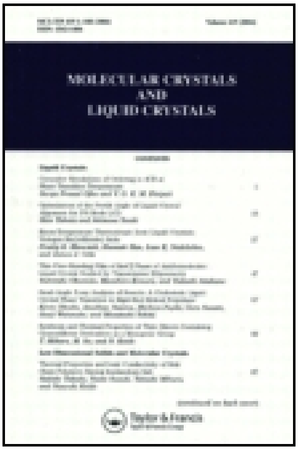

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Spatially Controlled Photoisomerizability of Azobenzene Moieties in Langmuir-Blodgett Monolayers of Ion-Paired Macrocyclic Amphiphiles

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Monolayers of ternary ion-paired macrocyclic amphiphiles consisting of a tetracationic cyclophane and two kinds of sulfonate surfactants with an azobenzene unit and either a single or double long chain alkyl unit were prepared by a Langmuir-Blodgett technique to elucidate the structure/property relation between a free space surrounding an azobenzene moiety and photoisomerizability in monolayers. It was found that an azobenzene unit with a hexyl group needs a minimum occupied area of about 0.5 nm^2 for sufficient *E/Z* photoisomerization.

Keywords: azobenzene; Langmuir-Blodgett; monolayer; macrocyclic amphiphile; electrostatic interaction

INTRODUCTION

Photochromic azobenzene (Az) underwent *E/Z* photoisomerization accompanying the alteration of a dipole moment so that a substrate surface binding Az exhibits reversible light-induced changes in surface energies such as wettability changes.[1] *E/Z* photoisomerizability of Az in prototypes of self-assembled monolayers (SAMs) and Langmuir-Blodgett (LB) monolayers is suppressed owing to their densely packed organized structures, since the Az requires a free volume for the photoisomerization. To improve the level of alteration of surface energies by light, a structural design to optimize monolayer organization of Az should be carried out. Our recent approach to use calix[4]resorcinarene derivatives as macrocyclic amphiphiles realizes excellent photoisomerizability of Az even in SAMs and LB monolayers.[2-4] The macrocyclic amphiphiles possess a rigid cyclic framework bearing a polar array and hydrophobic substituents as tails so that the cyclic polar heads orienting in a flat-laid manner determine precisely their monolayer structuring. This situation ensures a free space required for the photoisomerization of Az located at hydrophobic tails, because of a sum of cross-sectional areas of the tails sufficiently smaller than an occupied area of the cyclic framework.

Based on the concept of macrocyclic amphiphiles, we have recently developed a simple way to modify a polar macrocycle with various kinds of hydrophobic tails through coulombic interactions.[5] The ion-paired macrocyclic amphiphile with a cyclophane tetracation **1** as a polar head and Az-containing sulfonate surfactants **2** as tails was simply prepared at the air-water interface. A transferred monolayer of the amphiphile possesses Az units without aggregation and exhibits *E*-to-*Z* photoisomerizability of 74 % due to electrostatic anchor overcoming van der Waals interactions among Az units. We noticed,

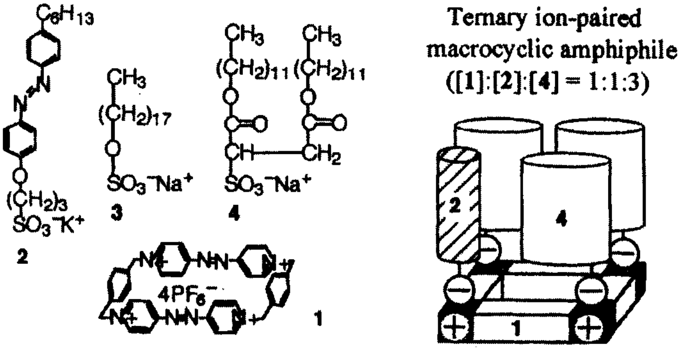

FIGURE 1 Chemical structure of compounds and schematic representation of a ternary ion-paired macrocyclic amphiphile.

however, that a level of 74 % of the *E*-to-*Z* photoisomerization in the monolayer is lower than that in solution (92 %). This fact lets us to control a free space of Az according to the concept of macrocyclic amphiphiles.[2] If a molecule with a larger cross-sectional area compared with Az coexists homogeneously in a monolayer, the photoisomerizability of **2** should be suppressed owing to the decrease of a free space. For this purpose, we chose two kinds of sulfonate surfactants of a single long-chain **3** as a slender molecule and of a double long-chain **4** as a fat molecule; **3** and **4** have a cross-sectional area of 0.20 nm^2 and 0.45 nm^2, respectively, while Az has that of 0.25 nm^2, as estimated by a CPK model. We report here the effect of a free space in LB monolayers on *E*-to-*Z* photoisomerizability by using a family of the ternary ion-paired macrocyclic amphiphiles consisting of **1**, **2** and either **3** or **4**. The structure/property relation leads to the evaluation of a minimum free space of Az for the photoisomerization.

EXPERIMENTAL

Tetracationic cyclophane **1** and Az-containing sulfonate **2** were prepared according to our previous papar.[5] **3** (Aldrich) and **4** (Sogo Pharmaceutical) were used after recrystallization from methanol and ethyl acetate, respectively.

Monolayers of ternary ion-paired macrocyclic amphiphiles consisting of **1**, **2** and either **3** or **4** were prepared by spreading solutions containing them on a pure water subphase employing a Lauda film balance (FW-1). Monolayers compressed at 0.5 mN m^{-1} were transferred on a hydrophilic silica plate by a vertical lifting method. Az contents of **2** in the ternary monolayers were controlled by varying molar ratios of **2** in the spreading solutions.

Absorption spectra were taken on a weak absorption spectrophotometer (MAC-1, JASCO). Ultraviolet light at 365 nm was obtained by passing light from a 500-W ultra-high pressure mercury arc (Ushio) through suitable glass filters (Toshiba).

RESULTS AND DISCUSSION

Transferred monolayers of ternary ion-paired macrocyclic amphiphiles with different contents of **2** were prepared by a Langmuir-Blodgett technique. A maximum absorption wavelength of **2** at 352 nm in each monolayer is well consistent with that in solution, indicating that the Az units exhibit a monomeric state without aggregation even in the monolayers. The controllability of Az contents in the monolayers was confirmed by absorption spectral measurements monitoring absorbances of Az. Absorbances ascribed to an Az unit of **2** toward an absorbance at 284 nm due to the azopyridinium units of **1** as an internal reference increased in a linear manner with the increase in molar ratios of **2** in spreading solutions in both monolayers containing either **3** or **4**. These results suggest that surface density of the monomeric Az is controllable simply by varying molar ratios of **2** in spreading solutions. Therefore, it is anticipated that the homogeneous monolayer formation and the control of Az density lead to the control of a free space for Az to affect the photoisomerizability.

Upon irradiation with 365 nm light, the Az of **2** in the monolayers underwent *E*-to-*Z* photoisomerization. The levels of photoisomerizability at photostationary states determined by changes in absorbances at 365 nm before and after photoirradiation are summarized in Table 1. Monolayers containing **3** displayed high photoisomerizability comparable to that in solution, while the photoisomerizability is suppressed by the increase in molar ratios of the fat molecule **4**. These results indicate clearly that the photoisomerization of **2** is regulated by changes in free spaces for Az due to the coexistence of **3** or **4**.

TABLE 1 Photoisomerizability of Az in monolayers.

Molar ratio	*E*-to-*Z* photoisomerizability/%	
	[1]:[2]:[3]	[1]:[2]:[4]
1:4:0	74 ± 6	74 ± 6
1:3:1	91 ± 3	70 ± 3
1:2:2	91 ± 5	62 ± 5
1:3:1	91 ± 7	44 ± 7

To comprehend the structure/property relation between a free space of Az and photoisomerizability in the monolayers, we estimated a two-dimensionally remaining molecular area of **2** by a CPK model under the assumption that **1**, **3** and **4** possess a cross-sectional area of 1.56 nm^2, 0.20 nm^2 and 0.45 nm^2, respectively. As seen in FIG. 2, the *E*-to-*Z* photoisomerizability plotted as triangles declines sharply at an occupied area of **2** of about 0.5 nm^2.

We attempted another way to estimate a cross-sectional area of each molecule. Taking into account the fact that an absorbance at 284 nm corresponding to the azopyridinium units of **1** is irrespective of the chemical composition of the monolayers, we estimated an occupied area of **1** to be 2.02 ± 0.08 nm^2 by spectral measurement of a monolayer consisting of **1** and **3**. The occupied areas of **3** and **4** were considered

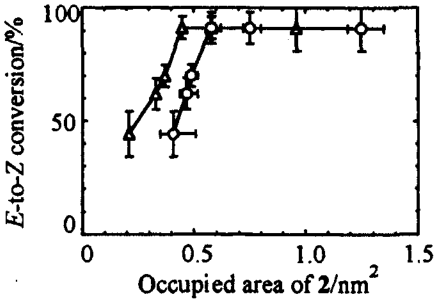

FIGURE 2 *E*-to-*Z* photoisomerizability of **2** in ternary monolayers as a function of occupied area of **2** estimated by a CPK model (triangle) and UV-Vis spectral analysis (circle).

to be 0.25 nm^2 and 0.53 nm^2, respectively, on the basis of the relation between a volume at 20 °C and a layer length of corresponding n-alkanes in a fluid state.[6] Using the occupied area of each molecule, we obtained the correlation between free molecular area of **2** and photoisomerizability as depicted in FIG. 2 as circles. In a manner quite similar to the estimation by a CPK model, the photoisomerizability decreased at an occupied area of around 0.5 nm^2. The value of 0.5 nm^2 is well consistent with an occupied area of *Z*-isomer of **2** which possess a hexyl group orienting perpendicularly to a substrate surface. We conclude consequently that the Az unit with a hexyl group requires a minimum free molecular area of 0.5 nm^2 for *E/Z* photoisomerization in densely packed LB monolayers.

CONCLUSION

We displayed that an Az unit requires a critical free occupied area of approximately 0.5 nm^2 for sufficient *E/Z* photoisomerization in monolayers, which can be deduced from a novel approach of controlling a free space of Az spatially by using a family of ternary ion-paired macrocyclic amphiphiles. This value may be helpful to design monolayer organizations exhibiting versatile photofunctional properties such as light-induced control of surface energy with improved efficiencies.

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