Mixed Monolayers of a Calix[4]resorcinarene with a Nematic Liquid Crystal and Their Bilayered Structuring

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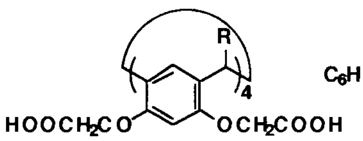
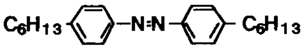
Perpendicular orientation of nematic liquid crystalline azobenzene (C6Azo) on a water surface was demonstrated by spreading a mixture of C6Azo with *O*-octacarboxymethylated calix[4]resorcinarene (CRA-CM) as a host. A host-guest mixed monolayer of C6Azo with CRA-CM formed a double-layered structure by further compression.

Our previous paper described that homogeneous host-guest mixed monolayers on water are formed by spreading a mixture of metal complexes of octaalkoxyphthalocyanines as novel macrocyclic amphiphiles with long-chain normal alkanes.[1] Recently, we have observed that the mixed monolayers are also assembled by mixing the phthalocyanine with nematic liquid crystals (LCs) and suggested that this molecular assembly provides us a novel model system for an ultrathin LC layer at an interface which plays an essential role in the alignment of bulk LC molecules.[2] In this system, a water surface acts as a substrate surface while flat-laid phthalocyanine molecules form an uppermost monomolecular layer which determines the mode of LC alignment.[3] In this respect, the crown isomer of *O*-octacarboxymethylated calix[4]resorcinarenes (CRA-CM) as macrocyclic amphiphiles is much attractive to fabricate the model system for an interfacial ultrathin LC layer, taking into account of the fact that their floating monolayers are very stable on water.[4] This viewpoint has led us to examine the behavior of mixtures of the macrocyclic compounds with a nematic liquid crystal on a water surface. We report here that homogeneous host-guest mixed monolayers are conveniently obtained from *O*-octacarboxymethylated calix[4]resorcinarenes (CRA-CMs) and a liquid crystalline azobenzene, which display bilayered structuring during compression.



R = $C_{11}H_{21}$: 11CRA-CM



C6Azo

4,4'-Dihexylazobenzene (C6Azo) is a monotropic liquid crystal and employed for this study, taking notice of its hydrophobicity. It melts at 37 ~ 38 °C, shows a transition temperature from isotropic to nematic phase at *ca.* 20 °C and crystallizes immediately during a cooling process.[5] Measurements of surface pressure-area (π-A) isotherms were performed on pure water (Milli-Q) filled in a Lauda FW-1 film balance. A spreading solution was prepared by mixing a 1:4 THF and chloroform solution of CRA-CM (*ca.* 10^{-5} mol dm^{-3}) and C6Azo. After the completion of solvent evaporation for 10 min, a monolayered film was compressed at a speed of 25 cm^2 min^{-1}, and the π-A isotherm was recorded. The subphase temperature was controlled at 20 °C where the guest is liquid crystalline. Visible absorption spectra of monolayers on water were recorded by a multi-channel photodiode MCPD-2000 (Ohtsuka Electronics) equipped with a quartz optical fiber.

Figure 1 shows π-A isotherm of 11CRA-CM at 20 °C in the presence of C6Azo in various mixing molar ratios. The shape of π-A isotherm curves of mixed monolayers with homogeneous appearance is not much altered by the addition of C6Azo and consists of three regions during compression; the first rise of surface pressure, a plateau and the second rise.

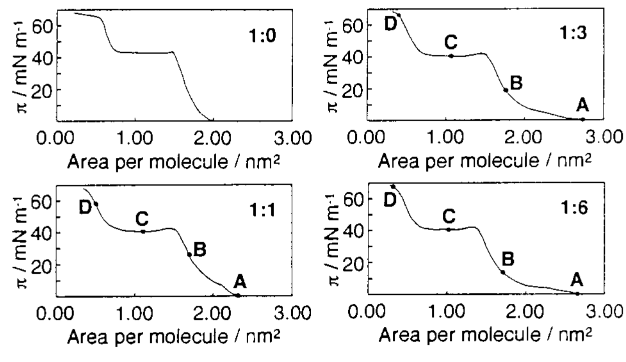


Figure 1. π-A isotherms of 11CRA-CM at 20 °C in the presence of C6Azo in 1:0, 1:1, 1:3, and 1:6 mixing molar ratios, respectively.

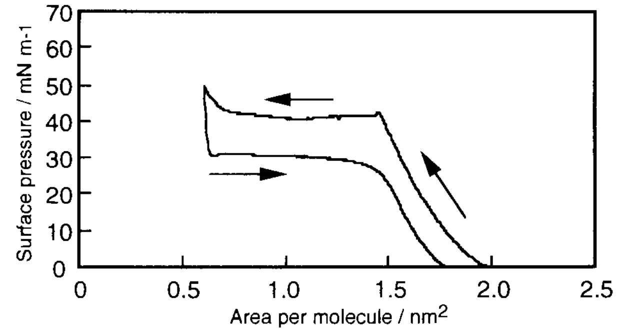


Figure 2. A π-A isotherm of 11CRA-CM at 20 °C during compression and expansion.

The occupied areas of 11CRA-CM estimated from the first and the second steep regions in the π-A isotherms were *ca.* 1.8 nm^2 and 0.9 nm^2, respectively, being in agreement with the base area of the macrocycle and exactly with a half of the base area. As shown in Figure 2, the isotherm for 11CRA-CM was reversible whereas the isotherm on the expansion process showed a slight hysteresis. The UV absorbances of a floating monolayer of 11CRA-CM at the occupied area (*A*) of *ca.* 0.7 nm^2, where the second abrupt increase in surface pressure emerges, is approximately twice of those at the break point of A = 1.5 nm^2. Brewster angle microscope observation (NLE-EMM633; Nippon Laser Electronics) of a floating monolayer showed a homogeneous appearance in the first steep rise whereas bright dots appeared and grew at the plateau region, suggesting layered structuring.[6] These all results indicate that reversible bilayering occurs specifically in the plateau region of a 11CRA-CM monolayer.

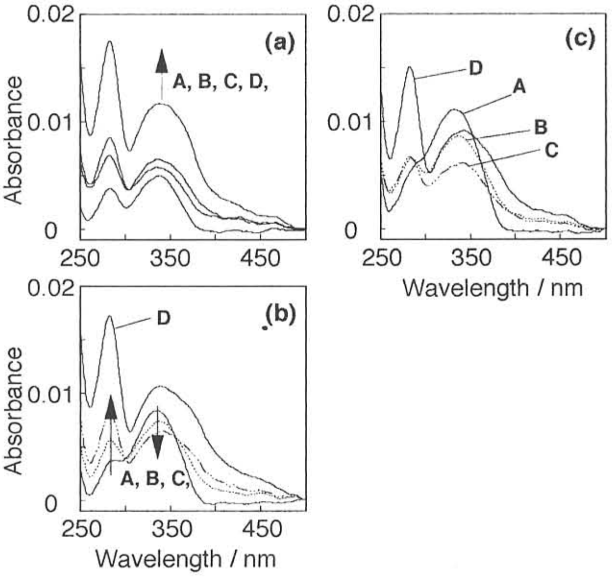


Figure 3. UV-visible absorption spectra of host-guest monolayers of 11CRA-CM and C6Azo in molar ratios of (a) 1: 1, (b) 1:3, and (c) 1:6, respectively, on a water surface before compression (spectrum-A), at the first rise (spectrum-B), at a plateau region (spectrum-C) and just before collapse (spectrum-D). These points are indicated in Figure 1.

The dynamic behavior of mixed monolayers was monitored by their UV absorption spectral changes during compression (Figure 3). There are two major absorption bands at 284 nm due to the calix[4]resorcinarenes and at *ca.* 335 nm due to the azobenzene. It is very likely that the absorption coefficient of 11CRA-CM is not modified during compression since the base of the macrocyclic framework lies flat on water. This fact gives us novel information that a change in the absorbance at 284 nm (OD_{284}) is caused by the alteration of the two-dimensional concentration of 11CRA-CM. An absorbance of C6Azo at 284 nm is relatively small so that A_{284} values can be employed for the rough estimation of two-dimensional concentrations of 11CRA-CM. This situation allows us to assume that OD_{335}/OD_{284} is a qualitative measure of the orientation of the azobenzene where OD_{335} is an absorbance of the azobenzene at λ_{max} = 335 nm. A smaller OD_{335}/OD_{284} suggests the preference of perpendicular orientation of C6Azo. As seen in Figure 3(a) for a 1:1 host-guest mixture, compression results in a linear increase in OD_{284} from spectrum-A through spectrum-C while OD_{335}/OD_{284} decreases gradually. This shows that compression induces a perpendicular reorientation of azobenzene as a guest molecule. It is noteworthy that absorbances in spectrum-D are approximately twice of those in spectrum-C, indicating that a 1:1 host-guest mixed monolayer is double-layered at A = 0.5 nm^2.

UV-visible spectral changes of a 1:3 host-guest mixed monolayer, as shown in Figure 3(b), are different from those of a 1:1 monolayer as follows. A new absorption band centered at *ca.* 380 nm as a shoulder appears during the compression (spectrum-C). This is caused by the J-aggregation of azobenzene molecules because of dense packing. Note that OD_{335} in spectrum-C is smaller than OD_{285} though a 3 molar amount of the azobenzene is mixed. Obviously, this reflects the perpendicular orientation of the azo-chromophore with respect to a water surface. Further compression results in bilayered structuring as revealed by spectrum-D where the absorbance is doubled. A 1:6 host-guest mixed monolayer exhibits spectral changes similar to those of a 1:3 mixed monolayer (Figure 3(c)) except for the more preferential formation of J-aggregates. It should be mentioned that even a 1:12 mixture forms a homogeneous host-guest molecular layer exhibiting a similar π-A isotherm. These results suggest that an excess amount of C6Azo molecules with a perpendicular orientation forms a multi-layered structure on a 11CRA-CM monolayer owing to the long range order of the liquid crystalline guest (Figure 4), just as in the case of octaalkoxyphthalocyanine metal complexes as hosts.[2]

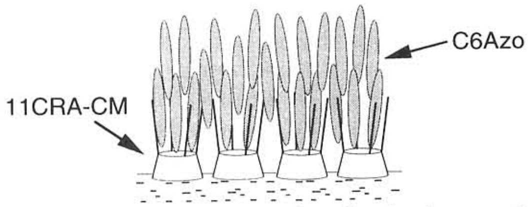


Figure 4. Illustrative presentation of molecular organization of a 11CRA-CM/C6Azo mixed monolayer on a water surface.

In summary, 11CRA-CM acts as an excellent host to include hydrophobic liquid crystalline azobenzene (C6Azo) because of its ability to form stable floating monolayers. Homogeneous host-guest mixed monolayers on a water surface are obtained at a subphase temperature where C6Azo is liquid crystalline and results specifically in the bilayered structuring by further compression.

References

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