

Ionic Self-Assembled Wormlike Nanowires and Redox Induced Transition

QIUHONG LI* and AIXIANG LI

College of Materials Science and Engineering, Shandong University of Technology, Zibo 255049, Shandong, P.R. China

*Corresponding author: E-mail: qhli@sdut.edu.cn

(Received: 14 April 2011;

Accepted: 19 October 2011)

AJC-10545

Wormlike nanowires have been prepared *via* the ionic self-assembly route from the cationic (ferrocenylmethyl)trimethylammonium iodide (FcMI) and the anionic sodium *bis*(2-ethyl-1-hexyl)sulfosuccinate (AOT). The formed FcM-AOT complexes have been proved to possess a composition of equal molar ratio. In response to redox stimuli, the nanowires can be changed into vesicles. The transformation of self-assembly aggregates induced by redox reactions were found to be brought out by drastic change in amphiphilicity of the supra-molecular complexes due to the oxidation ferrocenyl moiety.

Key Words: Ionic self-assembly, Ferrocene, Nanowires, Vesicle, Redox.

INTRODUCTION

Design and synthesis of artificial molecular switches has been a subject of intense study in recent years because of their potential applications in the creation of nanometer scale molecular devices¹⁻⁵. Supramolecular complexes formed through self-assembly are among the promising candidates for functional molecular devices and nanomaterials^{6,7}. 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, cheapness, flexibility and universality⁸⁻¹³.

In order to build molecular switches, it is a pre-requisite to include components that respond to external stimuli, such as pH, temperature, light, pressure, concentration and redox *etc.*^{4,14-18}. Among the various substances studied for these purposes, molecules or supramolecular complexes that are sensitive to the oxidation 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 importance in molecular recognition research due to their redox characteristics and can be chosen as a redox-switchable headgroup for supramolecular complexes¹⁹⁻²¹. Abe's group 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 disruption²². However, redox stimuli responsive supramolecular nanostructures based on ionic self-assembly of ferrocene derivate molecules without long tails and surfactant counter ions are less known²³.

The present paper describes an attempt to tune the self-assembly architecture of the supramolecular amphiphile formed through complexation between (ferrocenylmethyl)trimethylammonium iodide (FcMI) and AOT by electrochemical method. Through a facile ionic self-assembly route, wormlike nanowires are fabricated. Then, the nanowires formed through the ionic self-assembly will be changed into vesicles when FcMI is oxidized by constant potential due to the change of ferrocene moiety from hydrophobic Fc to hydrophilic Fc⁺.

EXPERIMENTAL

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

Methods: ¹H NMR spectra were obtained on a Bruker AV-400 NMR spectrometer at room temperature. Chemical shifts of the complexes were referenced to d = 2.50 ppm for DMSO. UV-VIS 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 solution for TEM was placed on a Formvar-covered TEM grid (200 mesh) and stained with a drop of 2 wt % uranyl acetate aqueous solution, then they were examined using a Hitachi 100CX-II TEM operating at 100 kV.

Electro-oxidation of the samples were made 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: 1.9 cm^2), a platinum plate counter electrode and a saturated calomel reference electrode (SCE), to which all potentials are referenced.

Binary complex preparation: Two aqueous solutions of AOT and FcMI with the same concentration (5.0 mmol L^{-1}) and volume (50 mL) were mixed under vigorous stirring. The obtained sample systems were kept at $25 \text{ }^\circ\text{C}$ in an incubator for 1 month. Then, the complex precipitates were collected and washed three times with triply distilled water to remove the produced salts and possible uncomplexed precursors. The binary complexes were dried under vacuum at room temperature for 24 h.

Preparation of samples from FcMI with different redox states: Samples with ferrocene group in reduced form (FcMI) were prepared by mixing AOT (5 mmol L^{-1}) and FcMI (5 mmol L^{-1}) aqueous solutions at a molar ratio of 1:1 under sonification for 1 h. Oxidized form (Fc^+MI) solution was obtained by electrolyzing the reduced form solution at a constant voltage $+0.75 \text{ V}$ for 20 h in a nitrogen gas stream. All samples were kept at $25 \text{ }^\circ\text{C}$ in an incubator.

RESULTS AND DISCUSSION

Macroscopic appearances and optical properties: UV-VIS spectrum measurements on FcMI-AOT mixture in solutions are performed to verify that FcMI molecules in solutions are oxidized and reduced by electrochemical method. Fig. 1 shows the UV-VIS 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 Fc^+MI ²⁴.

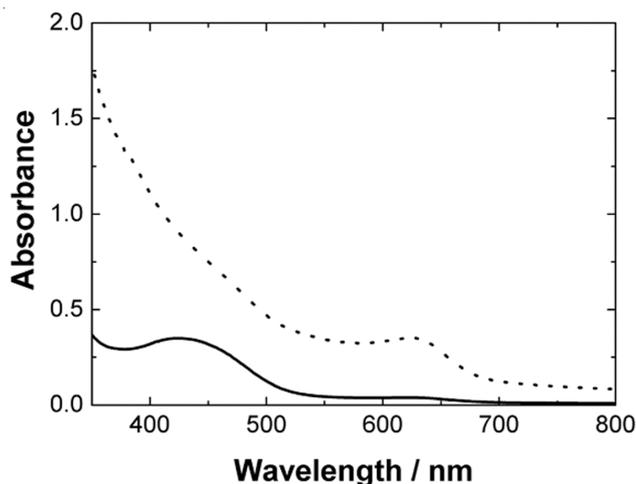


Fig. 1. UV-VIS absorption spectra for mixed solutions of reduced form (solid) and oxidized form (dot)

Aggregate characterization: The ionic self-assembly complex of FcM-AOT may aggregate and precipitate out of the mixed dilute aqueous solutions of FcMI and AOT due to the enhancement of hydrophobicity when they are mixed together, which leads to the formation of flocculent precipitate.

The morphology and composition of precipitated aggregates are characterized, respectively, by scanning electron microscopy (SEM), negative staining transmission electron microscopy (TEM) and ^1H NMR. As can be seen in Fig. 2a, the 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 . TEM image (Fig. 2b) shows that no clear contrast between the edge and central part is observed, thus indicating that the wormlike structures are solid nanowires. The stoichiometry between FcMI and AOT in the complex is determined as a 1:1 molar ratio by ^1H NMR spectroscopy by comparing the peak integral intensities (Fig. 3), which indicate that the complex is formed by ionic self-assembly of FcMI and AOT.

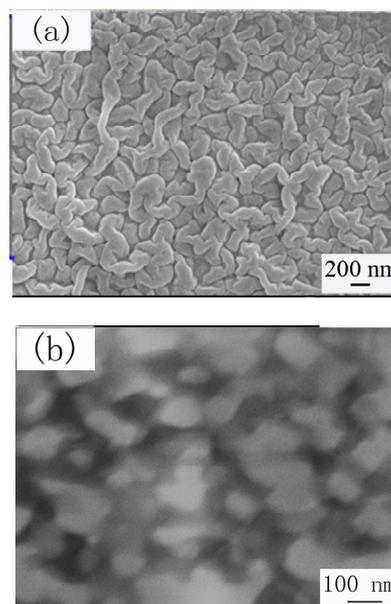


Fig. 2. Morphology of FcM-AOT aggregates observed by scanning electron microscopy (a) and transmission electron microscopy (b)

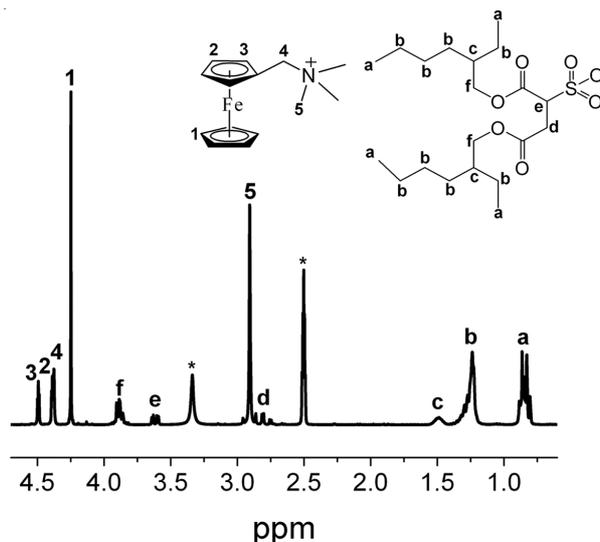


Fig. 3. ^1H NMR spectrum of FcM-AOT complex in $\text{DMSO}(d_6)$. The asterisks denote the solvent peaks

Subsequently, when FcMI and AOT mixed solution is oxidized by electrochemical method, 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. 4a) by transmission electron microscopy, consistent with the results observed with dynamic light scattering (Fig. 4b), 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. According to the reported property difference between oxidized and reduced ferrocene^{21,24}, the dramatic changes of ferrocene part from the hydrophobicity to hydrophilicity when it was oxidized aroused the transformation of amphiphilicity of the complexes, thus the self-assembled aggregate structures in solution are also changed accordingly.

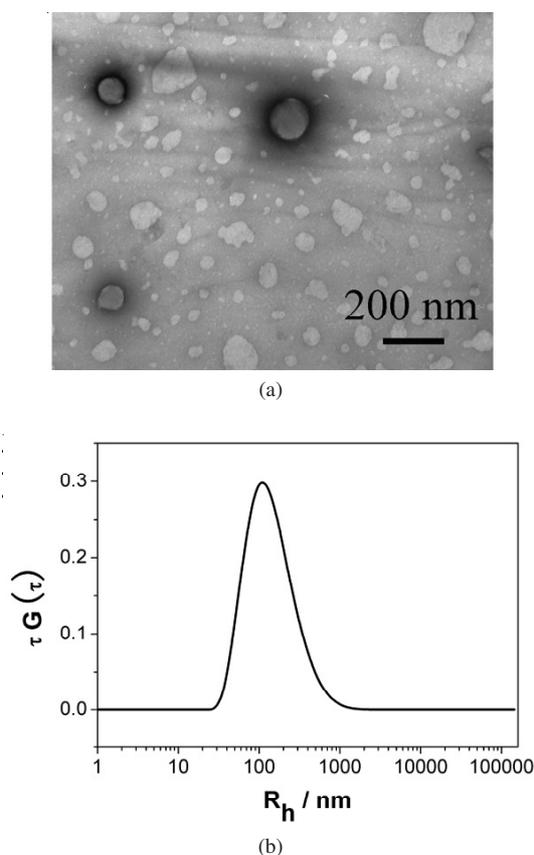


Fig. 4. (a) TEM micrograph and (b) apparent hydrodynamic radius (R_h) distribution determined by using light scattering of the vesicles observed in the system of Fc^+M -AOT solution

Conclusion

We have prepared FcM -AOT binary complexes based on ISA technique, which can be changed into vesicles in response

to electrochemical redox stimuli. Their structures are characterized, respectively, by ^1H NMR, SEM, TEM, UV-visible spectroscopy and dynamic light scattering measurements. Wherein, the change of amphiphilicity of the supramolecular amphiphiles due to the redox of the ferrocenyl moiety is responsible for the transformation of self-assembly structures from nanowires to vesicles. These novel findings may be applied in many areas including development of smart materials. We are currently exploring these possibilities.

ACKNOWLEDGEMENTS

The authors are thankful for the financial support from the Promotive research fund for Excellent Young and Middle-Aged Scientists of Shandong Province (BS2010CL039).

REFERENCES

1. E.R. Kay, D.A. Leigh and F. Zerbetto, *Angew. Chem. Int. Ed.*, **46**, 72 (2007).
2. H. Tian and Q.C. Wang, *Chem. Soc. Rev.*, **35**, 361 (2006).
3. K. Kinbara and T. Aida, *Chem. Rev.*, **105**, 1377 (2005).
4. T. Yasuda, K. Tanabe, T. Tsuji, K.K. Coti, I. Aprahamian, J.F. Stoddart and T. Kato, *Chem. Commun.*, **46**, 1224 (2010).
5. C. Wang, Q. Chen, F. Sun, D.Q. Zhang, G.X. Zhang, Y.Y. Huang, R. Zhao and D.B. Zhu, *J. Am. Chem. Soc.*, **132**, 3092 (2010).
6. J.M. Lehn, *Science*, **295**, 2400 (2002).
7. B. Song, Z. Wang, S. Chen, X. Zhang, Y. Fu, M. Smet and W. Dehaen, *Angew. Chem. Int. Ed.*, **44**, 4731 (2005).
8. Y.P. Wang, P. Han, H.P. Xu, Z.Q. Wang, X. Zhang and A.V. Kabanov, *Langmuir*, **26**, 709 (2010).
9. C.F.J. Faul and M. Antonietti, *Adv. Mater.*, **15**, 673 (2003).
10. Y. Zakrevsky, J. Stumpe and C.F.J. Faul, *Adv. Mater.*, **18**, 2133 (2006).
11. B. Jing, X. Chen, X.D. Wang, C.J. Yang, Y.Z. Xie and H.Y. Qiu, *Chem. Eur. J.*, **13**, 9137 (2007).
12. B. Jing, X. Chen, Y.R. Zhao, X.D. Wang, J.G. Cai and H.Y. Qiu, *J. Phys. Chem. B*, **112**, 7191 (2008).
13. C.F.J. Faul, P. Krattiger, B.M. Smarsly and H. Wennemers, *J. Mater. Chem.*, **18**, 2962 (2008).
14. S.Y. Liu and S.P. Armes, *Angew. Chem. Int. Ed.*, **41**, 1413 (2002).
15. M. Arotcarena, B. Heise, S. Ishaya and A. Laschewsky, *J. Am. Chem. Soc.*, **124**, 3787 (2002).
16. Y.P. Wang, P. Han, H.P. Xu, Z.Q. Wang, X. Zhang and A.V. Kabanov, *Langmuir*, **26**, 709 (2010).
17. A. Raudino, F. Lo Celso, A. Triolo and R. Triolo, *J. Chem. Phys.*, **120**, 3489 (2004).
18. J.F. Gohy, S.K. Varshney, S. Antoun and R. Jerome, *Macromolecules*, **33**, 9298 (2000).
19. E. Fan, C. Vicent, S.J. Geib and A.D. Hamilton, *Chem. Mater.*, **6**, 1113 (1994).
20. G. Cooke and V.M. Rotello, *Chem. Soc. Rev.*, **31**, 275 (2002).
21. J. Westwood, S.J. Coles, S.R. Collinson, G. Gasser, S.J. Green, M.B. Hursthouse, M.E. Light and J.H.R. Tucker, *Organometallics*, **23**, 946 (2004).
22. H. Sakai, H. Imamura, Y. Kondo, N. Yoshino and M. Abe, *Colloids Surf. A*, **232**, 221 (2004).
23. Q.H. Li, X. Chen, B. Jing, Y.R. Zhao and F.M. Ma, *Colloids Surf. A*, **355**, 146 (2010).
24. T. Saji, K. Hoshino and S. Aoyagui, *J. Am. Chem. Soc.*, **107**, 6865 (1985).