Supplementary Material for Chemical Communications

A surfactant-encapsulated polyoxometalate complex toward thermotropic liquid crystal

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Supplementary Information

1. Materials

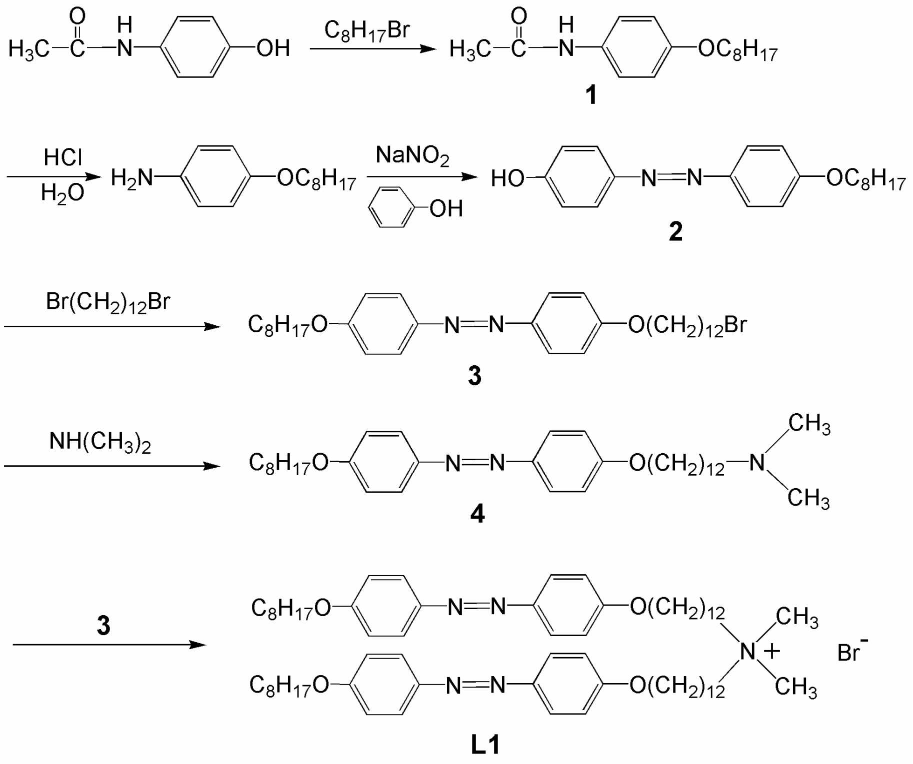
4-acetamidophenol was purchased from Aldrich. 1, 12-dibromododecane was obtained from Fluka. All these starting compounds for synthesis were used without further purification. All the used solvents are analytical grade. Doubly distilled water was used in the experiments. Silica gel (200-300 mesh) was used for column chromatography.

2. Measurements

^{1}H NMR spectra were recorded on a Bruker Avance 500 instrument using $CDCl_3$ as solvent and TMS as internal reference (0.00 ppm). Elemental analysis (C, H, N) were performed on a Flash EA1112 from ThermoQuest Italia S.P.A. FT-IR spectra were performed on a Bruker IFS66V equipped with a DGTS detector with a resolution of 4 cm^{-1}. IR measurements for characterization of molecules were carried out by KBr tablets. Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer TG/DTA-7 instrument and the heating rate is 10 ^{o}C min^{-1}. The phase behavior was studied using a polarising optical microscopy (Leica DMLP, Germany) with a hot stage. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204. The samples were examined at a scanning rate of 5 ^{o}C min^{-1} by applying several heating and cooling cycles from 30 to 220 ^{o}C. Variable-temperature WAXS experiments were performed on a Rigaku X-ray diffractometer (D/max 2500V, using Cu Kα_1 radiation of a wavelength of 1.54 Å) with a PTC-20A temperature controller.

3. Synthesis of di[12-(4'-octyloxy-4-azophenyl)dodecyloxy]dimethylamonium bromide (L1)

Synthesis of **L1** was carried out following the route as shown in Scheme S1. Detailed procedures are as follows:



Scheme S1. Schematic synthetic route of surfactant L1

4-octyloxyacetaniline (1). 4-acetaminophenol (8 g, 53 mmol) was dissolved in a solution of K_2CO_3 (7.7 g, 56 mmol) in 150 mL of acetone. To this solution was added 11.2 g (58 mmol) of 1-bromooctane. The mixture was stirred for 24 h under refluxing. The solvent was evaporated under reduced pressure and the residue was washed with water, drying in air to give the product **1**. The solid was used directly for next step reaction.

4-octyloxyazophenol (2). **1** (6.5 g, 20 mmol) was dissolved in a mixture of concentrated hydrochloric acid (25 mL) and water (150 mL). The solution was stirred for 10 h under refluxing. After the solution was neutralized to pH = 8 with a dilute sodium hydroxide solution, the white precipitate with light pink was filtered off and washed with water for 2 or 3 times, drying to give 4-octyloxyaniline in almost 100 % yield. Then, the obtained crude product was dissolved in a solution of concentrated hydrochloric acid (5 mL) and water (40 mL) in 70 mL acetone. Sodium nitrite (1.66 g, 24 mmol) in water (15 mL) was added dropwise to above solution at 5 ^{o}C. After stirring for additional half an hour, the diazo salt solution was obtained by filtration. An aqueous solution dissolved phenol (2.26 g, 24 mmol), sodium hydroxide (1.28 g, 32 mmol) and sodium carbonate (10 g, 100 mmol) was then added dropwise to the diazo salt solution under vigorous stirring maintaining temperature below

5 ^{o}C. The solution was stirred for further 2 h. After the solution was neutralized with a dilute hydrochloric acid solution, the precipitate was filtered off and treated with chloroform. The organic phase was washed with water, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated, and the residue was purified by column chromatography on silica gel using chloroform as eluent. Yield: 60 %.

4-(12-bromododecyloxy)-4'-octyloxyazobenzene (3). **2** (2.2 g, 6.7 mmol) was added to a solution of 1,12-dibromododecane (3.76 g, 11.5 mmol) and K_2CO_3 (2.82 g, 20 mmol) in 120 ml of acetone. This mixture was stirred for 24 h under refluxing. The solvent was evaporated, and the residue was treated with chloroform and filtered. The organic phase was washed with water, dried with anhydrous $MgSO_4$ and filtered. After evaporating solvent, the residue was purified by column chromatography on silica gel using chloroform/petroleum ether (1:1, v/v) as eluent. Yield: 70 %.

4-(12-N,N-dimethylaminododecyloxy)-4'-octyloxyazobenzene (4). A 33 % dimethylamine aqueous solution **(**0.62 g, 2.5 mmol**)** was added to a solution of **3** (0.5 g, 0.87 mmol) in 35 mL of ethanol. The mixture was stirred for 24 h under refluxing. The solvent was evaporated under reduced pressure, the residue was treated with chloroform, and the organic phase was washed with water, dried over anhydrous $MgSO_4$ and filtered. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using $CHCl_3/CH_3OH$ (15/1, v/v) as eluent. Yield: 84 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.88 (t, J = 5 Hz, 3 H), δ = 1.27-1.35 (m, 24 H), δ = 1.46-1.49 (m, 4 H), δ = 1.80-1.83 (m, 4 H), δ = 2.79 (s, 6 H), δ = 2.98 (t, J = 10 Hz, 2 H), δ = 4.03 (t, J = 5 Hz, 4 H), δ = 6.98-7.00 (d, J = 10 Hz, 4 H), δ = 7.85-7.87 (d, J = 10 Hz, 4 H).

Di[12-(4'-octyloxy-4-azophenyl)dodecyloxy]dimethylamonium bromide (L1). A mixture of 0.3 g (0.56 mmol) of **4**, 0.42 g (0.73 mmol) of **3** and 1.0 g (9.4 mmol) of anhydrous Na_2CO_3 in 80 ml of ethanol was refluxed for 24 h. The solvent was evaporated, the resulting reaction mixture was treated with chloroform, and the undissolved salt was removed by filtration. The filtrate was washed with water, dried with anhydrous $MgSO_4$, concentrated under reduced pressure. The residue was purified to give **L1** by column chromatography on silica gel using $CHCl_3/CH_3OH$ (10/1, v/v) as eluent Yield: 80 %. ^{1}H NMR ($CDCl_3$, 500MHz): δ = 0.89 (t, J = 5 Hz, 6 H), δ = 1.29-1.37 (m, 48 H), δ = 1.46-1.49 (m, 8 H), δ = 1.80-1.83 (m, 8 H), δ = 3.34 (s, 6 H), δ = 3.48 (t, J = 10 Hz, 4 H), δ = 4.03 (t, J = 5 Hz, 8 H), δ = 6.98-7.00 (d, J = 10 Hz, 8 H), δ = 7.91-7.93 (d, J = 10 Hz, 8 H). IR (KBr, cm^{-1}): ν = 3413, 2956, 2919, 2850, 1602, 1579, 1500, 1469, 1390, 1298, 1247, 1149, 1107, 1024, 1002, 842, 724, 557. Anal. Calc for surfactant L1 (1147.5): C, 69.08; H, 9.49; N, 6.11. Found: C, 68.64; H, 9.39; N, 6.06. Corresponding formula: $C_{66}H_{104}N_5O_4Br{\cdot}2H_2O$.

4. A typical procedure for preparation of SECs.

A polyoxometalate $K_{13}Tb(SiW_{11}O_{39})_2{\cdot}15H_2O$ (PM-1) was freshly prepared according to the procedures as described in the literature. SEC-1 was synthesized using the modified procedure: PM-1 was dissolved in aqueous solution (pH = 5.7), and then L1 in chloroform solution was added. The mixture was stirred for 4 h at 40 ^{o}C. The initial molar ratio of L1 to PM-1 was controlled at 10:1. The organic phase was separated and the complex was obtained by evaporating chloroform to dryness. Then, the sample was further dried in vacuum until the weight remained constant. IR (KBr, cm^{-1}): ν = 3461, 2956, 2920, 2850, 1602, 1581, 1500, 1470, 1390, 1298, 1248, 1149, 1107, 1024, 1002, 943, 893, 842, 837, 775, 729, 551. Anal. Calc for SEC-1 ($C_{858}H_{1412}N_{65}O_{160}W_{22}Si_2Tb$, 19458.71): C, 52.96; H, 7.31; N, 4.68. Found: C, 53.29; H, 7.05; N, 4.42. Therefore, the new polyoxometalate-based compound (**SEC-1**) should correspond to a tentative formula: $(L1)_{13}[Tb(SiW_{11}O_{39})_2]{\cdot}30H_2O$ (19458.71). SEC-2 was synthesized at room temperature followed the similar procedure as for SEC-1, using the surfactant L2 instead of L1. The initial molar ratio of L2 to PM-1 was controlled at 10:1. IR (KBr, cm^{-1}) for SEC-2: ν = 3460, 2956, 2918, 2850, 1636, 1484, 1468, 1379, 998, 952, 898, 798, 774, 721, 544, 521, 473. Anal. Calc. for **SEC-2** ($C_{494}H_{1050}N_{13}O_{83}W_{22}Si_2Tb$, 12761.63): C, 46.49; H, 8.29; N, 1.42. Found: C, 47.00; H, 8.26; N, 1.58, corresponding to a formula: $(L2)_{13}[Tb(SiW_{11}O_{39})_2]{\cdot}5H_2O$.

5. Structure Characterization of SEC-1 and SEC-2.

TGA showed a mass loss of 2.74% at the range of 30--110 ^{o}C due to crystal water in SEC-1. Combing the TGA and elemental analysis, SEC-1 should correspond to the following formula: $(L1)_{13}[Tb(SiW_{11}O_{39})_2]{\cdot}30H_2O$. Likewise, the TGA stage of SEC-2 (temperature range: 20 to 100 ^{o}C) corresponds to the loss of crystalline water (0.7%), and the calculated number of crystalline water is about 5. Therefore, the corresponding formula for SEC-2: $(L2)_{13}[Tb\ (SiW_{11}O_{39})_2]{\cdot}5H_2O$. It is important to note that the resulting complexes are stable in air, and no structural changes of PM-1 seem to take place on water subphase according to the identical IR and UV-vis spectra of PM-1, in SEC-1 and SEC-2. In the IR spectrum of the solid-state SEC-1, strong bands are observed below 1000 cm^{-1} for PM-1 vibrations. Characteristic IR absorption bands at 1248, 1500, 1602, 2850, and 2920 cm^{-1} suggest the presence of surfactant L1; Band at 3461 cm^{-1} is OH stretching mode for water molecules. In the case of SEC-2, bands at 2918 and 2850 cm^{-1} are assigned to CH_2 antisymmetric and symmetric stretching modes of L2 alkyl chains of SEC-2, respectively. Bands are observed below 1000 cm^{-1} for PM-1 vibrations; Band at 3460 cm^{-1} is OH stretching mode for water molecules. The detailed assignments are summarized in Table S1.

Table S1. Assignment for the vibration modes in the Infrared Spectra of SEC-1 and SEC-2.

SEC-1 (cm^{-1})	SEC-2 (cm^{-1})	assignment
3461	3460	O-H asymmetric stretching
2956	2956	CH_3 asymmetric stretching
2920	2918	CH_2 asymmetric stretching
2850	2850	CH_2 symmetric stretching
	1636	O-H scissor stretching
1602		C-C framework stretching
1581		C-C framework stretching
1500		C-C framework stretching
	1484	CH_2N scissor stretching
1470	1468	CH_2 scissor stretching
	1379	CH_3 symmetric stretching
1248		C-O-C asymmetric stretching
1149		C-N stretching
943	952	W-O_d asymmetric stretching
893	898	W-O_b-W asymmetric stretching
842		C-H stretching
837		W-O_C-W asymmetric stretching
775	774	W-O_C-W asymmetric stretching
729	721	CH_2 scissor stretching

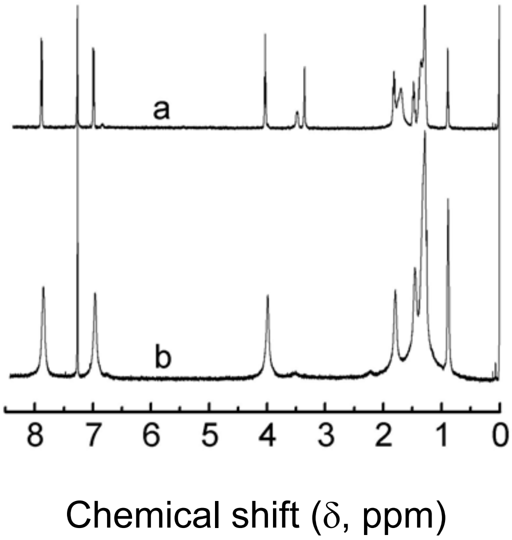


Figure S1. ^{1}H NMR spectra of L1 (a) and SEC-1 (b) in $CDCl_3$.

6. Thermal behavior of SEC-1 and L1.

Thermal behavior of SEC-1 and L1 were examined by DSC and TGA. Figure S1 depicted the DSC curves of SEC-1 and L1 for the first heating runs. The curves are different from their second heating curves respectively. This indicated that the first heating curves were in response to a loss of crystalline water. The transition temperatures and enthalpies of L1 and SEC-1 for the first cooling runs were summarized in Table S2. TGA curve (Figure S2) of SEC-1 showed no clear decomposition occurred between 20 and 220 °C.

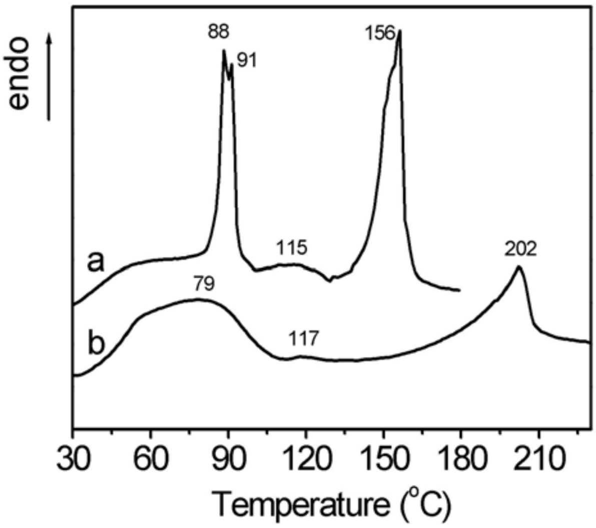


Figure S2. DSC curves of the virgin sample L1 (a) and SEC-1 (b) in the first heating run. (scanning rate: 5 °C min^{-1})

Table S2. The summary of transition temperatures (^{o}C) and enthalpies (J/g) on first cooling run.

Sample	LC phase, Transition and Enthalpy (in bracket)			
SEC-1	Iso	SmX_1	SmX_2	CC
	180 (5.4)	113 (3.46)	79 (12.28)	
L1	Iso	Sm1	Sm2	Cr
	147 (8.38)	117 (10.0)	82 (34.47)	

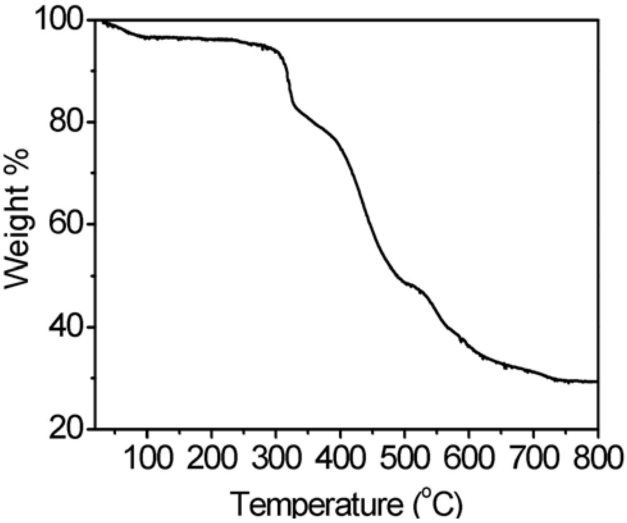


Figure S3. TGA curve of SEC-1 between 30 and 800 ^{o}C. (heating rate: 10 ^{o}C min^{-1})

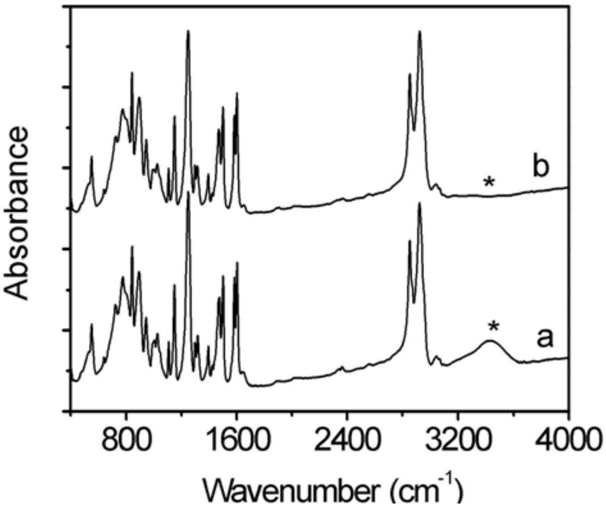


Figure S4. Infrared spectra of (a) virgin sample SEC-1 without heating experience at room temperature and (b) SEC-1 after heating to isotropic phase (220 ^{o}C) and cooling to room temperature.

7. X-ray diffraction of L1 and SEC-1.

WAXD results further confirmed the imperfect layered structures of L1. Figure S5A shows the typical variable-temperature patterns. At 130 °C, the diffraction pattern is constituted by many diffraction peaks in the small-angle region with a calculated periodicity of d = 4.71 nm. There is a strong diffraction peak in the wide-angle region ($2\theta = 20^{o}$), suggesting a LC crystalline structure. On cooling to 103 °C, the layer spacing d tends to 4.82 nm, indicating another high ordered layer LC phase. The diffraction pattern at room temperature is depicted in Figure S5Aa. Therefore, both of results of POM and WAXD suggest the presence of mesophases of L1.

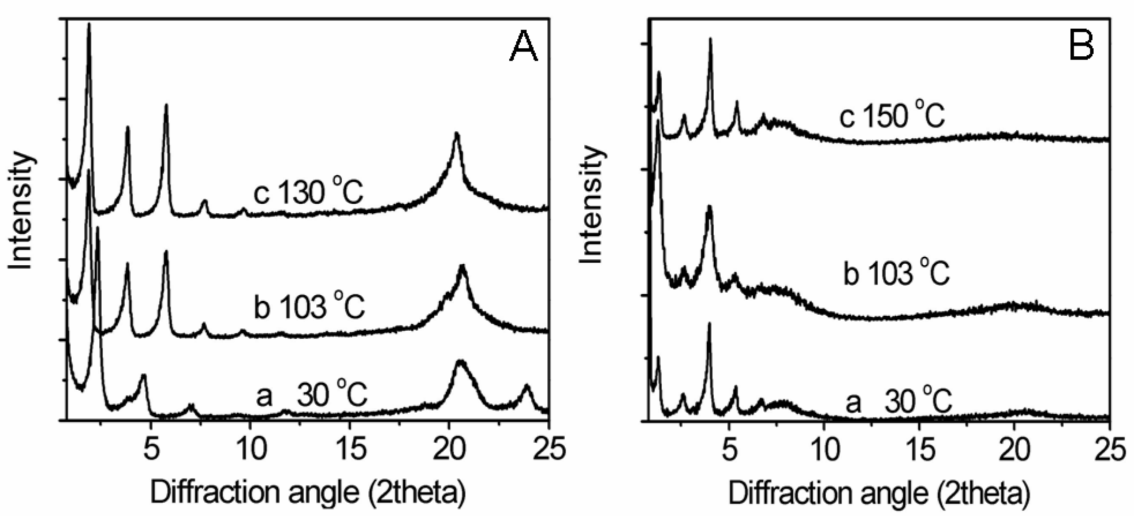


Figure S5. Wide-angle X-ray diffraction spectra of virgin sample L1 (A) and SEC-1 (B) during the first heating process.

Table S3. Estimated layer thickness and lateral distance from X-ray diffraction of L1 and SEC-1.

Sample		Layer spacing (nm)	Lateral distance (nm)
L1	Sm1	4.7	0.44
	Sm2	4.8	0.43
	Cr	4.0	0.42
SEC-1	SmX_1	6.5	0.45
	SmX_2	6.8	0.44
	CC	6.7	0.43