Negative Photochromism of a Spiropyran in a Langmuir–Blodgett Film

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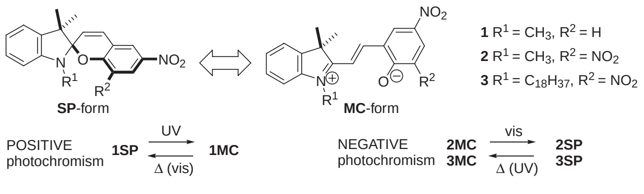
An indolinospiropyran possessing one long alkyl chain on the nitrogen atom of the indoline moiety and two nitro groups on the benzopyran ring, exhibiting negative photochromism in various organic solvents, showed negative photochromism in a Langmuir–Blodgett film. The change in the surface appearance was observed by atomic force microscopy after the visible light irradiation.

Photochromism is regarded as the switch of structures and properties of a molecule and a molecular assembly accompanied by a large change in absorption spectrum triggered by photoirradiation.[1] Organic photochromic compounds can be classified into two groups: one is thermally irreversible, exemplified by fulgides,[2] diarylethenes,[3] phenoxynaphthacenequinones,[4] and arylbutadienes.[5] The other is a rather larger group of thermally reversible ones,[6–8] including spiropyrans, naphthooxazines, naphthopyrans, azobenzenes, hexaarylbisimidazoles, and so on. Spiropyrans,[9] like **1**, are known as one of the representatives of the thermally reversible photochromic compounds. Upon UV light irradiation to the spiro form (**1SP**), the bond between the spiro carbon atom and the oxygen atom is cleaved to generate the colored zwitterionic merocyanine form (**1MC**). When the UV light irradiation is stopped and the sample is placed in the dark, the photogenerated **1MC** returns to the colorless **1SP** thermally (Scheme 1). This type of thermally reversible photochromism is called "positive photochromism" in this text.

When the environment of a spiropyran is highly polar, or when additional substituents which stabilize the zwitterionic MC form are attached on its π-conjugation system, as **2** for example, the colored MC form is more stable than the colorless SP form. In these cases, irradiation of visible light causes decoloration of MC to generate SP form. When SP form is placed in the dark, it returns to the colored MC form. Therefore, this thermally reversible photochromic system does not need the irradiation of UV light for its photochromism which may cause degradation of the compound,[10] though irradiation of UV light to the colorless form accelerates the rate of regeneration of the colored MC form (Scheme 1). It is called "negative photochromism."

If a long alkyl chain is introduced on the nitrogen atom of the indolium moiety of **2MC**, it then has a hydrophobic functional group as well as the hydrophilic zwitterionic moiety, as exemplified by **3**. Although the arrangement of these functional groups may be suitable to form Langmuir–Blodgett (LB) films which have ability to show photochromism, dense molecular packing sometimes prevents photochromic reaction.[11] However, LB films of spiropyrans reported so far, always using positive photochromic ones,[12] exhibited photochromism. If an LB film is composed of the negative photochromic spiropyran, we do not need to use UV light that damages spiropyran, yet it shows photochromism. This would open the ways of application of UV-degradable spiropyrans. We here report the preparation of LB films composed of **3MC** and its thermally reversible negative photochromism, which does not necessarily require UV irradiation.[13]



Scheme 1. Photochromism of spiropyrans.

Synthetic details of **3** are described in Supporting Information. ^{1}H NMR of **3** in DMSO-d_6 and $CDCl_3$ proved that **3** took the MC form exclusively. Photochromic absorption spectral change of **3** in DMSO (λ_{max} 532 nm, ε_{max} 3.5×10^4 mol^{-1} cm^{-1} dm^3) is shown in Supporting Information. Upon visible light (>500 nm) irradiation, the absorption band in the visible region decreased until the solution became almost colorless. When the resulting solution was kept in the dark at room temperature for 6 h, the initial spectrum was almost restored. Although the similar spectral changes induced by the photoreaction and thermal treatment were observed in ethanol, acetone, and chloroform, the change was not observed in hexane and in toluene because of the little solubility of **3** in these solvents. Thus, **3** shows negative photochromism in many polar solvents.

Figure 1 shows a pressure-area (π-A) isotherm of **3MC** when spreading its chloroform solution on ultrapure water at 15 °C. It gave a monolayer isotherm with a pressure lift-off area at 0.94 nm^2 and a molecular-occupied area at 0.40 nm^2, which was estimated from the extrapolation of the steepest region of π-A isotherm to the zero pressure.

These values are coincident with the areas of the largest and the secondly largest rectangular faces, respectively, when the hydrophilic merocyanine moiety of **3MC** is regarded as a rectangular parallelepiped. This result suggests that **3MC** molecule would orient in a face-on manner on the water surface at zero

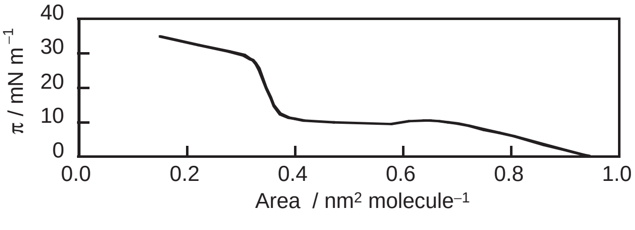


Figure 1. Pressure-area isotherm of **3MC** on ultrapure water at 15 °C.

pressure, and the MC plane arose gradually to separate the hydrophobic alkyl chain from the water surface during the compression procedure.

The single layer deposition of **3MC** monolayer was undertaken in the upstroke onto a cleaned glass plate under the dimmed red light. Transfer was performed at 13.5 mN m^{-1} by standard vertical deposition with the rate of 5 mm min^{-1}. Transfer ratio was equal to 1.0, indicating that monolayer was successfully transferred onto the glass plate.

The UV–vis absorption spectral change of the LB film of **3MC** upon 518-nm light irradiation is shown in Figure 2a. Before visible light irradiation, the film was slightly pink ($\lambda_{\max}$ 535 nm, $\varepsilon_{\max}$ 3.8×10^4 mol^{-1} cm^{-1} dm^3). That the ε of the LB film is larger than that in solution would indicate the orientation of the transition moment is fairly parallel to the glass surface. After visible light irradiation, the color disappeared. It took 2–3 days to restore the original absorption spectrum completely when it was placed in the dark at room temperature (Figure 2b). It took longer time than that in DMSO because of the sterically congested environment.

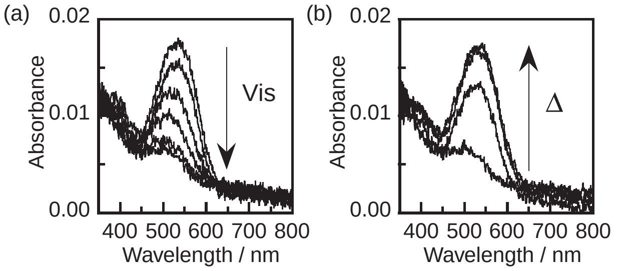


Figure 2. Photochromic absorption spectral changes of an LB film of **3MC**. (a) Visible light irradiation (518 nm) (irradiation time/min: 0, 1, 5, 10, 20, and 60). (b) Thermal back reaction at room temperature (thermal treatment/day: 0, 1, 2, and 3).

The change in surface morphology of the LB film of **3MC** by white light irradiation with a xenon lamp was observed by the atomic force microscopy (AFM).[14] Before irradiation, the surface was rather flat, and some holes (diameter 20–30 nm, depth ca. 2 nm) were observed (Figure 3a). We judged that the surface of the glass plate was exposed at the bottom of the hole because (i) the depth of the holes was always about 2 nm, (ii) the length of the alkyl chain of **3** when it is extended with trans conformation was about 2.2–2.3 nm (PM3 semi-empirical MO calculations) and the alkyl chains could slant to some extent in order to gain the greater van der Waals interactions between the alkyl chains. After irradiation, the depth of the holes became shallower (Figure 3b). Although it could be attributed to the breakdown of the packing of the alkyl chains caused by the ring closure of the merocyanine form, the possibility that the holes were partially buried to become so small for the AFM probe (radius of its tip sphere is ca. 15 nm) that it could not measure the depth of the holes accurately, cannot be ruled out. Although the change in absorption spectrum was reversible, the recovery of the ordered structure of the film has not been confirmed.

In summary, we have succeeded to prepare an LB film of **3MC**, negative photochromic merocyanine form of spiropyran **3SP**, with two nitro groups on the phenolate moiety and a long alkyl chain on the nitrogen atom of the indolium group. It showed thermally reversible negative photochromism as its LB film. Upon irradiation of visible light, the surface of the LB film, observed by AFM, showed some change in appearance caused by the structure change in the molecular level.

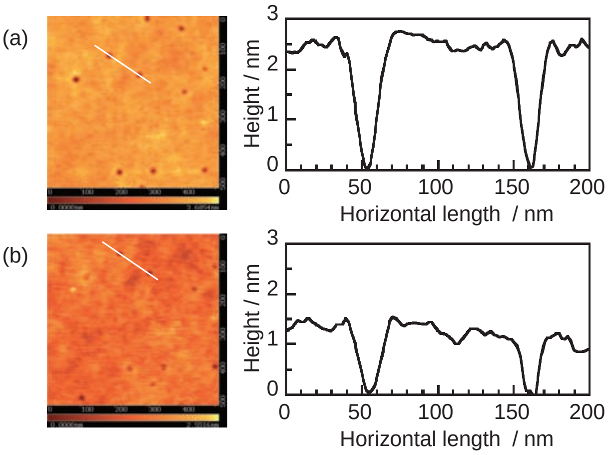


Figure 3. AFM images of an LB film of **3MC**. (a) Before white light irradiation. (b) After white light irradiation for 90 min. The figures on the right side indicate the cross-sectional height profiles for the solid lines shown in the AFM images.

References and Notes

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14 The AFM image was taken using SII SPA300/SPI3700 in the contact mode equipped with a microcantilever of SN-AF1 with a spring constant of 0.02 N m^{-1}.

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