Preparation of Monolayers of Ion-Paired Macrocyclic Amphiphiles to Estimate a Critical Free Space Required for Azobenzene Photoisomerization

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A novel family of ion-paired macrocyclic amphiphiles consisting of a tetracationic cyclophane and long-chain sulfonates was developed to form stable monolayers incorporating azobenzene moieties with tailor-made photoisomerizability.

We have proposed the concept of macrocyclic amphiphiles consisting of a cyclic framework with molecular rigidity as a polar head and hydrophobic substituents as tails.[1] We have so far reported disk-shaped metallophthalocyanines substituted with eight alkoxyl chains[2] and crown isomers of calix[4]resorcinarene derivatives with a cylindrical skeleton.[1,3] The uniqueness of this kind of amphiphiles can be summarized as follows. First, owing to the cyclic array of polar sites, the polar and cyclic heads float on water surface in a flat-laid conformation so that occupied areas of the molecules are determined critically by the plane areas of the cyclic skeletons. Consequently, an efficient space as a two-dimensional free space is ensured in a floating monolayer of a macrocyclic amphiphile because a sum of the cross-sectional areas of hydrophobic tails is much smaller than that of the occupied area of the macrocyclic polar head. Second, the existence of suitable free spaces in monolayers leads to the formation of stable hybrid monolayers incorporating normal alkanes[2a] or liquid crystals[2b] as guest molecules and provides an efficient free space required for *E-to-Z* photoisomerization of azobenzenes.[1] Thirdly, macrocyclic amphiphiles, in particular, derived from calix[4]resorcinarenes display effective adsorptivity on polar surfaces to give densely packed, self-assembled monolayers due to the multi-point hydrogen bonding between the polar heads and polar residues on substrate surfaces.[1,3,4]

During our further studies on macrocyclic amphiphiles, a preparative way to a polar macrocycle with different kinds of hydrophobic substituents has been needed to extend our concept for the fabrication of self-assembled monolayers with versatile functionality. We report here a convenient method to prepare floating and transferred monolayers of a novel family of ion-paired macrocyclic amphiphiles assembled by the coulombic interactions between a cyclophane tetracation as a polar and cyclic head and sulfonate surfactants as tails. The sort of hydrophobic tails can be selected by a suitable choice of a mixture of anionic surfactants. Consequently, a critical free space sufficient to the photoisomerization of an azobenzene having a sulfonate in monolayers is available simply by mixing the tetracation with long-chain sulfonates.

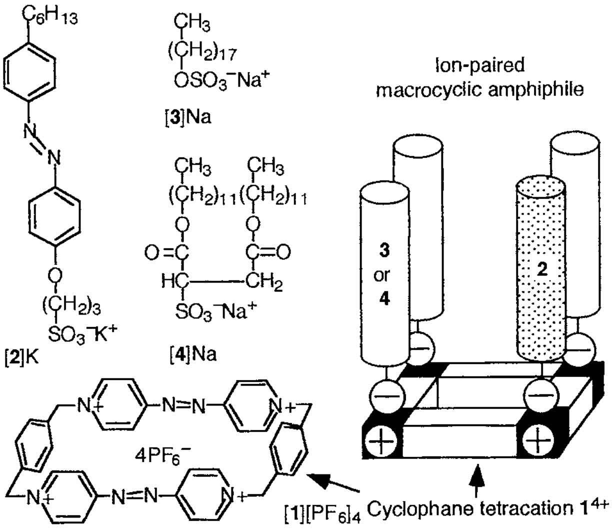

Figure 1. Chemical structures used in this study and an illustration of an ion-paired macrocyclic amphiphile.

We employed the cyclophane tetracation $\mathbf{1}^{4+}$ on account of the following anticipation.[5] First, the cationic and rigid molecular framework consisting of aromatic rings arranged in a face-to-face conformation acts as a novel type of polar and cyclic head, as illustrated in Figure 1, to result in a flat-laid orientation on a water surface when coupled with long-chain sulfonates as hydrophobic tails. Second, an ion-paired complex with less solubility in water is readily prepared by mixing the tetracation with the sulfonates to form a floating monolayer on a water surface.[6] Thirdly, the coulombic interaction is so strong to overcome the hydrophobic interactions of long chains so that functional tails having a sulfonate is incorporated homogeneously in monolayers with any mixing ratios.

Solutions of mixtures of $[\mathbf{1}][PF_6]_4$ and $[\mathbf{2}]K$ in THF/H_2O (v/v 9:1) were spread on a water subphase to be subjected to measurements of π-A isotherms and UV-Vis spectra and Brewster angle microscope observation. Whereas no monolayer was obtained by spreading each component separately, the formation of homogeneous monolayers was observed when solutions dissolving both components were spread on water as a result of an ion-paired complexation. The limiting occupied area of 1.51 nm^2 for a 1:4 mixture of $[\mathbf{1}][PF_6]_4$ and $[\mathbf{2}]K$ was not far from the area of the cyclic framework of $\mathbf{1}^{4+}$ of 1.56 nm^2 which was estimated by a CPK model. A floating monolayer was transferred onto a fused silica plate by the vertical lifting method with a transfer ratio of approximately unity. On the other hand, a floating monolayer prepared from a linear tetracation, 1,1'-[1,4-phenylenebis(methylene)]bis[4-(4-methylpyridinioazo)-pyridinium] hexafluorophosphate and $[\mathbf{2}]K$ was remarkably unstable at a constant surface pressure so that a transferred monolayer was hardly obtained. These results reveal that the cyclic structure with a high rigidity of $\mathbf{1}^{4+}$ plays an essential role in the generation of stable monolayers.

Transferred monolayers were comprised specifically of a 1:4 mixture of $\mathbf{1}^{4+}$ and $\mathbf{2}^-$ ($[\mathbf{1}][\mathbf{2}]_4$), being irrespective of mixing molar ratios, as revealed by the fact that UV absorption spectra of the as-formed mixtures exhibiting λ_{max} at 284 nm and 352 nm due to the azopyridinium of **1** and the azobenzene of **2**, respectively, are essentially identical with the ion-paired complex of $[\mathbf{1}][\mathbf{2}]_4$,

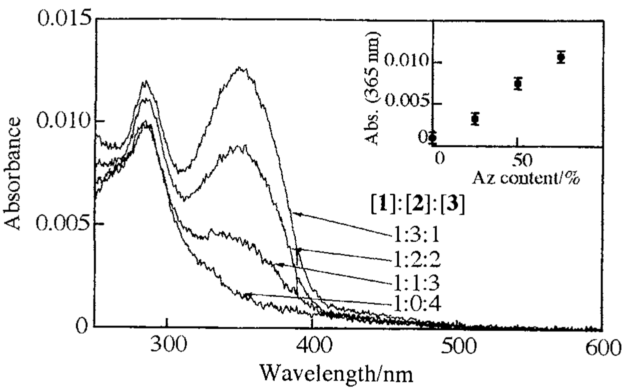

Figure 2. UV-Vis spectra of monolayers of mixtures of $[\mathbf{1}][PF_6]_4$, $[\mathbf{2}]K$ and $[\mathbf{3}]Na$ with different molar ratios transferred on silica plates. The inset indicates absorbance at 365 nm of the monolayers as a function of azobenzene (Az) content.

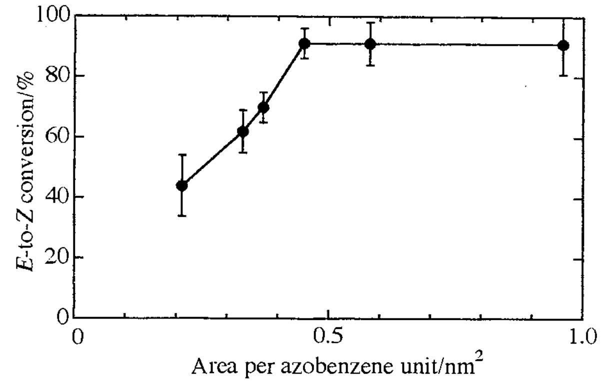

Figure 3. Relationship between *E*-to-*Z* photoisomerizability and remaining molecular area of the azobenzene monoanion **2** in transferred monolayers of ion-paired macrocyclic amphiphiles.

which was isolated and purified. In order to estimate the flat-laid conformation of the cyclic system, a monolayer of a 1:4 ion-paired complex of $[\mathbf{1}][PF_6]_4$ and octadecyl sulfate ($[\mathbf{3}]K$) was deposited on a silica plate. Polarized absorption spectra of the complex recorded by probe light at an incident angle of 45° suggested that the azopyridinium moieties of $\mathbf{1}^{4+}$ orient in parallel with the substrate plane because the oblique transmittance change ratio of $\Delta T_s/\Delta T_p$[7] at 284 nm was about 1.5, as has been reported by Orrit *et al.*[8]

It was confirmed that photoisomerization of $[\mathbf{1}][PF_6]_4$ is thoroughly suppressed even in solution owing to the steric effect. Photoirradiation of a transferred monolayer of the $[\mathbf{1}][\mathbf{2}]_4$ with 365 nm light resulted in the formation of 74% *Z*-isomer of **2**.[9] The *E-to-Z* photoisomerizability as high as that observed for the alternative macrocyclic amphiphiles, calix[4]resorcinarenes,[1c] suggests that the rigid cyclophane structure as a polar head guarantees a free space required for the photoisomerization in monolayers. To manipulate free spaces surrounding the azobenzene moiety of $\mathbf{2}^-$ in monolayers of the tetracation **1**, the azobenzene sulfonate $\mathbf{2}^-$ was replaced partially by the single-chain anion $\mathbf{3}^-$ or the double-chain sulfonate $\mathbf{4}^-$ to form ternary component systems. In both cases for $\mathbf{3}^-$ and $\mathbf{4}^-$, absorbances at 352 nm due to the azobenzene were linearly reduced as the increase of fractions of $\mathbf{3}^-$ or $\mathbf{4}^-$. Figure 2 shows UV-Vis spectra of transferred monolayers of the ternary systems comprised of $\mathbf{1}^{4+}$, $\mathbf{2}^-$ and $\mathbf{3}^-$ with various molar ratios as an example. No shift of the π,π^*-absorption band in monolayers enabled us to estimate *E-to-Z* photoisomerizability in these monolayers. As the fraction of the alkyl chains increased, the *E-to-Z* photoisomerizability was enhanced in monolayers containing single-chain $\mathbf{3}^-$, while it was reduced by the incorporation of the double-chain $\mathbf{4}^-$. Figure 3 summarizes the *E-to-Z* photoisomerizability as a function of free spaces for each azobenzene moiety in monolayers, which were calculated under the estimation that the occupied areas of $\mathbf{1}^{4+}$, $\mathbf{2}^-$, $\mathbf{3}^-$ and $\mathbf{4}^-$ are 1.56 nm^2, 0.25 nm^2, 0.20 nm^2 and 0.45 nm^2, respectively, according to CPK models. As seen in Figure 3, the sufficient conversion into Z-isomer levels off at 0.45 nm^2 per azobenzene unit, indicating that the *E-to-Z* photoisomerizability in monolayers requires this critical two-dimensional free volume. The value of 0.45 nm^2 is considerably consistent with the occupied area of Z-isomer estimated by the CPK model of **2** whose hexyl moiety orients perpendicular to the substrate plate.

In conclusion, a simple way to prepare novel monolayers enabling the manipulation of the photoisomerizability of azobenzenes has been developed by using ion-paired macrocyclic amphiphiles consisting of the tetracationic cyclophane as a rigid molecular building block. A critical free space of 0.45 nm^2 required for the *E-to-Z* photoisomerization of *p*-hexylazobenzene in densely packed monolayers was estimated by using ternary ion-paired macrocyclic amphiphiles containing long-chain alkyl anions as two-dimensional diluents. The present results provide novel information for designing photoresponsive thin films to fabricate optical,[10] electrical[11] and electrochemical[12] photoswitching devices.

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