A surfactant-encapsulated polyoxometalate complex towards a thermotropic liquid crystal†

Wen Li,[a] Weifeng Bu,[a] Haolong Li,[a] Lixin Wu*[a] and Min Li[b]

Received (in Cambridge, UK) 9th March 2005, Accepted 2nd June 2005
First published as an Advance Article on the web 29th June 2005
DOI: 10.1039/b503550c

A novel surfactant-encapsulated terbium-substituted heteropolyoxotungstate complex $[L1]_{13}[Tb(SiW_{11}O_{39})_2]\cdot 30H_2O$ (SEC-1) bearing mesomorphous groups was successfully prepared by the ionic self-assembling route, exhibiting characteristic thermotropic liquid-crystalline behavior.

Polyoxometalates (PMs) have received considerable interest in chemistry and material science because of their potential application such as in optical, electric and magnetic fields.[1] Recently, an important progress of PM chemistry is that PMs are enwrapped with a water-insoluble shell composed of ionic organic molecules based on cooperatively electrostatic interactions so that the surfactant-encapsulated clusters (SECs) can be processed conveniently into thin films by spin coating, simple casting, and LB techniques.[2] In some cases, the organic surfactant cation not only plays a structural role but also has a strong effect on the properties of these hybrids.[3] Additional properties of the hybrid materials based on PM are expected to be obtained by the appropriate choice of organic components.[3c]

Liquid crystals are fascinating organic functional materials which can automatically self-assemble to various mesophases through organized packing of organic molecules in a certain temperature range and provide extra features such as the ability to respond to external stimuli.[4] Therefore, a logical problem is how to incorporate PMs into liquid crystalline (LC) matrices. Such hybrids combining the characteristics of LC materials with PMs are expected to bring exciting synergistic properties. For example, the optical and magnetic properties of PMs can be incorporated into LCs. Based on the anisotropic and organized nature of LCs, the properties of PMs can probably be modified and new functional materials can be constructed.

Motivated by this target, in this communication, we report the preparation of a surfactant-encapsulated cluster (SEC-1) and its characteristic thermotropic LC behavior. The azobenzene-containing surfactant L1,† as shown in Fig. 1, was prepared according to modified routes of literature.[5–7] The polyoxometalate $K_{13}Tb(SiW_{11}O_{39})_2\cdot 15H_2O$ (PM-1) was synthesized by following a literature procedure.[8] SEC-1 was obtained according to a modified method.[2] PM-1 (0.165 g) was dissolved in aqueous solution (pH = 5.7) and then 0.283 g of L1 in chloroform was added to the solution dropwise. After stirring for 4 h at 40 °C, the organic phase was separated and evaporated to dryness. The residue was further dried under vacuum until the weight remained constant. In contrast to PM-1 which is only soluble in water, the obtained complex is immiscible in water but readily dissolves in organic media. This indicates that PM-1 has been successfully encapsulated. Combining the results of thermogravimetric analysis (TGA) and elemental analysis, SEC-1 should correspond to the chemical formula: $(L1)_{13}[Tb(SiW_{11}O_{39})_2]\cdot 30H_2O$.

Differential scanning calorimetry (DSC) curves (Fig. 2) give phase transitions of L1 and SEC-1 in their first cooling and the second heating process. Comparing these curves with those of the first heating run of both virgin samples L1 and SEC-1 (Fig. S2†), we know that the primary heating run results in the loss of crystalline water in SEC-1, which is proved by IR and TGA measurements. Upon cooling, L1 exhibits three phase transitions at 147, 114 and 82 °C, respectively. Similar phase behavior is found in SEC-1, which undergoes three exothermic transitions at 180, 113 and 79 °C, respectively. The broad peak of SEC-1 at 180 °C should correspond to a slow phase transition from isotropic phase to a LC phase.

LC behaviors of SEC-1 and L1 are also identified by polarizing optical microscopy (POM) as shown in Fig. 3. On cooling from isotropic phase, L1 displays clear birefringence at 130 °C (Fig. 3a), suggesting a characteristic liquid-crystalline phase. On further cooling, broken texture is observed at 103 °C (Fig. 3b), suggesting a highly ordered smectic phase. In the case of SEC-1, clearing of the LC phase is firstly observed at 160 °C, which displays a fine-grain texture though it is not a typical one (Fig. 3c). When the LC phase is cooled to below 113 °C, a similar but clear mesophase texture is seen at 103 °C as shown in Fig. 3d, suggesting another liquid-crystalline phase. To determine the LC effect of L1, SEC-2 was prepared following the same procedure as for SEC-1, using dioctadecyldimethylammonium (L2) without azobenzene groups instead of L1. However, LC behavior was not observed in SEC-2 according to the results of DSC and POM. As a consequence, we can see that the mesomorphous L1 plays an important role for the formation of LC in SEC-1.

The mesophases and structures of SEC-1 are further investigated by using X-ray diffraction (XRD), seen in Fig. 4. When SEC-1 is cooled from isotropic liquid to 150 °C, four equidistant small angle diffractions are observed apparently (Fig. 4a), which attribute to a typical layered structure (SmX_1) and the layer spacing is calculated to be 6.50 nm. The diffuse peak at $2\theta \approx 20^\circ$ (d = 0.45 nm) indicates a decreasing of the lateral correlation among neighboring alkyl chains. On further cooling to 103 °C, the layer spacing increase to 6.80 nm as shown in Fig. 4b, suggesting

---

[a] *Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, Jilin University, Changchun, China. E-mail: wulx@jlu.edu.cn; Fax: +86 431 5193421; Tel: +86 431 5168481*
[b] *Department of Material Science and Engineering, Jilin University, Changchun, China*

† Electronic supplementary information (ESI) available: detailed synthesis and characterization of L1, SEC-1 and SEC-2. See http://dx.doi.org/10.1039/b503550c

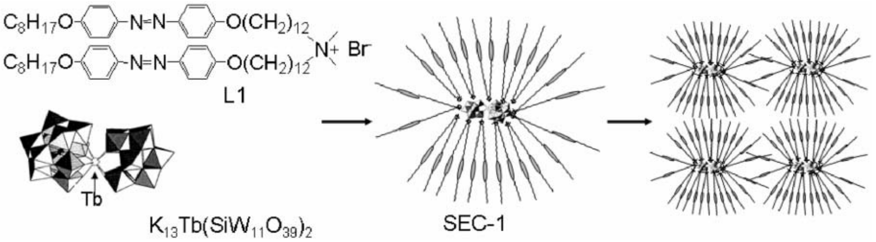

Fig. 1 The schematic chemical structures of L1, PM-1, SEC-1 and proposed layered aggregates of SEC-1.

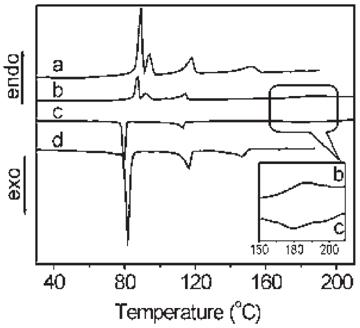

Fig. 2 DSC thermograms of SEC-1 and surfactant L1 on the first cooling and second heating process with a rate of 5 °C $\min^{-1}$: a, L1 (second heating); b, SEC-1 (second heating); c, SEC-1 (first cooling); d, L1 (first cooling).

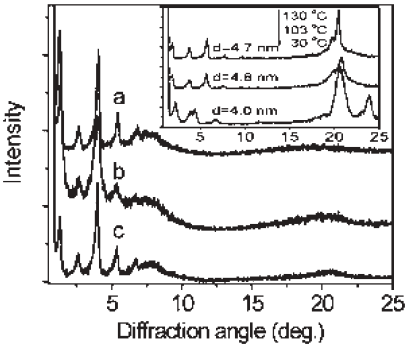

Fig. 4 Variable-temperature wide-angle X-ray diffraction of SEC-1: (a) 150, (b) 103 and (c) 30 °C. (Inset: temperature-dependence XRD of surfactant L1.)

another lamellar mesophase (SmX_2). The diffraction pattern at room temperature (Fig. 4c) gives the layer distance 6.69 nm. XRD results also confirmed the smectic phases of L1 (Fig. 4 inset).[9] Quite strong diffraction intensity and narrow peak at wide angles imply that L1 exists in a crystalline and a highly ordered state even in the LC phase after eliminating the heating history. However for SEC-1 at room temperature, the presence of broad wide-angle diffraction at $2\theta \approx 20°$ ($d = 0.43$ nm) nm indicates it is not in a crystalline but in a highly ordered aggregated state or colloid crystal (CC). The regularity of layer spacing change of SEC-1 is in agreement with that of L1. In fact, PM-1 consists of two lacunary Keggin structures of $SiW_{11}O_{39}{}^{2-}$ linked by a terbium ion[10] and the long-to-short axis ratio is 2:1; hence, most of the L1 molecules are proposed to align along its long axis, which is favourable for ordered and oriented packing in self-assembly lamellar structure through the hydrophobic interaction between alkyl chains.[3a,3b] Considering the radius (0.52 nm) of Keggin-type PMs,[11] the short-axis diameter of PM-1 is about 1 nm. Combing the length of L1 (3.45 nm, calculated by MM2 force field method) and the short-axis diameter of PM-1, the total thickness of a single SEC-1 should be around 7.9 nm. The ideal molecular length is larger than the layer distance measured by XRD in mesophase. Herein, we conclude that in the smectic structures the alkyl chains are partially interdigitated or tilted. Another possibility is the conformational disorder of chains. But the present data can not give further evidence to identify the mesophases more exactly. Hence, the mesophase sequence of SEC-1 can be summarized as I-SmX_1-SmX_2-CC.

It is worth noting that the lamellar LC phase of SEC-1 is derived from the synergistic effect between PM-1 and L1. The ellipsoid structure of PM-1 is favorable for the formation of lamellar structure and the LC behavior of SEC-1 is induced by L1. Up to date, some organic–inorganic hybrid materials with liquid-crystalline behavior have been explored.[3c,12–14] Moreover mesostructured supramolecular assemblies combining giant mixed-valent polyoxomolybdates and surfactants have also been

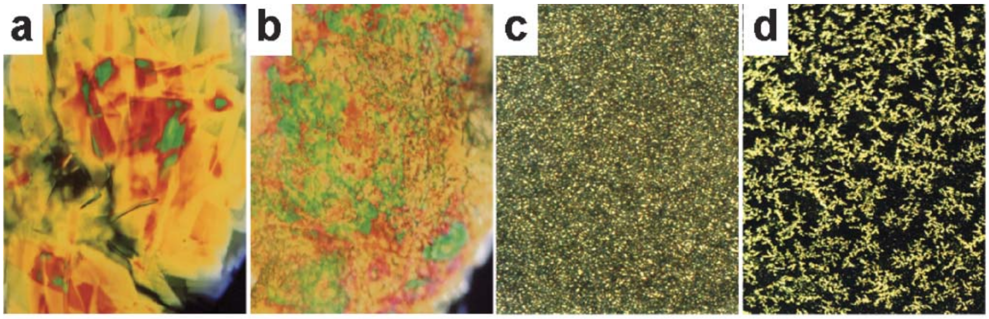

Fig. 3 Optical textures of the surfactant L1 and SEC-1: (a) L1 at 130 °C; (b) L1 at 103 °C; (c) SEC-1 at 160 °C; (d) SEC-1 at 103 °C. (×400).

obtained, in which the inorganic clusters were organized into LC-like alignment with long-range ordered structure.[15] The present paper reports a novel hybrid material based on polyoxometalate, which displays thermotropic liquid-crystalline behavior. The strategy is a general and facile method to fabricate PM-based LC molecular materials by using mesogroup-containing surfactant to encapsulate PM.

This work was supported by Natural Science Foundation of China (20473032), Major State Basic Research Development Program (G2000078102), PCSIRT of Ministry of Education of China, Innovation Fund of Jilin University. We also thank Prof. D.H. Yan from CIAC of CAS for his helpful discussion.

Notes and references

1 (*a*) E. B. Wang, C. W. Hu and L. Xu, *Introduction to Polyoxometalate Chemistry*, Chemical Industry Press: Beijing, 1998; (*b*) T. Yamase, *Chem. Rev*, 1998, **98**, 307; (*c*) E. Coronado and C. J. Gómez-García, *Chem. Rev.*, 1998, **98**, 273.

2 (*a*) D. G. Kurth, P. Lehmann, D. Volkmer, H. Cölfen, M. J. Koop, A. Müller and A. Du Chesne, *Chem. Eur. J.*, 2000, **6**, 385; (*b*) D. Volkmer, A. Du Chesne, D. G. Kurth, H. Schnablegger, P. Lehmann, M. J. Koop and A. Müller, *J. Am. Chem. Soc.*, 2000, **122**, 1995; (*c*) D. G. Kurth, P. Lehmann, D. Volkmer, A. Müller and D. Schwahm, *J. Chem. Soc., Dalton Trans.*, 2000, 3989; (*d*) W. Bu, H. Fan, L. Wu, X. Hou, C. Hu, G. Zhang and X. Zhang, *Langmuir*, 2002, **18**, 6398.

3 (*a*) W. Bu, L. Wu, X. Zhang and A. Tang, *J. Phys. Chem. B.*, 2003, **107**, 13425; (*b*) W. Bu, H. Li, W. Li, L. Wu, C. Zhai and Y. Wu, *J. Phys. Chem. B.*, 2004, **108**, 12776; (*c*) T. Zhang, C. Spitz, M. Antonietti and F. J. Faul Charl, *Chem. Eur. J.*, 2005, **11**, 1001.

4 D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, *Handbook of Liquid Crystals*, Wiley-VCH, Weinheim, Germany, 1998.

5 M. Shimomura, R. Ando, T. Kunitake and B. Bunsen-Ges, *Phys. Chem.*, 1983, **87**, 1134.

6 Y. Okahata, R. Ando and T. Kunitake, *Bull Chem. Soc. Jpn.*, 1979, **52**, 12, 3647.

7 R. Ueoka and Y. Matsumoto, *J. Org. Chem.*, 1984, **49**, 3774.

8 R. D. Peacock and T. J. R. Weakley, *J. Chem. Soc. A.*, 1971, 1836.

9 Ordered lamellar structure was observed from the temperature-dependence XRD of L1, the strong diffraction peak in wide-angle region ($2\theta \approx 20^\circ$) suggesting a high ordered smectic structure. In contrast, SEC-1 showed diffuse peaks in wide-angle region. The difference is result from the effect of PM-1.

10 R. Ballardini, E. Chiorboli and V. Balzani, *Inorg. Chim. Acta*, 1984, **95**, 323.

11 C. Rocchoccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, 1983, **22**, 207.

12 N. Kanayama, O. Tsutsumi, A. Kanazawa and T. Ikeda, *Chem. Commun.*, 2001, 2640.

13 K. Kanie and T. Sugimoto, *J. Am. Chem. Soc.*, 2003, **125**, 10518.

14 F. Camerel, M. Antonietti and C. F. J. Faul, *Chem. Eur. J.*, 2003, **9**, 2160.

15 S. Polarz, B. Smarsly and M. Antonietti, *Chem. Phys. Chem.*, 2001, **7**, 457.