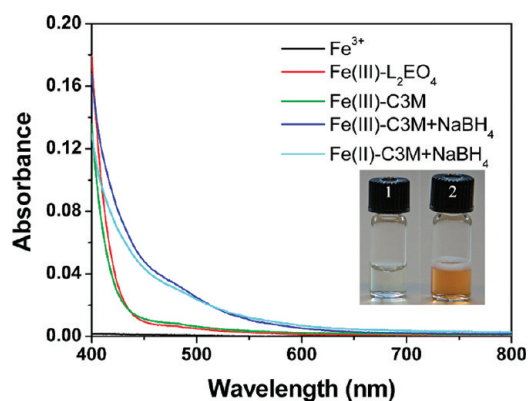


Figure 1. UV–vis spectra of Fe(III)-C3Ms before and after reduction with NaBH₄. For comparison, the spectra of Fe³⁺ ions, Fe(III)–L₂EO₄ coordination complexes, and the freshly prepared Fe(II)-C3Ms were also provided. The insets demonstrate the macroscopic feature of the Fe(III)-C3Ms solution (1) and reduced Fe(III)-C3Ms (2) solution, respectively.

relatively stable rod-like structures.^{23,24} Upon being taken up into the micelles, they might alter the shape of the micellar core, which may be unambiguously detected with TEM, thereby providing direct experimental proof that uptake can indeed occur in redox-responsive micelles.

RESULTS AND DISCUSSION

Characterization of the Responsiveness of Iron Micelles to Reduction. As reported in previous literature, coordination occurs immediately upon mixing Fe³⁺ and L₂EO₄

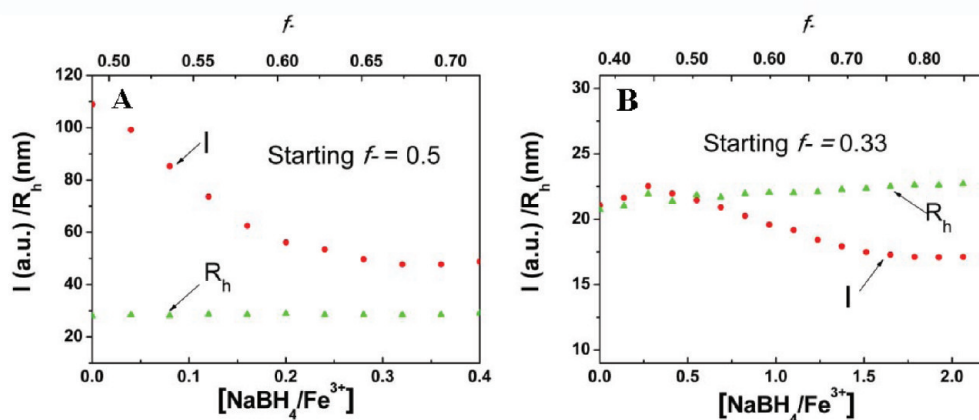


Figure 2. Variation of the scattered light intensity and the hydrodynamic radii, R_h , upon addition of NaBH_4 to the Fe(III)-C3Ms.

in aqueous solution.²² The coordination center is negatively charged, which allows electrostatic attraction with the positively charged PMVP₄₁–PEO₂₀₄. As a result, micelles are formed at charge-balanced mixing ratio, that is, at a charge fraction of $f^- = 0.5$. The solution of Fe(III) micelles is yellowish and shows weak absorbance in the 400–800 nm range, as illustrated in Figure 1. However, upon reduction of Fe^{3+} by NaBH_4 , the system immediately turned reddish, while a large amount of bubbles was also produced. The reddish color is similar to that of freshly prepared Fe^{2+} micelles, suggesting that transformation from Fe^{3+} to Fe^{2+} occurred. This was also verified by the fact that the UV–vis spectra of the reduced Fe(III)-C3Ms and that of the Fe(II) micelles (in the presence of NaBH_4 as background) were similar (Figure 1).

The reduction of Fe(III)-C3Ms was also reflected in the change of scattering intensity. As demonstrated in Figure 2A, the scattering intensity of the charge-balanced micellar system decreases as the reduction proceeds. Since the reduced intensity is proportional to the product of CM , where C is the weight concentration of the micelles in kg/m^3 that is proportional to the aggregation number and M is the mass of one micelle. This suggests either a mass loss from the micelles for constant concentration of micelles or a decrease in micellar concentrations for constant aggregation number. Although the dynamic light scattering results demonstrates that the average hydrodynamic radii, R_h , of the micelles remained nearly unchanged, the polydispersity of the micelles increased. This confirms that loss of material from the micelle cores occurred.²³ Since the net charge at every coordinating center increases from -1 to -2 upon reduction, the negative charges in the micellar core should be in excess by $1/3$ at fixed composition. This must result in repulsive forces in the micelles, causing material to be expelled from the core. This, then, may explain why the scattering intensity of the micelles decreases.

The decrease of the electron contrast of the core has been observed by TEM. As can be seen in Figure S1,

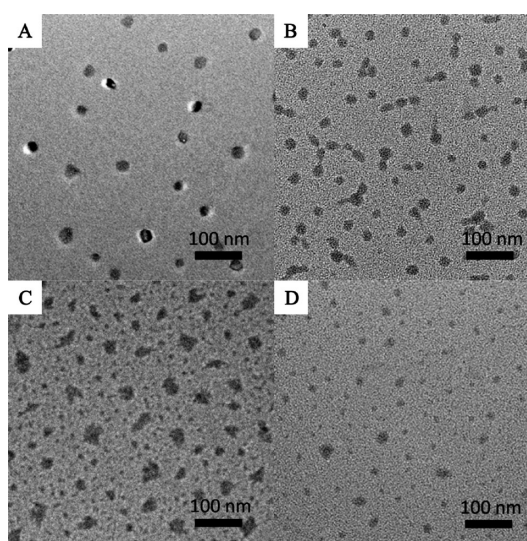


Figure 3. Fe(III) micelles at different situations: (A) $f^- = 0.50$; (B) $f^- = 0.60$; (C) $f^- = 0.70$; (D) $f^- = 0.40$.

after reduction the size of the micellar core becomes more polydisperse, and the contrast of the core has decreased. This should not be surprising, as the presence of excess charges disfavors electrostatic micelle formation due to the formation of water-soluble coacervate complexes.²⁶ As demonstrated in Figure 3B, C, and D, both the shape and the contrast of the micelles formed at $f^- = 0.40$, 0.60 , and 0.70 are not as well-defined as that at $f^- = 0.50$ in Figure 3A.

Reduction of the micelles also triggers a decrease of the zeta potential. Before reduction, the $f^- = 0.5$ micelles have a vanishingly small zeta potential, consistent with the charge-balanced nature of the micelles. However, the zeta potential of the micelles decreases to around -2 mV after reduction. Although this is a very small change, it provides proof for the appearance of excess negative charges. As analyzed in the first section, one expects a negative charge excess of about $1/3$; that is, after reduction of the original $f^- = 0.50$ Fe(III) micellar system, Fe(II) micelles will be

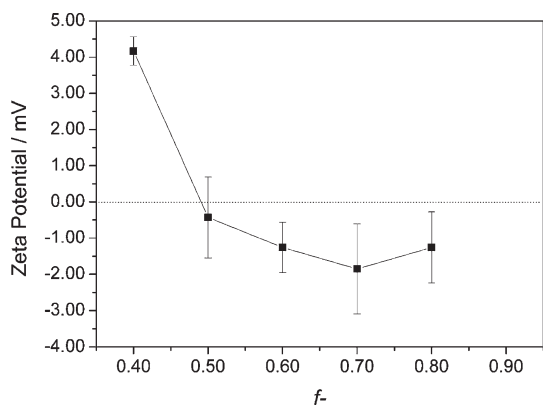


Figure 4. Variation of zeta potentials of the micelles with variation of the charge ratio.

obtained with roughly $f^- = 0.67$. The fact that one does not observe a significant negative zeta potential is because of the presence of a thick PEO corona outside the micellar core, which would bury most of the mobile countercharges. The negative charges are mainly concentrated on the micellar core, and the concentration of countercharges decays from there according to the Debye screening length given by the following equation at room temperature (25 °C):

$$\kappa^{-1} \text{ (nm)} = \frac{0.304}{\sqrt{I}}$$

where κ^{-1} is expressed in nanometers (nm) and I is the ionic strength expressed in molar concentration (M or mol/L, further discussion of I refers to Experimental Section). In our micellar system, the micellization and coordination processes release altogether 1 mM 1:1 type electrolyte, giving a Debye length of 4.8 nm. Since the thickness of the corona is around 10 nm,¹⁷ substantial screening of the negative charge occurs within the corona, so that the remaining fraction of mobile counterions and the corresponding zeta potential become rather low.¹⁹ As demonstrated in Figure 4, the observed variation of the zeta potential of the micelles is qualitatively consistent with the shift in the charge fraction, which verifies that the excess of negative charges indeed occurs as the charge composition deviates from $f^- = 0.50$.

Uptake of MEPE Using Negatively Charged Micelles. The above results suggest that reduction indeed causes an excess of negative charges on the micellar core. Therefore, it can be expected that extra positively charged species can be sequestered into the micellar core owing to a tendency to restore the charge balance. Considering the size of the micellar core, positive species that would “fit” there are molecules or particles of a few nanometers. However, it is difficult to “see” their uptake in the micellar core. As stated in the first section, in order to verify that the sequestered species is indeed in the micellar core, it is important to be able to distinguish it from the species that are already

present. Hence, special selection of “cargo” has to be made. For this reason, MEPE, which is a rigid supramolecular polymer connected by coordination bonds (see Scheme 2), was chosen. Since it is positively charged, MEPE is expected to be easily sequestered by the micellar core, and because of its rigidity, MEPE is also expected to change the shape of the core considerably.

We have prepared the MEPE according to literature methods²⁴ and further examined its morphology by TEM. Contrary to expectation, we did not see the regular rod-like structures as reported in the literature; instead, some irregular nanometer-sized patches, short rods, and dots were observed, as demonstrated in Figure 5A. We attribute this phenomenon to the poor solubility of MEPE in water (10% methanol solution). To make sure no precipitates were involved in our next experiments, the concentration of the MEPE supernatants was carefully determined by titration with an oppositely charged polyelectrolyte (polystyrene sulfonate, PSS) and used in the following experiments. First of all, uptake of MEPE was checked in the directly prepared $f^- = 0.60$ C3Ms. It can be clearly observed in Figure 2B that some of the micelles formed in the sample at $f^- = 0.60$ have tails, and the contrast is weaker than in the $f^- = 0.5$ system. However, upon mixing with MEPE, the contrast increases considerably and banana-bundle-like micelles were formed (Figure 5B). The variation of the micellar shape is attributed to the sequestering of MEPE in the micellar core. If the negative charge fraction is increased even further, a different situation arises. As shown in Figure 5C, when $f^- = 0.70$ micelles are used as a starting configuration, one observes formation of fiber-like structures upon sequestering MEPE. A bird's-eye view of the fiber-like structures can be found in Figure S2.

Considering that the electrostatic micelles in our study are rather labile, it was expected that exchange of core materials with the bulk solution occurs any way regardless of the starting f^- for micelles. To clarify that the variation of the micellar morphology was indeed induced by the uptake of MEPE, instead of by the exchange of core materials with the bulk solution, we also examined the micellar morphology of $f^- = 0.5$ micelles in the presence of MEPE. We found no considerable change of the micelle structures up to a MEPE concentration of 1/3 of the core materials, which is a similar situation to reduction-triggered excess of charges for the micelles (refer to Figure S3 in the Supporting Information). This suggests that variation of the negatively charged micellar morphology in the presence of MEPE is indeed caused by sequestering of MEPE in the core.

Reduction-Triggered Sequestering of MEPE. The aforementioned experiments suggest that MEPE may be sequestered by negatively charged micellar systems. This encouraged us to carry out reduction-triggered uptake of MEPE into micelles. After addition of NaBH_4

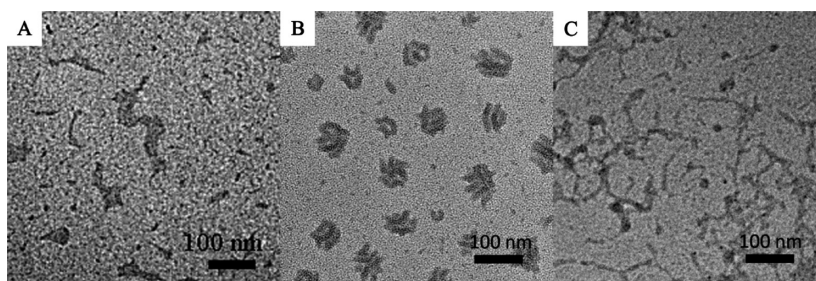


Figure 5. TEM image of (A) MEPE; (B) $f^- = 0.60$ Fe(III)-C3Ms + MEPE; (C) $f^- = 0.70$ Fe(III)-C3Ms + MEPE.

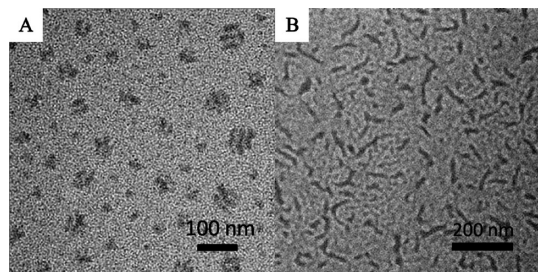
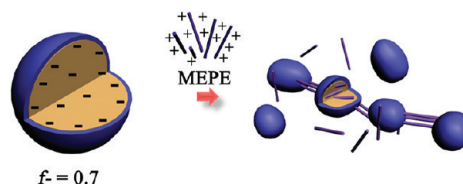


Figure 6. Uptake of MEPE using reduced Fe(III) micelles; original $f^- = 0.40$; $f^- = 0.50$. After reduction, the f^- shifts to 0.57 and 0.67, respectively.

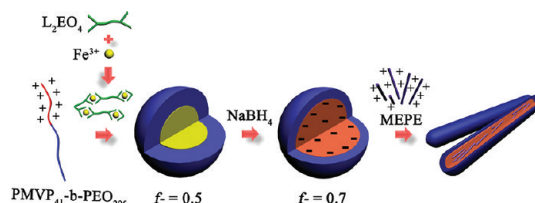
to a Fe(III)-C3Ms system prepared at $f^- = 0.4$, MEPE was added stoichiometrically to the system. Indeed, banana-bundle-like micelles were observed again (Figure 6A). The pattern is very similar to that obtained by directly mixing $f^- = 0.60$ Fe(III)-C3Ms with MEPE, suggesting that reduction-triggered uptake of MEPE indeed occurred. Theoretically, the reduction induces an increase of f^- from 0.40 for the original Fe(III)-C3Ms to 0.57 for the resultant Fe(II)-C3Ms. This means that the reduction has produced a shift in charge fraction to approximately $f^- = 0.60$ so that the reduced system indeed has a similar charge fraction to that in the directly prepared $f^- = 0.60$ Fe(III)-C3Ms. This also suggests that uptake of MEPE occurs regardless of the valence of the coordinated iron ions.

Reduction triggered uptake of MEPE was also tested in Fe(III)-C3Ms at other negative charge fractions. It is interesting to find that if we started from $f^- = 0.50$ Fe(III)-C3Ms, where reduction is expected to lead to Fe(II) micelles with $f^- = 0.67$, the resulting micellar morphology (Figure 6B) is more regular than that obtained by directly mixing $f^- = 0.70$ Fe(III)-C3Ms with MEPE (Figure 5C). This suggests that the negative charges in the reduced systems are more confined in the micellar core.

The mechanism of the significant topology variations can be attributed to the charge distribution in the micellar core. If the negative charges were obtained by directly mixing excess Fe(III)-L₂EO₄ with PMVP₄₁-PEO₂₀₄, the charges will be more diffuse in the micellar structures and not stick firmly to the core. This was verified by the zeta potential measurements (Figure 4), which suggests that some Fe(III)-L₂EO₄ is located on

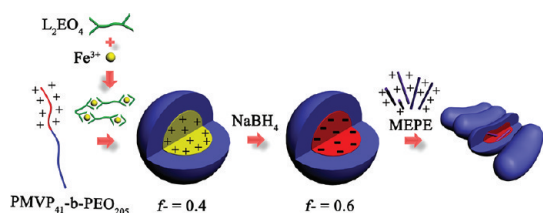


Scheme 3. Illustration of Fibril Formation by Directly Mixing $f^- = 0.7$ Fe(III)-C3Ms with MEPE



Scheme 4. Illustration of the Deformation of Original $f^- = 0.5$ Fe(III)-C3Ms upon Reduction-Triggered Uptake of MEPE

the surface of the micellar corona, allowing a small negative potential. In this case, the positively charged MEPE will adhere to the surface of the charged micelles and link them to fibrils, as illustrated in Scheme 3. In contrast, if the excess negative charges were achieved by reduction of the originally charge-neutral micelles, the charges might be well-confined in the micellar core owing to the existing entanglement with PMVP₄₁-PEO₂₀. In the latter case, MEPEs may be taken into the core, which leads to elongation of the core, as demonstrated in Scheme 4. As to the formation of banana-like structures upon uptake of MEPE by Fe(III)-C3Ms with f^- around 0.6, the small quantity of the excess in negative charges enables an easier entrapment of them in the core. This, in turn, may take up only a comparably small amount of oppositely charged MEPE, so that the deformation of the micelles is not as significant as that in higher f^- systems. The micelles may then take the morphology of the cluster of a few short rigid segments of MEPEs, which looks like banana bundles, as demonstrated in Scheme 5. So far, we have mapped out a coherent figure for the Fe(III)-C3Ms: they may indeed develop excess charges upon redox stimuli; these excess charges are less diffusing and better confined in the core when compared with those in the micelles of



Scheme 5. Illustration of Redox-Triggered Uptake of MEPE in Electrostatic Micelles Based on Fe(III)-Metallosupramolecules

direct preparation. This suggests that by applying a redox stimulus, one can indeed get a smart loading system.

SUMMARY

We have shown in this paper the direct observation of redox reaction-induced uptake of oppositely charged species using charged electrostatic micelles based on coordination polymers. The use of a rigid

“cargo”, namely, MEPE, causes deformation of the micelles after uptake, which can be directly observed under TEM. We have shown that the uptake process could occur regardless of the methods utilized to introduce excess charges, *i.e.*, whether the excess negative charges were acquainted by reduction or by directly mixing iron coordination polymer in excess. It is also noteworthy that the uptake of positively charged MEPE occurs in both cases with minor differences: in the reduced systems, the negative charges are confined more closely in the micellar core than in the directly mixed ones. Our results not only provide direct proof for the tendency of micellar systems with excess charges to take up oppositely charged species but also indicate that the electrostatic micelles in our study have potential applications in redox-gated uptake and release systems.

EXPERIMENTAL SECTION

Materials. The bis-ligand L_2EO_4 and diblock polyelectrolyte poly(*N*-methyl-2-vinylpyridinium iodide)-*b*-poly(ethylene oxide) (PMVP₄₁-*b*-PEO₂₀₅, $M_w = 18.5$ K, PDI = 1.05, about 90% quaternized) used in this work were prepared according to previously reported procedures.¹⁷ Bis-terpyridine ligand 1,4-bis(2,2':6',2''-terpyridin-4'-yl)benzene came from Alfa Aesar Chemical with a purity of 97%. Other chemicals (FeCl₂·6H₂O and NaBH₄, Beijing Chemicals Company, AR) were used without further purification.

Methods. *Sample Preparation. Preparation of Fe(III) Micelles (Scheme 1).* Stock solutions of PMVP₄₁-*b*-PEO₂₀₅ (abbreviated as BP in this work), L_2EO_4 , and FeCl₃ were prepared at appropriate concentrations using ultrapure water. To prepare the Fe(III) coordination complexes, 5 mM L_2EO_4 solution and freshly prepared 50 mM FeCl₃ (or FeCl₂) solution were mixed at equal molar ratio. The coordination complex solutions were then added in stoichiometric amounts to a PMVP₄₁-*b*-PEO₂₀₅ aqueous solution ([+] = 1 mM) to reach charge-balanced mixing. Here, [+] stands for the molar concentration of positive charges carried by the polyelectrolyte PMVP₄₁-*b*-PEO₂₀₅. The negative charge fraction or mixing ratio is defined as $f^- = [-]/([+] + [-])$, with [-] being the molar concentration of the negative charges of the Fe(III) coordination polymer.

Preparation of MEPE (Scheme 2). MEPE was obtained by mixing the bis-terpyridine ligand 1,4-bis(2,2':6',2''-terpyridin-4'-yl)benzene and FeCl₂·6H₂O in water at the molar ratio of 1:1. The system immediately turned dark purple, indicating coordination between Fe²⁺ and the bis-ligands occurs. After refluxing for 24 h under a nitrogen atmosphere, the product was treated following the method in the literature,²⁵ to obtain a blackish power, which is inert to oxygen at room temperature. The UV–vis spectrum of the product was the same as that reported for MEPE in the literature,²⁵ suggesting the success of preparation of MEPE in our study.

TEM Observation. A JEOL 2100F TEM was employed to observe the morphology of micelles. Drops of samples were put onto 230 mesh copper grids coated with Formvar film. Excess water was removed by filter paper, and samples were then allowed to dry in ambient air at room temperature, before TEM observation.

Dynamic Light Scattering. Dynamic light scattering measurements were performed with an ALV light-scattering apparatus, equipped with a 400 mW argon ion laser operating at a wavelength of 514.5 nm. A refractive index matching bath of filtered cis-decalin surrounded the cylindrical scattering cell, and the temperature was controlled at ±0.5 °C using a Haake C35 thermostat.

Zeta Potential. The electrophoretic mobility of the particles was determined with a Zeta PALS (zeta potential analyzer, Brookhaven Instruments). Twenty cycles were carried out for each run, and altogether 5 runs were done for each sample. The measuring temperature was 25 °C. For analyzing the screening length, κ^{-1} , of micellar core at room temperature, the equation $\kappa^{-1} = (0.304)/(\sqrt{I})$ nm was used, where I is the ionic strength in units of mol/kg. For 1 mM (charge concentration) charge-compensated micelle solutions in this work, the small inorganic ions released upon complex coacervate core micelle formation, including K⁺, Cl⁻, and I⁻, can be considered as a mixture of 1 mM KI and 3 mM KCl. Both are 1:1 type electrolytes, and both contribute to I . The solution density was approximately the same as water. Thus, I was obtained to be about 4×10^{-3} mol/kg. Therefore, $\kappa^{-1} = (0.304)/(\sqrt{I}) = 4.8$ nm. In the case of partially charge compensated micelles, namely, in the case where f^- deviates from 0.5, I will be further increased and the electric double layer will be even thinner.

UV–Vis Measurement. Spectra for all the samples were recorded on a Hitachi spectrophotometer in the visible range 400–800 nm. The scan rate for each measurement was 10 nm/min.

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Supporting Information Available: Figures S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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