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Interfacial Behaviors of Azocalixarene Derivatives at the Air / Water Interface and Photochromism in the Langmuir-Blodgett Films

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Abstract: The interfacial behaviors of the non-typical amphiphilic compound *p*-methylphenylazocalix[4]arene **1** and *p*-chlorophenylazocalix[4]arene **2** at the air/water interface and photochromism in the Langmuir-Blodgett films were studied by surface pressure-area isotherm and UV-Vis spectra. The results indicate that they can form stable monolayers at the air / water interface although they have no hydrophobic alkyl chains, and their LB film underwent reversible *trans-cis* photoisomerization on UV and daylight illumination.

Keywords: Azocalixarene, photochromism, monolayer, LB film.

The azocalixarenes is a novel chromogenic compound and their spectra properties have been reported. A number of them have been applied as selective ionophores in extractive process[1] or as selective ligands in ion selective electrodes and optical sensors based on spectra changes[2]. Some amphiphilic azocalixarene derivatives with hydrophobic long alkyl chains were synthesized and their interfacial behaviors at the air / water interface have also been investigated[3]. However, the photochromism of the azocalixarene derivatives in LB film has not been reported. In present work, the compounds 5, 11, 17, 23-tetrakis-[(4-methylphenyl)azo]-25, 26, 27, 28-tetrahydroxy calix[4]arene **1** 5, 11, 17, 23-tetrakis-[(4-chlorophenyl)azo]-25, 26, 27, 28-tetrahydroxy calix[4]arene **2** (**Figure1**) were prepared by the diazo-coupling of calix[4]arene and *p*-methyl or *p*-chloro phenyl diazonioms in non-aqueous solution, respectively. The compounds **1** and **2** were characterized by ^{1}H NMR, ^{13}C NMR, MS, IR and elemental analysis[4]. We found that **1** and **2** can form stable monolayers at the air / water interface although they have not hydrophobic alkyl groups. And the experiments by UV absorption spectra observations showed that the LB film underwent reversible *trans-cis* photoisomerization on UV and daylight illumination.

When compounds **1** and **2** were spread from chloroform solution onto water surface respectively, stable monolayers can be formed. **Figure 2** showed π-A isotherms of **1** and **2** monolayers on pure water. It is observed that both no compressed plateau and the

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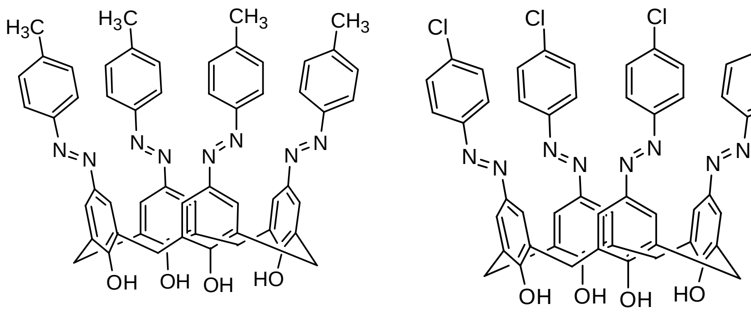
limiting molecular area are 0.30 and 0.35 nm^2/molecule. And **1** and **2** monolayers have higher surface pressure (above 60 mN/m). According to the proposal of Coleman[5], when the molecular area is under 0.65 nm^2, calix[4]arene molecules may take an orientation parallel to the air-water interface. Obviously, azocalixarene derivative **1** and **2** orient parallel at the air-water interface. Why can form their stable monolayers? At wood has reported that the bipolar amphiphilic calixarene without hydrophobic alkyl chains can self-organized to form two-dimensional bilayers in aqueous solution due to arene π-π stacking interaction[6]. The reason of azo calix[4]arenes **1** and **2** monolayers can also ascribed to arene π-π stacking interaction.

The photoisomerization of azo compound can be easily detected by the UV-Vis absorption spectra because the *cis* and *trans* configuration change also caused the change of the absorption spectra[7]. **Figure 3** and **Figure 4** show UV-Vis absorption spectra of the LB films of azocalixarene derivatives **1** and **2**, respectively. It is clearly seen that the absorptions remarkably decrease after illumination at 365 nm for 30 min. It implies that the *trans*-to-*cis* photoisomerization has been preceeded. Then the absorptions obviously increase after the illumination with daylight for 30 min. It means that the *cis*-to-*trans* photoisomerization proceeded to some extent. These phenomena indicated

Figure 1 The structures of azocalixarene **1** and **2**



1 **2**

Figure 2 π-A isotherms of the monolayers of **1** and **2**: (a) **1** on the surfaces of pure water (b) **2** on the surfaces of pure water

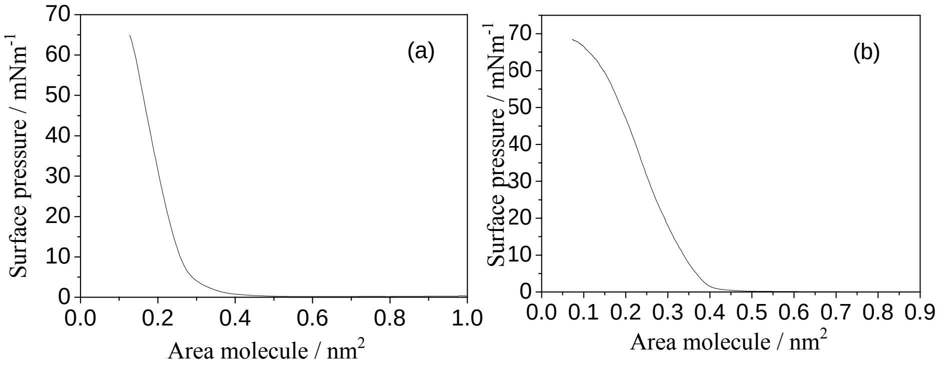


Figure 3 Change of absorption spectrum of LB films of 1(18-layer) on quartz before (A) and after (B) illumination at UV 365 nm for 30 min and and illumination with daylight for 30 min (C).

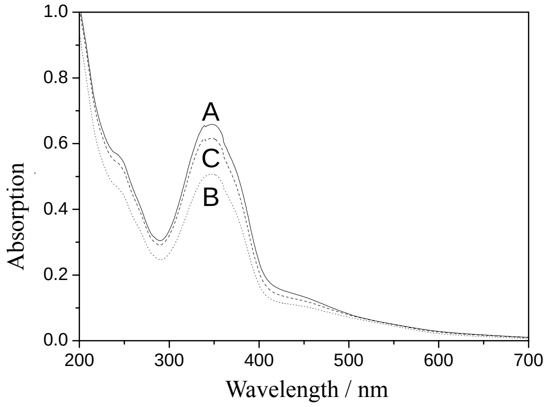
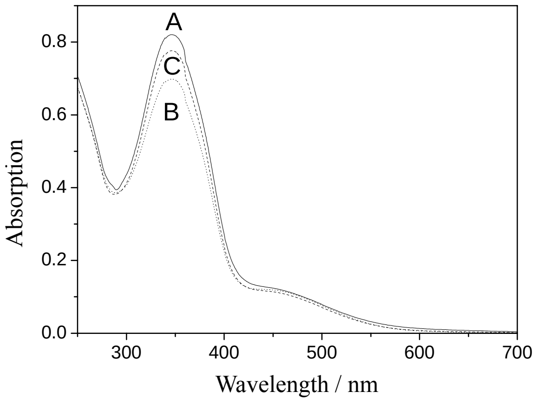


Figure 4 Change of absorption spectrum of LB film of 2 (30-layer) on quartz before (A) and after (B) illumination at UV 365 nm for 30 min and then after illumination with daylight for 30 min (C).



that the *trans*-to-*cis* and *cis*-to-*trans* photoisomerization of both **1** and **2** in the LB films is reversible on illumination at UV 365 nm and daylight.

In conclusion, the non-typical amphiphilic azocalixarene derivatives can form stable monolayers at the air / water interface although without long alkyl chain, and the LB films can undergo reversible *trans*-*cis* photoisomerization on illumination at 365 nm and daylight.

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