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Acidichromism in the Langmuir–Blodgett films of novel photochromic spiropyran and spirooxazine derivatives

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Two novel photochromic spiropyran (SP) and spirooxazine (SO) derivatives without substituted long alkyl chains were synthesized. They can form stable Langmuir monolayers at the air–water interface and can be transferred to solid substrates successfully through vertical dipping as Z-type Langmuir–Blodgett (LB) films. LB films of both of the compounds showed typical photochromism. An additional acidichromism was found for the LB films. The LB film of SO turned red upon exposure to HCl gas. Consecutive exposure to NH_3 gas caused the film to turn blue. The red colour and blue colour can be changed reversibly upon alternate exposure to HCl and NH_3 gas. For the LB film of the SP derivative, due to the protection of the spiropyran by the substituted group, the acidichromism was not obvious in the initial exposure to the HCl and NH_3 gases. However, after several repeated exposures to HCl and NH_3 gas alternately, the acidichromism became obvious. This paper presents a new route for SO and SP LB films changing from the "spiro" form to the merocyanine form through acidichromism besides the well-known photochromic route of this system.

Introduction

Photochromism of spiropyran (SP) and spirooxazine (SO) has been extensively investigated due to their wide applications in optical information storage,[1–4] molecular switching devices[5] and other fields.[6] The photochromism of spiropyran and spirooxazine is based on the reversible colour change between the closed "spiro" structure and an open planar merocyanine (MC) structure. Acidichromism describes the reversible colour changes depending on the pH in solution or upon exposure to HCl and NH_3 alternately in films.[7–9] Acidichromism of photochromic species has potential applications in pH or acid and base gas sensors, photo- and chemical-switching systems and gas controlled reversible colour-change devices. Up to now, photochromism of spiropyran and spirooxazine has been widely investigated in various matrices such as sol–gel systems,[10–12] polymer dispersions,[13–15] bilayer lipid membranes[16,17] and Langmuir–Blodgett films.[18–21] The Langmuir–Blodgett technique provides a good way to orient and assemble molecules into an ordered array and assures the formation of ultrathin organic films at the molecular level.[22] In this paper, we report a novel property of the LB films of SO and SP derivatives (Scheme 1) besides their photochromism. It has been found that the LB films show reversible colour change between the "spiro" form and "open" form upon exposure to HCl and NH_3 alternately. While such kind of chromism was reported for the LB films of some J-aggregates of merocyanine dyes,[23] this is the first report on the acidichromism of the LB films of SO and SP derivatives.

Experimental

1,3,3-Trimethyl-9′-({3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propanoyl}oxy)-3′*H*-spiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine] (SO) was synthesized from the condensation of 1,3,3-trimethyl-9′-hydroxy-3′*H*-spiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine] with 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propanoic acid using dicyclohexylcarbodiimide (DCC) as dehydrant and 4-dimethylaminopyridine (DMAP) as catalytic agent. 1,3,3-Trimethyl-9′-hydroxy-3′*H*-spiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine] was obtained by condensation of 1,3,3-trimethyl-2-methyleneindoline with 1-nitroso-2,3-dihydroxynaphthalene in dry ethanol.[24] 3-[3,5-Di(*tert*-butyl)-4-hydroxyphenyl]propanoic acid was prepared as described previously.[25] Mp = 112–114 °C. MS: *m*/*z*, 604(M^+), 589(M−15). ^{1}H NMR: 1.48(s, 6H, CH_3), 1.52(s, 18H, CMe_3), 2.79(s, 3H, NCH_3), 2.98(t, 2H, CH_2), 3.10(t, 2H, CH_2COO), 6.58–8.23(m, 10H, Ar-H).

The synthesis of 1′-[2-({3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propanoyl}oxy)ethyl]-3′,3′-dimethyl-2*H*-spiro[chromene-2,2′-indoline] (SP) was based on the condensation of 1′-hydroxyethyl-3′,3′-dimethyl-6-nitro-2*H*-spiro[chromene-2,2′-indoline] and a 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propanoic acid.[26] The 1′-hydroxyethyl-3′,3′-dimethyl-6-nitro-2*H*-spiro[chromene-2,2′-indoline] was obtained according to the literature.[27] Mp = 184–186 °C. MS: *m*/*z*, 612(M^+). ^{1}H NMR: 1.15(s, 3H, CH_3), 1.24(s, 3H, CH_3), 1.41(s, 18H, CMe_3), 2.58(t, 2H, CH_2), 2.81(t, 2H, CH_2COO), 3.45(t, 2H, NCH_2), 4.23(t, 2H, NCH_2CH_2), 6.5–8.2(m, 11H, Ar-H).

A chloroform (distilled before use) solution of SP or SO (1×10^{-3} mol dm^{-3}) was spread on millipore water surface (18 MΩ cm). After the evaporation of the chloroform for 10 minutes, surface pressure (π)–area (A) isotherms were recorded on a KSV 1100 LB trough with a barrier compressing speed of 10 mm min^{-1}. Quartz substrates were cleaned by mixed chromic acid and washed with water thoroughly. The substrates were made to be hydrophobic before deposition by rubbing the substrates with ferric stearate. The LB films were deposited on quartz substrates by the vertical dipping method at 2 mN m^{-1}. The dipping speed was 10 mm min^{-1} both downward and upward. UV-Vis spectra of the transferred LB films were measured with a JASCO UV-530 spectrophotometer. To investigate the acidichromism, the LB films were exposed to HCl and NH_3 gas separately for 1 minute. The films were purged with N_2 gas before spectral measurements.

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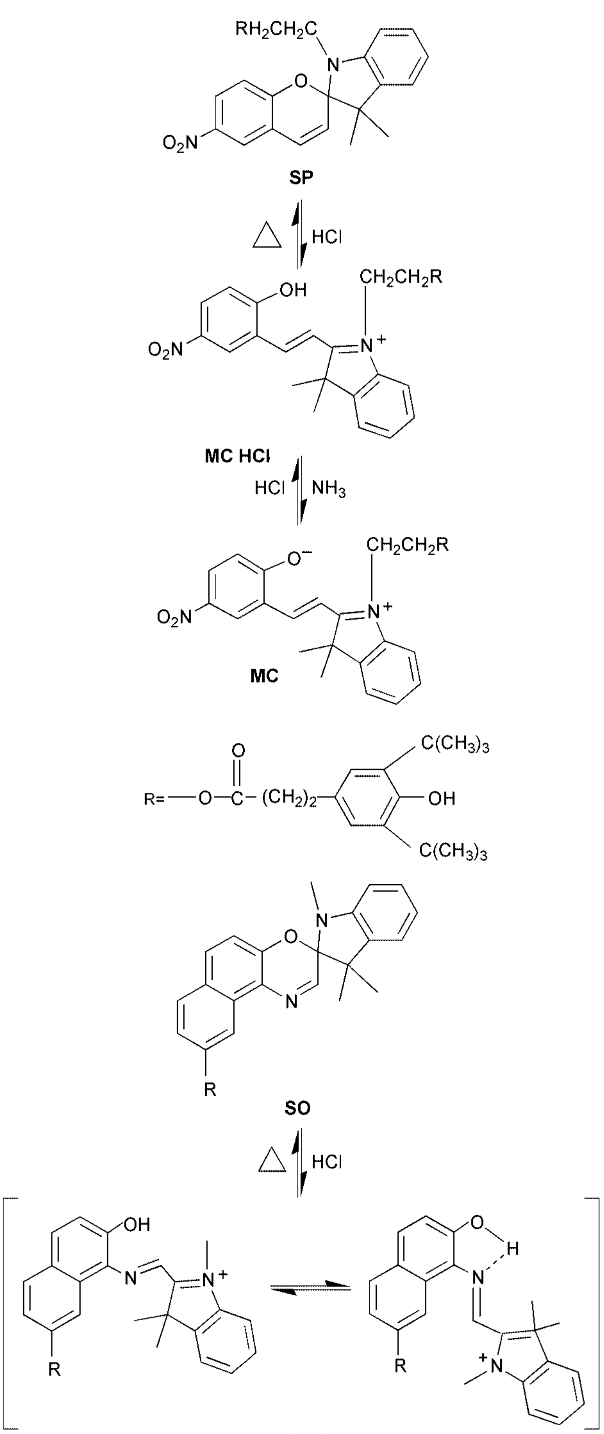


Scheme 1 Possible structural change of SP and SO in acidichromism.

Results and discussion

Fig. 1a shows the π–A isotherms of SP and SO derivatives on plain water surface. It is interesting to note that both of the compounds can form monolayers at the air–water interface although they have no substituted long-alkyl chain. The onsets of the surface pressures are at 1.3 and 1.1 nm^2 $molecule^{-1}$ for SP and SO, respectively. In comparison with those reported for the monolayer of long-chain SP derivatives,[28] which showed the onset of surface pressure at around 0.8 nm^2 $molecule^{-1}$, it can be regarded that a true monolayer was formed for SP at the air–water interface. The relatively larger molecular area of SP compared to those of long-alkyl chain substituted spiropyran is due to the short substituent which may lie flat at the air–water interface before compressing. Besides, a phase transition is observed for SP at 2.8 mN m^{-1}. For SO, a relatively small area is found, which may be due to the different substituent position. On the other hand, these monolayers are stable. We have measured the monolayer relaxation at 2 mN m^{-1} for SP and 10 mN m^{-1} for SO, respectively. It was found that within 40 minutes measurement, no decrease of molecular areas was detected.

The monolayers of SP and SO can be transferred onto solid substrates by a vertical deposition method. Fig. 1b shows the optical densities of the SP (λ_{max} = 267 nm) and SO (λ_{max} = 237 nm) LB films transferred at 2 mN m^{-1} as a function of layer numbers. Linear relationships are obtained for both of the LB films, showing the uniform transformation of the monolayer onto solid substrates. On the other hand, transfer ratio showed that the LB films were fabricated as a Z-type film, *i.e.*, the transfer ratio was nearly unity in the upward, while it was near zero in the downward. Fig. 2a and 2b shows the UV-Vis spectra of the 20-layer LB films of SP and SO deposited at 2 mN m^{-1}, respectively. Obvious photochromism was observed for LB films of SP and SO. The coloured forms of SP and SO are found at 569 and 614 nm, respectively. In comparison with those in solution,[29,30] the MC form of SP in the LB films showed a large red shift, suggesting the head to tail arrangement or J-aggregates of the molecules in LB films. These properties are essentially the same as those reported for the LB films of long-chain derivatives.[28]

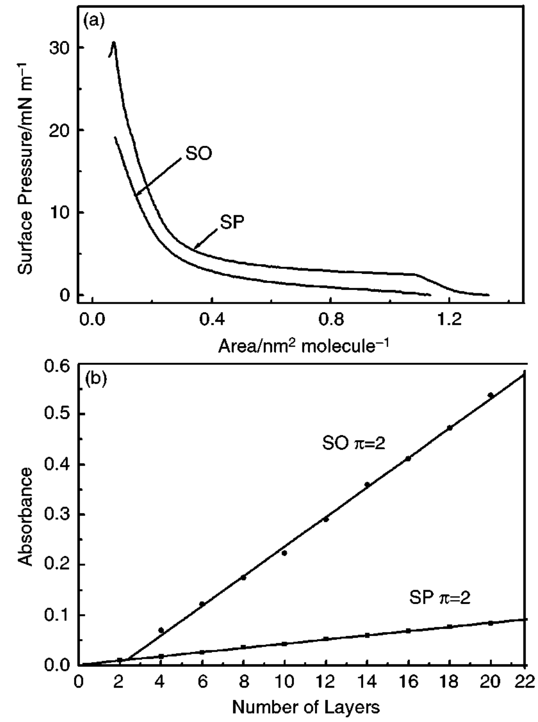


Fig. 1 (a) Surface pressure (π)–area (A) isotherms of the SP and SO monolayers at the air–water interface at 20 °C. (b) Plots of the optical density as a function of layer number of the LB film. The transferred pressure was 2 mN m^{-1}. The detected wavelength was 267 and 237 nm for SP and SO, respectively.

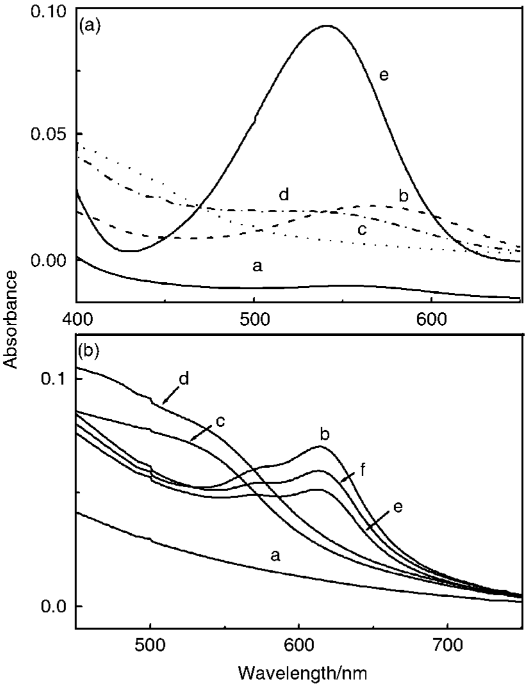


Fig. 2 (*a*) UV-Vis spectral changes in the LB film of SP before (a) and after (b) UV irradiation (254 nm). Upon exposure to HCl (c) and NH_3 (d) gas. (e) SP in methanol solution after UV light (254 nm) irradiation. (*b*) Photochromism and acidichromism in the LB film of SO. (a) and (b): spectra of the SO LB film before (a) and after (b) irradiation; (c) and (d): spectra of the film in (a) and (b) upon exposure to HCl gas, respectively, (e) and (f): spectra of the film (c) and (d) upon exposure to NH_3 gas, respectively.

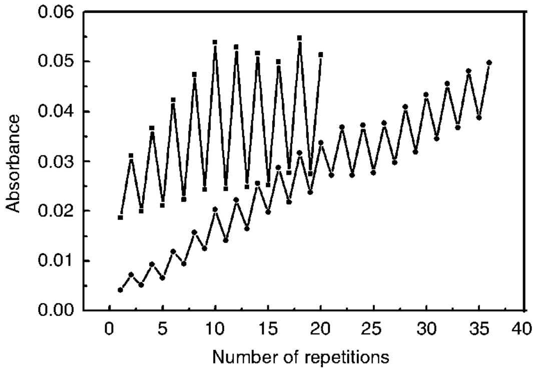
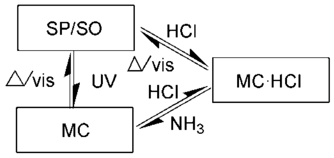


Fig. 3 Plots of the optical density as a function of the repeated exposure number to HCl and NH_3 gases. The LB films were transferred both at 2 mN m^{-1}. The detected wavelength was 556 and 612 nm for SP and SO, respectively.



Scheme 2 Photochromism and acidichromism in the LB film of SP and SO.

Interesting properties were found for the acidichromism of their LB films. When the LB film of SO was exposed to HCl gas, it turned red immediately. This colour is different from either the "spiro" form or the MC form of SO. Fig. 2b shows the spectral change of the "spiro" SO LB film upon exposure to HCl gas. A new absorption peak was observed at 513 nm in the spectrum. This absorption is different from those of the UV-irradiated species, which shows absorption at 614 nm. We ascribed the form as MC·HCl tentatively. The red colored MC·HCl gradually returned to the "spiro" form in the dark. However, when the LB film of this form was subjected to NH_3 gas, the film turned blue immediately and the same spectrum as that of photo-produced MC was obtained. This indicates that the "spiro" SO can be transferred to the MC form through such kind of chemical treatment without photoirradiation. On the other hand, when the photoirradiated blue-coloured MC LB film was exposed to HCl gas, it also turned red as the "spiro" SO film. In the case of SP LB film (Fig. 2a), although similar properties were found after several repeated treatments to the alternate exposure to HCl and NH_3 gases, the acidichromism is not obvious initially. Fig. 3 shows the optical densities of the colored species as a function of cycle numbers. In the case of SO LB film the change of optical density is about 0.03. In the case of SP LB film, however, the change in optical density of the colored species is very low in the initial cycles. After 10 cycles, this change of optical density approaches to a constant of 0.01. It is clear that the gas sensing ability of SP LB film was much weaker than SO.

Gabbutt *et al.* have investigated the acidichromism of spiropyran derivatives in solution and proposed that in acidic conditions SP could form various colored protonated rotamers.[31] This is applicable to our cases. Scheme 1 shows one kind of the protonated rotamers. In the case of SO, the rotamer can form an intramolecular hydrogen bond between the nitrogen atom in the oxazine ring of SO and OH in the naphthyl ring, while this is not the case for SP. Therefore the protonated product of SO is more stable and the acidichromism is much more obvious than that of SP. In addition, in the case of SP, the large substituent group is attached to the N-atom of the indole ring, while in the case of SO, the group is far from the indole ring. Owing to the protection of the color-changeable center in the SP LB film, its acidichromism was weaker than the SO LB film.

The above photochromism and acidichromism can be combined as illustrated in Scheme 2, where SP/SO, MC and MC·HCl stand for the "spiro", MC and HCl adduct of MC, respectively. SP and SO can be changed into the MC form reversibly by photoirradiation. Such change can also be realized through the consecutive exposing to HCl and NH_3 gas without photoirradiation through an intermediate MC·HCl form. Moreover, the colour change between the MC·HCl and MC was reversible. While photo-switched reversible changes between SO and MC are widely reported, the route through the HCl and NH_3 is reported here. This further provides a possibility for SO and SP derivatives to be used as gas sensing materials.

Conclusions

Two SP and SO derivatives, although without long alkyl chain substituents, were found to form stable monolayers at the air–water interface. The Z-type LB films of the two compounds can be deposited by conventional LB technique. Both of the LB films showed photochromism similar to those reported for other SP and SO derivatives. Besides the photochromism, a new route for the transformation of the "spiro" form to MC form through acidichromism was presented.

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