



Electrochemical Controlled Supramolecular Switches Formed by Ionic Self-Assembly

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Controlling aggregates transformations are achieved in this work by electrochemical method without the adding of a third substance. In response to redox stimuli, the self-assembly nanostructures of supramolecular amphiphile formed by ionic self-assembly technique can change between nanowires and vesicles. The transformation of self-assembly aggregates induced by redox reactions were found to be brought out by drastic change in amphiphilicity of the supramolecular complexes due to the oxidation and reduction of a ferrocenyl moiety. The novel finding may be applied in many areas including development of smart materials.

Key Words: Ferrocene, Redox, Switch, Nanowires, Vesicles.

INTRODUCTION

As a new class of materials, supramolecular switches with noncovalent structures have attracted significant interest in the past few decades¹⁻³. They can undergo reversible physical or chemical changes and adjust their aggregated nanostructures in response to external stimuli such as pH^{4,5}, light⁶, temperature^{7,8}, molecules⁹ and redox¹⁰⁻¹². In order to build molecular switches, it is a pre-requisite to include components that respond to external stimuli. Among the various substances studied for these purposes, molecules or supramolecular complexes that are sensitive to the redox state of one or more components are a logical choice.

As an important type of organometallic electron mediators, ferrocene (Fc) and its derivatives have received a lot of attention in molecular recognition research due to their redox characteristics and can be chosen as a redox-switchable headgroup for supramolecular complexes^{13,14}. It is well known that ferrocene can be oxidized to hydrophilic ferrocenium utilizing mild oxidants such as ferric chloride, hydrogen peroxide, silver (Ag⁺) and cerium (Ce²⁺)^{15,16}. When applying electrochemical means, ferrocene undergoes reversible oxidation and reduction¹⁷. The interconversion between Fe(II) and Fe(III) states results in hydrophobicity-hydrophilicity transition of the hydrophobic block of amphiphiles.

The technique of ionic self-assembly (ISA), *i.e.*, the coupling of oppositely charged building blocks by electrostatic attraction, has been extensively exploited to fabricate various

supramolecular systems with vivid properties due to its advantages of easiness, reliability, low-cost, flexibility and universality¹⁸⁻²¹. Abe's group²² found spontaneous vesicle formation by mixing a single-chain cationic surfactant modified with ferrocenyl group and an anionic surfactant, which could be redox-controlled on their reversible formation and disruption. For this motivation, we have just recently investigated the formation of vesicles self-assembled from sodium *bis*(2-ethyl-1-hexyl)sulfosuccinate (AOT) and oxidized form N,N-dimethyl-aminomethylferrocene (Fc⁺M), which can be reversibly modulated by adding oxidant and reducing agent²³. However, the disruption and regeneration processes of vesicles can only be repeated twice because of the introduction of the third substance (oxidizing or reducing agent), which causes precipitate formation due to an increase in ionic strength. Compared with chemical methods, the electrolytic oxidation-reduction reaction gives a better reversibility in the assembled state between the reduced and oxidized forms because of without the adding of a third substance. That is to say, the electrolytic redox reaction do not disturb the system.

The present paper describes an attempt to reversibly control the self-assembly architecture of the supramolecular amphiphile formed through complexation between (ferrocenylmethyl)-trimethylammonium iodide (FcMI) and AOT by electrochemical method without using oxidizing and reducing agents. The self-assembly architecture of the supramolecular amphiphile can change between nanowires and vesicles in response to redox stimuli due to the change of ferrocene moiety from hydro-

phobic ferrocene to hydrophilic Fc^+ by electro-oxidation of FcMI. Moreover, the change can be controlled reversibly for at least three times.

EXPERIMENTAL

(Ferrocenylmethyl)trimethylammonium iodide (Alfa-asear) and sodium *bis*(2-ethyl-1-hexyl)sulfosuccinate (98 %, Aldrich) were used as received. The other chemical reagents were analytical grade. Water used in the experiment was triply distilled.

Oxidized and reduced formed complex preparation:

Samples with ferrocene group in reduced form (FcMI) were prepared by mixing AOT ($5 \times 10^{-3} \text{ mol dm}^{-3}$) and FcMI ($5 \times 10^{-3} \text{ mol dm}^{-3}$) aqueous solutions at a molar ratio of 1:1 under sonification for 1 h. Oxidized form solution was prepared by electrolyzing the reduced form solution at a constant voltage of +0.7 V *versus* SCE for 5 h in a nitrogen gas stream. Electrolysis for 1 h at -0.1 V *versus* SCE in a nitrogen gas stream oxidized form solution gave re-reduced form solution. The voltage was controlled with a CHI 604A electrochemical workstation by using a double-compartment glass cell with three-electrode configuration, comprised of a platinum plate working electrode (geometric area: 0.019 cm^2), a platinum plate counter electrode and a saturated calomel reference electrode (SCE), to which all potentials are referenced.

Characterization: UV-visible absorption spectra were recorded in a quartz cell (light path of 10 mm) on a HP 8453E spectrometer to verify the redox states of FcMI molecules. Scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F system (operated at 3.0 kV). The sample was prepared by casting the aqueous solution of FcM-AOT complexes onto a clean silicon slide, followed by drying under vacuum at room temperature. The dried sample was then coated by gold. The produced mesophase structures were characterized using a Rigaku D/Max 2200PC diffractometer with a graphite monochromator and CuK_α radiation ($\lambda = 0.154 \text{ nm}$). The morphology of the aggregates were observed by negative staining transmission electron microscopy (TEM). To do so, a drop of the sample solution was placed on a Formvar-covered TEM grid (200 mesh) and stained with a drop of 2 wt % aqueous solution of uranyl acetate. The excess solution was wicked away with filter paper under the grid. After being dried at room temperature, they were examined using a Hitachi 100CX-II TEM operating at 100 kV. The sizes of aggregates with oxidized and re-oxidized forms in aqueous solutions were detected with a Wyatt Technology DAWN HELEOS instrument poised at 25 °C by using a 12-angle replaced detector in a scintillation vial and a 50 mW solid-state laser ($\lambda = 658.0 \text{ nm}$). All solutions were filtered through a 0.45 μm filter.

RESULTS AND DISCUSSION

Optical properties of FcM-AOT aggregates before and after being oxidized: UV-visible spectrum measurements on FcMI-AOT mixture in solutions are performed to verify that FcMI molecules in solutions are oxidized and reduced. Fig. 1 shows the UV-visible spectra of the reduced and oxidized forms FcMI-AOT mixed solutions. It can be seen that the characteristic absorption peak for Fc^+MI (627 nm) becomes much

clear after oxidation, while the absorption peak for reduced FcMI (427 nm) disappears, which is a strong evidence for conversion of FcMI to $\text{Fc}^+\text{MI}^{24}$. At the same time, the visual observation of reduced and oxidized mixed solutions shows the different interaction of FcM-AOT and $\text{Fc}^+\text{M-AOT}$. As can be seen from Fig. 1 (insert a), the direct mixing of FcMI and AOT leads to the formation of flocculent precipitates. When FcMI-AOT aqueous solution is oxidized by constant potential, the aqueous mixture exhibits a slightly green transparent opalescence [Fig. 1 (insert b)] instead of flocculent precipitates, indicating the formation of some new aggregates.

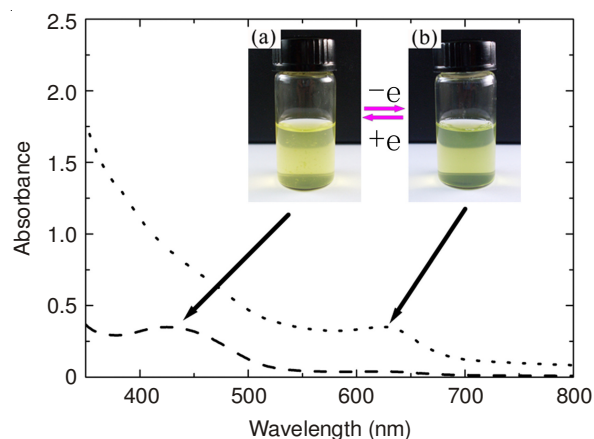


Fig. 1 UV-visible absorption spectra for mixed solutions; (a) reduced form, (b) oxidized form. Insert : photographs for systems of FcM-AOT (a) $\text{Fc}^+\text{M-AOT}$ (b).

Morphology characterization of FcM-AOT aggregates before and after being oxidized: When AOT is mixed with reduced form FcMI, due to the enhancement of hydrophobicity, they can form FcM-AOT complexes by ISA. The morphology and composition of the self-assembled aggregates are characterized, respectively, by scanning electron microscopy (SEM), negative staining transmission electron microscopy (TEM) and ^1H NMR and the relevant work has been reported²⁵. The flocculent precipitates formed by FcM and AOT are actually of reticular structure interweaved by large amounts of one-dimensional wormlike structure with diameters of approximately 100 nm (Fig. 2a). The stoichiometry between FcMI

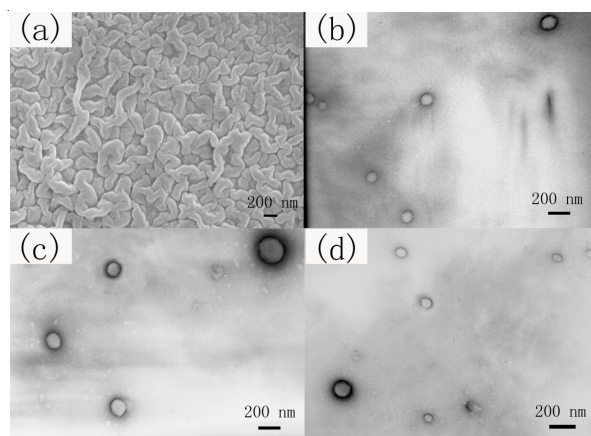


Fig. 2. SEM images of FcM-AOT aggregates (a) and negative staining TEM image of $\text{Fc}^+\text{M-AOT}$ aggregates after oxidization (b), after oxidation and again oxidation (c) and after the third oxidation

and AOT in the complex is determined as a 1:1 molar ratio by ^1H NMR spectroscopy by comparing the peak integral intensities, which indicate that the complex is formed by ionic self assembly of FcMI and AOT.

Subsequently, when FcMI and AOT mixed solution is oxidized by constant potential +0.7 V for 5 h, the flocculent precipitates will disappear and the aqueous mixture exhibits a slightly green transparent opalescence. The uranyl acetate-stained closed spherical vesicles formed in the system containing Fc^+MI and AOT can be observed with their outer diameters in the range of 50–200 nm (Fig. 2b) by transmission electron microscopy (TEM), consistent with the results observed with dynamic light scattering (DLS) (Fig. 3a), showing an average hydrodynamic diameter of about 110 nm. That is to say, the oxidation of FcMI leads to the transformation of self-assembled aggregates from nanowires to vesicles.

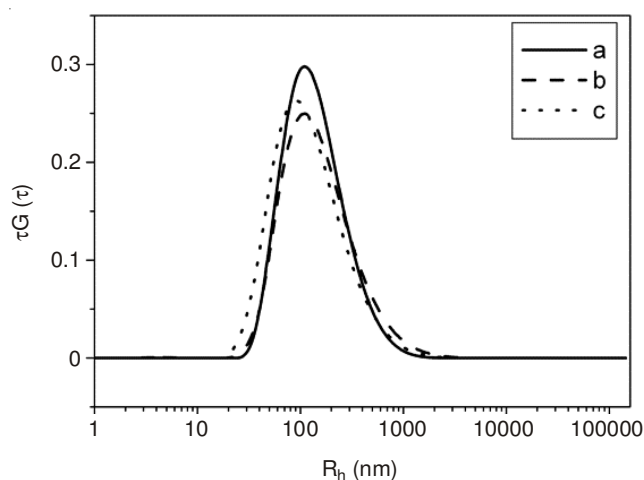


Fig. 3. Apparent hydrodynamic radius (R_h) distribution determined by using light scattering of the vesicles observed in the system of Fc^+MI and AOT mixed solution after oxidation (a), after oxidation and again oxidation (b) and after the third oxidation (c)

In order to reveal the reversibility of the self-assembly architecture, a electrochemical reduction stimulus (constant potential -0.1 V for 1 h) was applied to the vesicles. Due to the transition from Fc^+MI to FcMI and the change of complexes amphiphilicity, vesicles disintegrate and disappear and large amount of flocculent precipitates are re-formed. Then, re-generation of vesicles can be realized after the twice oxidation of the sample as seen in Fig. 2c. Dynamic light scattering result (Fig. 3b) shows the average hydrodynamic diameter of the re-formed vesicles is also about 108 nm, similar to that of the vesicles after the first oxidation. Such a morphology transition exhibits a reversible modulation on aggregate structures by electrochemical method. Moreover, the construction-deconstruction process can be controlled reversibly for at least three times (Fig. 2d and Fig. 3c).

Transition mechanism of self-assembled aggregates induced by electrochemical redox: Fig. 4 shows the transition mechanism of self-assembled aggregates induced by electrochemical method. The interconversion of ferrocene moiety between hydrophobic Fc to hydrophilic Fc^+ results in the structure change of self-assembly aggregates. The wormlike nanowires are formed by ionic self-assembly when FcMI and

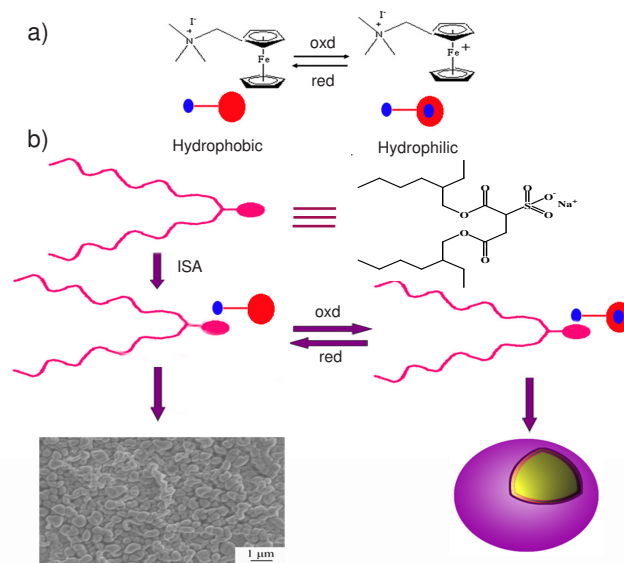


Fig. 4. (a) The redox responsive properties of FcMI; (b) schematic representation of the reversible transformation between nanotubes and vesicles of the FcM-AOT complex in response to redox stimuli

AOT are mixed together due to the increase of hydrophobicity. Then, when FcMI is oxidized by constant potential, the nanowires will disappear gradually due to the enhancement of hydrophilicity. The oxidized Fc^+MI -AOT complex with Fc^+ as a hydrophilic head, which looks like an amphiphile and can self-assemble into vesicles. The ferrocene rings in the vesicles are stacked in a manner that gives an UV-visible absorption band at 623 nm, which is blue-shifted from the corresponding band of the monomeric Fc^+MI at 629 nm (Fig. 5), indicating that they adopt an H-aggregate arrangement (face to face) in the complex. Meanwhile, the reduction of oxidized form FcMI (Fc^+MI) leads to the dissociation of vesicles and the re-formation of nanowires. That is to say, the self-assembly architecture of supramolecular amphiphile can change reversibly between nanowires and vesicles in response to redox stimuli by electrochemical method without adding oxidizing and reducing agents.

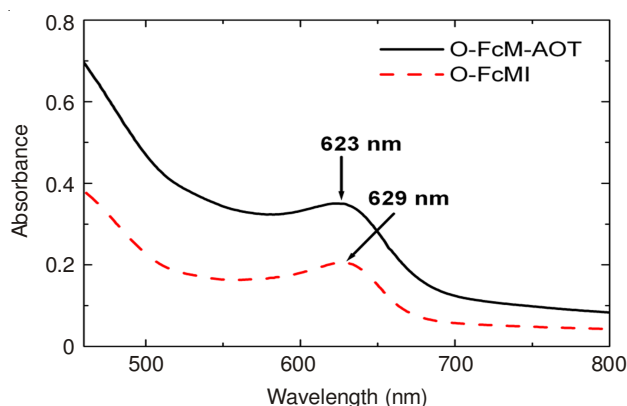


Fig. 5. UV-visible spectra of Fc^+MI (dash) and vesicle (solid) aqueous solutions (Both concentrations are 2.5 mol L^{-1})

Conclusion

We have demonstrated a novel supramolecular switch based on ionic self-assembly technique, which can be changed

reversibly between nanowires and vesicles in response to electrochemical redox stimuli. Compared with chemical oxidation-reduction reaction, the electrolytic redox reaction gives a better reversibility in the assembled state between the reduced and oxidized forms because of without the introducing of a third substance. Meanwhile, the changes of amphiphilicity of the supramolecular amphiphiles due to the redox of the ferrocenyl moiety is responsible for the transformation of self-assembly structures between nanowires and vesicles. The novel finding may be applied in many areas including development of smart materials. We are currently exploring these possibilities.

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