Monolayers of Calix[4]resorcinarenes with Azobenzene Residues Exhibiting Efficient Photoisomerizability

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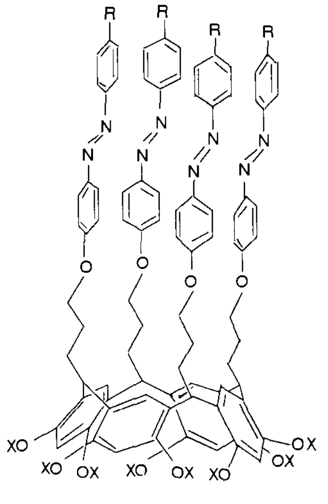
Azobenzenes tethered from the lower rim of crown conformer of *O*-octacarboxymethoxylated calix[4]resorcinarenes display efficient E-to-Z photoisomerizability in densely packed monolayers on a water surface, in LB films and in surface-adsorbed monolayers, respectively.

Molecular layers incorporating photochromic moieties have been attracting increasing interest in conjunction with photofunctionalization of material surfaces including the photoregulation of various functionalities[1] and alignment of liquid crystals.[2] Azobenzenes have been employed extensively for these purposes owing to their good availability and reasonable photofatigue-resistance. However, problems arise from the fact that *E*/*Z* photoisomerization of the chromophores is accompanied by a relatively large sweep volume so that the geometrical photoisomerization takes place hardly in LB films of long-chain amphiphiles incorporating an azobenzene unit.[3] The photoisomerizability in densely packed films has been so far ensured by using polymeric chains as hydrophilic head groups[4,5] or bulky hydrophilic head groups,[6] cyclodextrin inclusion complexes[7] and by mixing of amphiphilic azobenzenes with a shorter alkyl surfactant.[8]



1: R = $CH_3(CH_2)_3$-
X = H

4a: R = H
X = CH_2COOH

4b: R = cydohexyl
X = CH_2COOH

Taking notice of a unique structure of the crown isomer of calix[4]resorcinarene (CRA), we prepared CRA crown isomer (**1**) substituted with four azobenzenes at its lower rim and examined the photoisomerizability in densely packed monomolecular layers.[9] Though the base area of CRA (*ca.* 1.3 nm^2) is larger than that of the cross-sectional area of four azobenzenes (*ca.* 1.0 nm^2), the extent of *E*-to-*Z* photoisomerization is still restricted in a densely packed monomolecular layer. We report here that azobenzenes tethered from an octacarboxymethoxylated CRA (CRA-CM) skeleton, which possesses a larger base area of *ca.* 1.7 nm^2, exhibit efficient photoisomerizability even in densely packed monolayers.

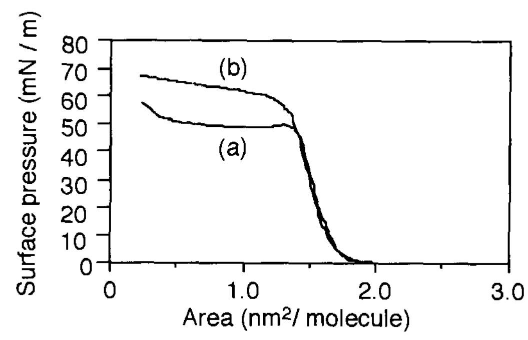


Figure 1 Surface pressure/area isotherms of (a) **4a** and (b) **4b** on water at 20 °C.

CRA-CM with four 3-chloropropyl residues (**2**)[10] was converted into the corresponding 3-iodopropylated CRA-CM (**3**),[11] followed by the reaction with a 4-hydroxyazobenzene and alkaline hydrolysis to give an amphiphilic CRA-CM (**4**) having unsubstituted (**4a**)[12] or *p*-cyclohexylated azobenzenes (**4b**),[13] respectively.

Figure 1 shows π-A isotherms of **4a** and **4b**, both of which agree with each other except for collapse pressures. A higher collapse pressure for **4b** is evidently due to the introduction of cyclohexyl substituent which shows a cross-sectional area similar to that of azobenzene. The occupied areas are estimated to be 1.7 nm^2 and prominently in line with those of crown conformers of CRA-CM substituted with long-alkyl chains at the lower rim instead of azobenzenes.[14] This indicates that an occupied area of CRA derivatives on a water surface is practically determined by the base area of CRA framework irrespective of the nature of substituents at the upper rim.

Figure 2 shows absorption spectra of **4a** and **4b** on a water at various surface pressures. It is worthy to stress that both of absorbance and wavelength at λmax = *ca.* 350 nm are not altered at all during surface compression for both derivatives. This makes a sharp contrast to our previous observation that **1** with an occupied area of 1.3 nm^2 displays a considerable blue shift of the π, π*-absorption band due to the H-aggregation during compression.[9] Figure 2 tells us also that λmax of **4** in monolayers is very close to that in solution, informing that essentially no aggregation is formed even in densely packed monolayers. Observation with Brewster angle microscopy revealed that monolayers of both **4** on a water subphase exhibit a homogeneous appearance during compression. These all results draw the conclusion that **4** forms quite stable monolayers on water while the occupied areas are strictly determined by the area of the hydrophilic upper rim of the cyclic skeleton so that molecular interactions among the chromophores are effectively suppressed.

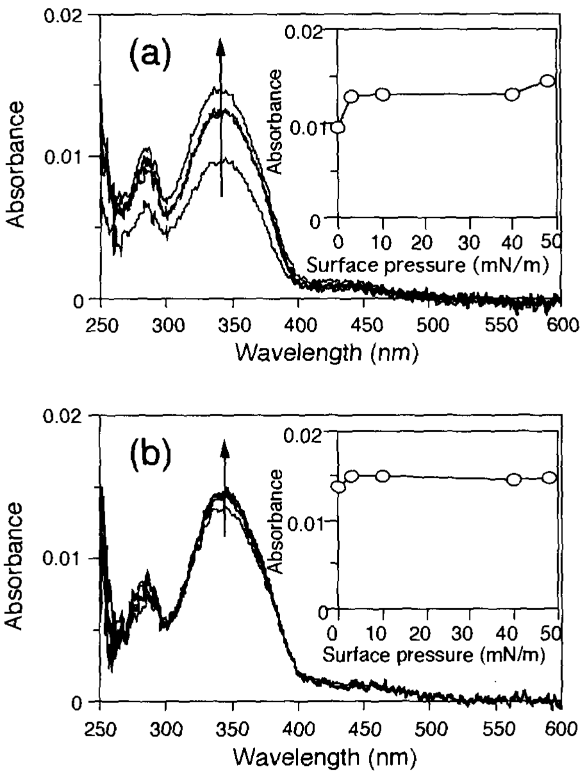


Figure 2 Spectral changes of (a) **4a** and (b) **4b** on a water surface at various surface pressures. Each inset shows absorbances at λmax as a function of surface pressure.

Aiming at approaching to our final goal to achieve surface-assisted photocontrol of liquid crystal alignment,[2] monolayers of **4** on substrate plates were prepared by the following two methods; Langmuir-Blodgett (LB) deposition and an adsorption technique from a solution.[10] LB film deposition was carried out using a Lauda film balance at 20 ± 1 °C . Monolayers were transferred onto cleaned quartz substrates by vertical dipping at a surface pressure of 20 mN min^{-1}. Surface adsorption of **4a** and **4b** was carried out by immersing cleaned quartz plates in a 2-butanone solution under gentle shaking at 60 °C, followed by rinsing out in pure 2-butanone shortly. Occupied areas of **4a** and **4b** adsorbed on a quartz plate was estimated spectroscopically to be 1.9 nm^2 and 2.0 nm^2, respectively.

Table 1 summarizes the *E*-to-*Z* photoisomerizability of azo-chromophores of **4a** and **4b** upon irradiation with 365 nm light in monolayers on a water surface, in LB films and in adsorbed monolayers, respectively. All of monolayers display reasonable photoisomerizability irrespective of the methods for assembling monomolecular layers. This is evidently owing to the macrocyclic structure of **4**, the occupied areas of which are determined by the upper rim with the eight polar substituents.

Table1. The level of *E*-to-*Z* photoisomerization in CRA-CM monolayers

Monolayer	Content of Z-isomer[a] 4a	Content of Z-isomer[a] 4b
On a water surface[b]	61	59
LB film	73	72
Adsorbed film	87	85
In THF[c]	99	99

a) At photostationary states upon irradiation with 365 nm light.
b) At a surface pressure of 10 mN/m.
c) Solution photochemistry.

These facts indicate that CRA-CM derivatives provide a promising way to assemble well-defined monomolecular layers embedding photoreactive moieties.

References and Notes

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10 A solution of 2,8,14,20-tetrakis(3-chloropropyl)-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene, ethyl bromoacetate and potassium carbonate in acetone was refluxed under nitrogen for 24 h, followed by conventional work-up to give colorless crystals of mp 110.0-110.5 °C in a 79% yield.
11 A solution of **2** and sodium iodide in 2-butanone was refluxed for 12 h to give a product which was purified by silica gel column chromatography and recrystallization from 2-propanol. Colorless crystals of mp 128-129 °C in a 90% yield.
12 A mixture of **3** and *p*-hydroxyazobenzene and potassium carbonate in DMF was stirred for 12 h at room temperature, followed by a conventional work-up to give the corresponding octaester of **4a** as orange crystals of mp 75-76 °C in a 85% yield. The octaester was stirred in a mixture of THF and an aqueous solution of KOH for 1.5 h at room temperature to give an orange solid of mp 220-222 °C in a 82% yield.
13 A similar method for the preparation of **4a** was applied to obtain **4b** as orange crystals of mp 228.5-230 °C in a 68% overall yield.
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