Self-assembly of small molecules: An approach combining electrostatic self-assembly technology with host–guest chemistry

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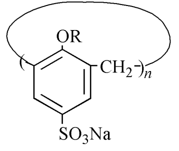
A fluorescence probe study, surface tension and dye solubilization tests indicate that the water-soluble calixarene, 5,11,17,23,29,35,41,47-octosulfonato-49,50,51,52,53,54,55,56-octododecyloxycalix[8]arene (**1**$_8$-C$_{12}$) acts as a "unimolecular" micelle in water. By forming guest–host-type complexes with **1**$_8$-C$_{12}$, lipophilic dyes, such as methyl yellow (MY), *p*-hydroxyazobenzene (HAB) and 1-(*p*-phenylazophenylazo)-2-naphthol (Sudan III), dissolve in aqueous solution. By dipping a charged substrate in the **1**$_8$-C$_{12}$–dye solution and a cationic polyelectrolyte solution alternately, these small molecular dyes were successfully self-assembled into multilayer films.

Fabricating organic ultra-thin films is of great interest due to their potential use in many fields. One important strategy is the so-called Langmuir–Blodgett self-assembly process, which usually requires amphiphilic molecules. Another strategy, the electrostatic self-assembly (ESA) technology,[1] which is based on the electrostatic attraction between opposite charges, was developed by Decher and Hong in 1991.[2] Based on this approach, molecules carrying at least 2 charges, including synthetic polyelectrolytes and charged polypeptide,[3] low molar mass compounds[4] and inorganic nanoparticles,[5] can be self-assembled successfully. Because this method has the advantages of (1) no limit on the size and shape of the substrate and (2) no need for complicated equipment,[4] it has attracted more and more attention in recent years.[1] However, no suitable strategy is available for the self-assembly of low molar mass molecules that are neither amphiphilic nor carrying charges.

Only limited work has been done so far on inclusion chemistry in polyelectrolyte multilayers. Some charged inclusion compounds have been used for electrostatic multilayer build-up.[1,6,7] Neutral hosts can be introduced into the multilayer films using their inclusion complexes with charged guests.[8,9] Calixarenes are cavity-shaped cyclic molecules made up of benzene units. They have received increasing attention during the last decade due to their ability to form host–guest-type complexes with a variety of organic or inorganic compounds and their ready accessibility as well.[10–12] Sulfonated calixarenes **1**$_n$ ($n = 4$, 6, 8) are water-soluble and carry 4, 6 and 8 charges respectively (Scheme 1), so they are suitable to assemble with a cationic polyelectrolyte to fabricate an ultra-thin film. For example, **1**$_6$-C$_{12}$ has been assembled with the cationic polyelectrolyte poly(dimethyldiallyammonium bromide) (PDDA) successfully, and the resulting ultra-thin film shows sensitivity to certain organic vapors as a surface acoustic wave (SAW) device.[6] In addition, Shinkai *et al.* reported that **1**$_6$-C$_{12}$, which bears 6 long hydrophobic alkyl chains, does not act as a common surfactant, but as a "unimolecular" micelle in water.[13] It can form host–guest-type complexes with lipophilic dyestuffs such that the dyestuffs can dissolve in aqueous solution. We think such sulfonated calixarene-dye complexes can also be assembled with a cationic polyelectrolyte, and thus provide a way to assemble low molar mass compounds into an ultra-thin film. This strategy is represented in Scheme 2.



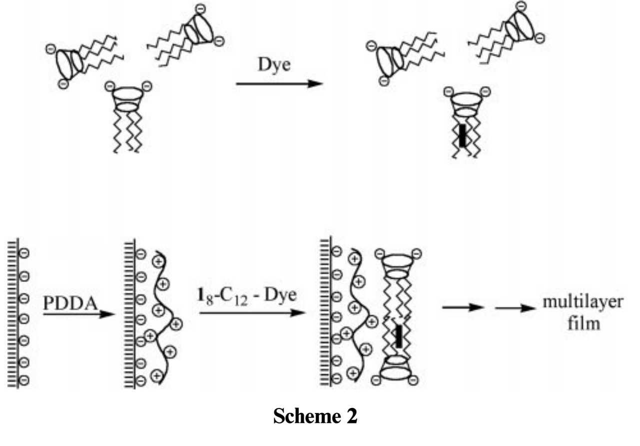
1$_n$: R = H, $n = 4, 6, 8$
1$_6$-C$_{12}$R: $= n$-C$_{12}$H$_{25}$, $n = 6$
1$_8$-C$_{12}$: R $= n$-C$_{12}$H$_{25}$, $n = 8$

Scheme 1

Experimental

Materials and instrumentation

5,11,17,23,29,35,41,47-Octosulfonato-49,50,51,52,53,54,55,56-octododecyloxycalix[8]arene (**1**$_8$-C$_{12}$) was synthesized according to Shinkai *et al.*'s method.[13] The structure and purity of the resulting product were determined spectroscopically. Poly(dimethyldiallyammonium bromide) (PDDA; Aldrich) was used as received. Sodium dodecyl sulfate (SDS) was recrystallized from ethanol twice. The dyes used are methyl yellow (4-dimethylamino azobenzene, MY, $\lambda_{max} = 408$ nm in methanol), *p*-hydroxyazobenzene (HAB, $\lambda_{max} = 348$ nm in methanol), Sudan III [1-(*p*-phenylazophenylazo)-2-naphthol, $\lambda_{max} = 504$ nm in methanol] (all from Aldrich). The fluorescent probe, 4-*N*,*N*-dimethylaminoflavone (DMFV), was donated by Prof. S. K. Wu (Institute of Photographic Chemistry, Chinese Academy of Sciences). Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Surface tensions were measured in pure water at



Scheme 2

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30 °C by the Wilhelmy method. UV-vis spectra were measured on a Shimadzu 2100 spectrophotometer. Atom force microscopy (AFM) measurements were carried out in air at room temperature on a Nanoscopy IIIA (Digital Instruments, Inc.) in the tapping mode. Commercial silicon probes (model TESP-100) with a typical resonant frequency around 300 KHz were used to obtain the images.

Solubilization of dyes

For the solubilization test of MY, excess MY was added to solutions of $\mathbf{1}_8$-C_{12} (0–1 × 10^{-4} M). After stirring for 5 h and then standing overnight, the supernatant liquid was decanted. To determine the concentration of the dye, the filtrate was diluted with ethanol–water (1 : 1 v/v) and its absorbance was measured. The solubilization test of MY in SDS was carried out in the same way. Similarly, the solubilization of HAB and Sudan III was performed by the same method.

Fabrication of $\mathbf{1}_8$-C_{12}–dye/PDDA multilayer films

For the fabrication of self-assembled films, the substrate used was a quartz slide that had been treated in a boiling H_2SO_4–H_2O_2 mixture (7 : 3 v/v) for 30 min before use to create a clean and hydrophilic surface and then rinsed with water thoroughly. It has been verified that the electrostatic self-assembly can be carried out on a hydrophilic glass surface,[14] so no further surface modification was needed. The multilayer films were fabricated by alternately dipping the substrate into the PDDA solution and the $\mathbf{1}_8$-C_{12}–dye solution. In detail, the substrate was first dipped into a solution of PDDA (0.2%) for 2 min. After washing with water thoroughly, it was dipped into a solution of $\mathbf{1}_8$-C_{12} (1 × 10^{-4} M) that had been saturated with dye (after filtering) for 2 min and then washed with water thoroughly. The cycle was repeated until the desired layer number was reached. For the UV-vis measurement the process was interrupted and the sample was air-dried before measurement. The samples for AFM measurements were fabricated on freshly cleaved mica.

Results and discussion

"Unimolecular" micellar behavior of $\mathbf{1}_8$-C_{12}

It is well known that many water-insoluble materials, for example, lipophilic dyestuffs, can dissolve in aqueous surfactant solutions. In the case of an ionic surfactant, the micelles, which involve lipophilic dyestuffs, can be regarded as "macroions", and so may be assembled with a polyelectrolyte carrying the reverse charge. Unfortunately, this strategy is not successful, because the micelle structure will be destroyed in the dry state. Therefore, a "unimolecular" micelle, in which the alkyl chains are connected through covalent bonds and not only by hydrophobic interactions, is needed to meet this target. In this study, we synthesized $\mathbf{1}_8$-C_{12}, an analogue of $\mathbf{1}_6$-C_{12}. First we examined whether it acts as a "unimolecular" micelle in water like its analog.

Fluorescence. A fluorescent probe was used to investigate the aggregation behavior of $\mathbf{1}_8$-C_{12} in water. It has been proved that the fluorescence intensity (I_F) and emission maximum of DMFV show a strong solvent dependence.[15] Fig 1 shows the I_F of DMFV in the presence of various concentrations of $\mathbf{1}_8$-C_{12}. As a comparison, the effect of SDS on the fluorescence of DMFV was also investigated.

In a solution of a common surfactant such as SDS, the I_F of DMFV does not increase significantly until the concentration of surfactant reaches *ca.* 2 × 10^{-3} M, at which point aggregation begins and the probe enters into the hydrophobic microphase. But for $\mathbf{1}_8$-C_{12}, the I_F of the probe increases immediately and no CMC can be observed (see Fig. 1), indicating that it acts as a "unimolecular" micelle. The fluorescence intensity of DMFV increases more significantly in $\mathbf{1}_8$-C_{12}, and the emission maximum of DMFV shifts to shorter wavelength in $\mathbf{1}_8$-C_{12} (λ_{em} = 499 nm) as compared with that in SDS (λ_{em} = 513 nm), indicating that the "unimolecular" micelle of $\mathbf{1}_8$-C_{12} is more hydrophobic due to the fact that the alkyl chains are preorganized *via* covalent bonds.

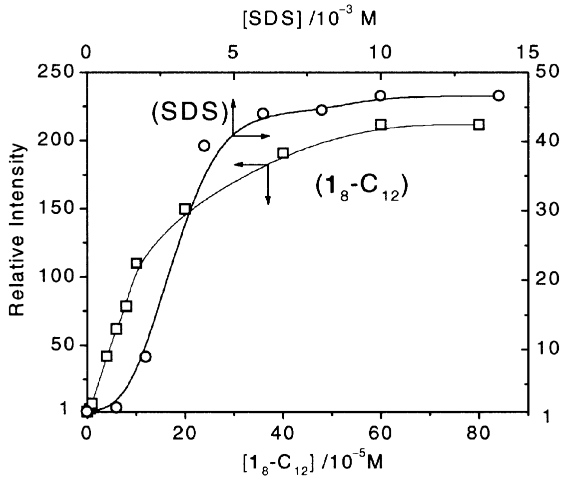

Fig. 1 Relative fluorescence intensity of DMFV (1.5 × 10^{-5} M) in the presence of various concentrations of $\mathbf{1}_8$-C_{12} (□) or SDS (○). λ_{ex} = 360 nm, λ_{em} = 499 nm for $\mathbf{1}_8$-C_{12}, λ_{ex} = 360 nm, λ_{em} = 513 nm for SDS.

Surface tension. Usually the surface tension of water drops upon adding surfactant. The surface tension of an SDS solution decreases gradually with increasing SDS concentration and flattens out at *ca.* 5 × 10^{-3} M, which corresponds to the CMC of SDS. In contrast, the surface tension of the $\mathbf{1}_8$-C_{12} solution is almost the same as that of pure water (Fig 2), indicating that it is not surface-active. This observation also verifies that $\mathbf{1}_8$-C_{12} acts as a monomer or an oligomer rather than forming a monolayer assembly at the air–water interface.[13]

Solubilization of lipophilic dyes. The solubilization of lipophilic dyestuffs is frequently used to evaluate the solubilization power of surfactants. In aqueous SDS, the solubilization of MY was observed only above the CMC and the concentration increased linearly with increasing SDS concentration (Fig. 3). In contrast, the solubilized MY concentration increases with the concentration of $\mathbf{1}_8$-C_{12} linearly from zero $\mathbf{1}_8$-C_{12} concen-

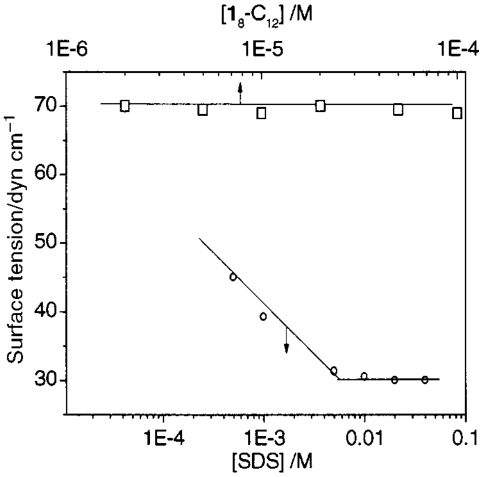

Fig. 2 Surface tension plotted against concentration of $\mathbf{1}_8$-C_{12} (□) or SDS (○).

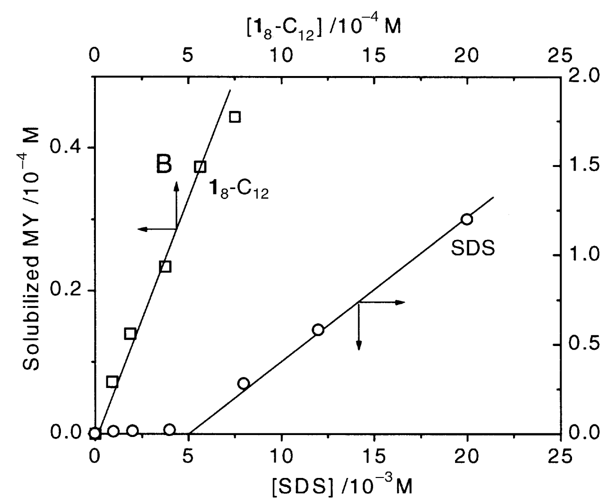

Fig. 3 Solubilization of MY in various concentrations of $\mathbf{1}_8$-C_{12} (□) or SDS (○) at 30 °C.

tration with no threshold effect. This result also suggests that $\mathbf{1}_8$-C_{12} acts as a unimolecular micelle in water.

Self-assembly of dyes

Three lipophilic dyes, HAB, MY and Sudan III, were dissolved up to saturation in $\mathbf{1}_8$-C_{12} solutions ($[\mathbf{1}_8\text{-}C_{12}] = 1 \times 10^{-4}$ M) and then the $\mathbf{1}_8$-C_{12}–dye solutions were used to fabricate self-assembled multilayer films with the cationic polyelectrolyte, PDDA. The processes were monitored spectrometrically, and the results are shown in Fig. 4, 5 and 6, respectively. In all three cases, homogeneous colored films were obtained, indicating that the self-assembly processes were carried out successfully.

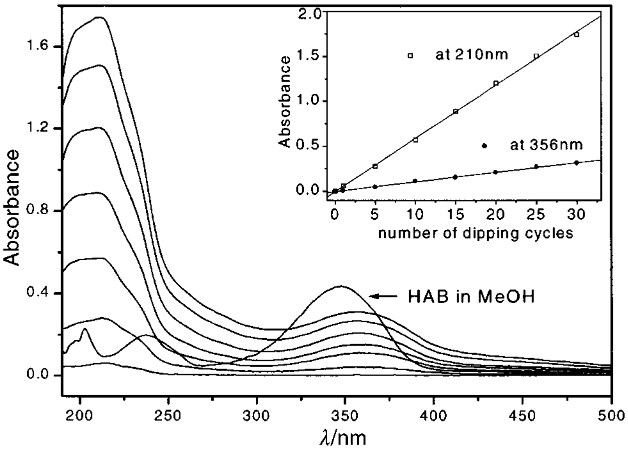

Fig. 4 UV-vis spectra of $\mathbf{1}_8$-C_{12}–HAB/PDDA multilayer films with various dipping cycles. Dipping cycles (from bottom to top): 1, 5, 10, 15, 20, 25, 30. Inset: absorbance at 210 (□) and 356 nm (●) against number of dipping cycles.

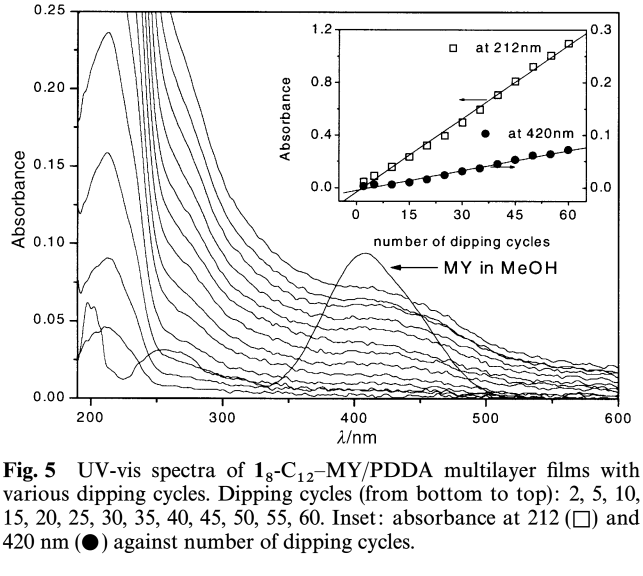

Fig. 5 UV-vis spectra of $\mathbf{1}_8$-C_{12}–MY/PDDA multilayer films with various dipping cycles. Dipping cycles (from bottom to top): 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60. Inset: absorbance at 212 (□) and 420 nm (●) against number of dipping cycles.

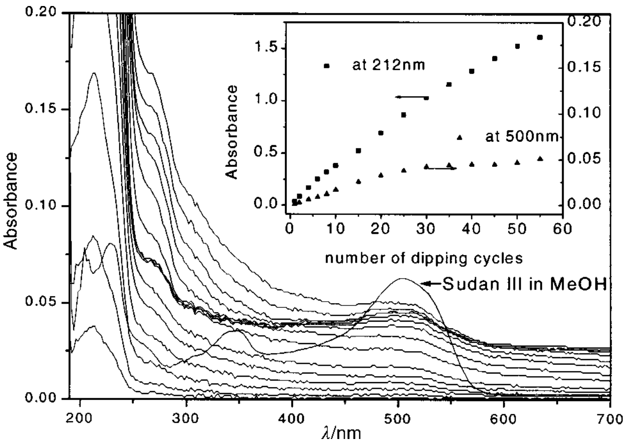

Fig. 6 UV-vis spectra of $\mathbf{1}_8$-C_{12}–Sudan III/PDDA multilayer films with various dipping cycles. Dipping cycles (from bottom to top): 1, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55. Inset: absorbance at 210 (■) and 500 nm (▲) against number of dipping cycles.

In methanol, HAB shows an absorption maximum at 348 nm, which corresponds to a $\pi \rightarrow \pi^*$ first singlet electron transition. In the absorption spectra of the film of $\mathbf{1}_8$-C_{12}–HAB/PDDA, except for the absorption band at 210 nm, which is attributed to the phenyl groups of $\mathbf{1}_8$-C_{12} and HAB, another band appears clearly at 356 nm, which is assigned to be the absorption band of HAB (Fig. 4). This result suggests that HAB has assembled successfully. The increases in the absorbance at both 210 and 356 nm are linear with layer number (see inset), indicating that the fabrication is uniform. It was known that λ_{max} of an azo dye is sensitive to the environment and the aggregation state of the chromophores. From Fig. 4 we can see that λ_{max} of the multilayer film remains constant at 356 nm, regardless of the number of dipping cycles. This means that the environment and the aggregation state of the chromophores in the film does not change in different layers. The absorption band of HAB in the film was red-shifted by *ca.* 8 nm relative to that in methanol. This result suggests that the $\mathbf{1}_8$-C_{12}–HAB complexes may be aligned partially parallel to each other in each layer[8] or that J-like aggregations may form in the film, as reported by other groups,[16–18] since the dye is not necessarily confined to any single calixarene molecule in the hydrogel-like solid film; thus it is possible for the dye molecules to aggregate in a hydrophobic area composed of alkyl chains.

In the case of MY, in addition to the absorption band at 212 nm, a flat absorption band appears in the visible range, suggesting the successful assembly of the dye in the film (Fig. 5). The absorption band at *ca.* 420 nm corresponding to that of MY (λ_{max} of MY in methanol is 408 nm) is not very clear. Two reasons may contribute to the appearance of a flat absorption band. The first is the low ratio of MY to $\mathbf{1}_8$-C_{12}, and the other may be the aggregation of the chromophores. Partial H-aggregations may form in the film, but a considerable amount of nonaggregated dye is present all the same.[17,19] The linear relationship between the absorbance at 210 and 420 nm and the number of dipping cycles indicates reproducible deposition (see inset).

The case of Sudan III appears to be more complex. In agreement with the colored film observed by the naked eye, strong absorption occurs in the visible range up to 550 nm,

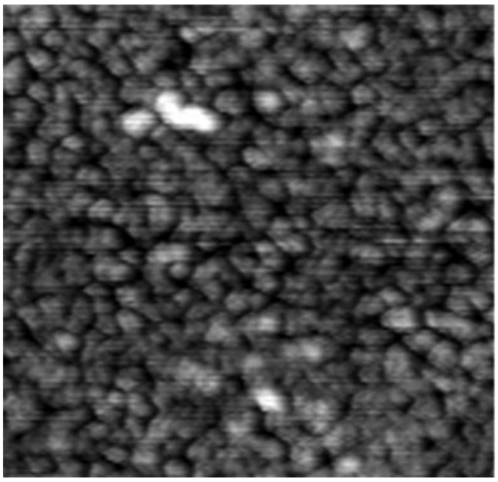

Fig. 7 AFM image of a 4-bilayer $\mathbf{1}_8$-C_{12}–MY/PDDA multilayer film fabricated on mica.

and an absorption maximum appears at about 500 nm corresponding to that of the dye, which shows an absorption band at 504 nm in methanol (Fig. 6), indicating the successful assembly of the dye. Closer observation shows that the absorbance at 212 nm increases nearly linearly with the dipping cycle number, but at 500 nm no such linear relationship was found (see inset). The result suggests that the assembly process is smooth while partial H-aggregation of the chromophore in the film and the extent of the aggregation vary with increasing number of dipping cycles. Similar results have been reported by Laschewsky *et al.*[1,19,20] They found that, due to strong and varying aggregation of the chromophores, the absorption maximum of an ESA film may vary from one adsorption cycle to another.

To study the orientation of the chromophores in the plane, the multilayer films were observed under polarization microscopy. No birefringence between crossed polarizers was observed, indicating that the dyes have an isotropic distribution in the plane.[17] Although dye aggregation may occur in all cases, it does so in a much less than dramatic manner. At the same time, a less defined sublayer structure is characteristic of an ESA multilayer film. So it is not strange that the dyes distribute isotropically in the plane on the macroscopic level.

The surface morphology of the films that were fabricated on mica was determined by atom force microscopy. A typical image is shown in Fig. 7. For the 4-bilayer $\mathbf{1}_8$-C_{12}–MY/PDDA film, the mean roughness was determined to be 2.11 nm, suggesting that the film fabricated by this method is rather smooth.

Conclusion

The water-soluble calixarene $\mathbf{1}_8$-C_{12} acts as a "unimolecular" micelle in water. Lipophilic dyes, such as HAB, MY and Sudan III, have been used to form guest–host-type complexes with the calixarene and dissolve in its aqueous solution. By dipping a charged substrate in the $\mathbf{1}_8$-C_{12}–dye solution and a cationic polyelectrolyte solution alternately, the small molecular dyes were successfully self-assembled into multilayer films.

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