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Influence of Monolayer State on Spectroscopy and Photoisomerization of an Amphiphilic Styryl-Pyridinium Dye on a Solid Substrate

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Received October 17, 2006. In Final Form: December 28, 2006

The spectroscopy and photochromic properties of transferred monolayers of the amphiphilic styryl-pyridinium dye 4-(3',4'-dimethoxystyryl)-N-octadecylpyridinium perchlorate (DMPOP) were studied at different conditions during their transfer. The emission maxima of the monolayers transferred from the air–water interface in the liquid-expanded phase are strongly dependent on the surface pressure applied during the transfer process, even at values when the area per molecule is 2–3 times larger than the area occupied by a chromophore. In monolayers transferred from the liquid-condensed phase, the presence of a different kind of aggregates was observed. The fluorescence emission properties of the monolayers can be reversibly modulated by photoinduced *E*–*Z* isomerization. A blue shift up to 72 nm in the emission maximum, depending on the transfer conditions of the films, can be obtained by irradiation with blue light, and partially recovered (a red shift of up to 26 nm) with UV radiation. The rate at which the first process (*E*→*Z*) takes place is drastically reduced in monolayers transferred from the liquid-condensed phase as compared to those transferred from the liquid-expanded one. However, the rate of the reverse reaction (*Z*→*E*) is not significantly altered. These properties make DMPOP a promising material for the preparation of Langmuir–Blodgett films, whose properties can be effectively controlled by the transfer conditions and subsequently optically modulated, for potential applications as photonics devices for data storage.

Introduction

Photochromism is defined as a reversible light-driven transformation of a chemical species^{1,2} between two isomeric forms. A photochromic compound is a bistable system that can be interconverted by optical radiation of two different wavelengths. The two isomers differ in the electron distribution, and therefore also in their physical and chemical properties such as absorption spectrum, refractive index, dielectric constant, redox potential, chelate formation, etc. When embedded in a proper medium (e.g., polymer, liquid crystal, etc.), the properties of the host can be switched by photoirradiation. Examples are rewritable holographic systems,^{3,4} photosensitive optical waveguide components,^{5,6} reversible photoinduced phase transition of liquid crystals,^{7,8} and optoelectronic systems.^{9,10} Therefore, this kind of system has attracted much interest recently due to its potential

application for information storage and construction of molecular switches.^{11,12}

Styryl dyes are a class of photochromic compounds of potential interest in the fabrication of useful photonics devices. Their large hyperpolarizability not only makes them good candidates for the preparation of nonlinear optical (NLO) materials, but also confers a high sensitivity to the environment, which can be measured by absorption and fluorescence spectroscopy (solvatochromic effect¹³). The substituents in the aromatic ring strongly influence the photophysical and photochemical properties of these compounds. For example, unsubstituted styryl dyes show reversible photoisomerization and -cyclization depending on the media.¹⁴ Strong electron-donating groups give rise to locally excited (fluorescent) and twisted intramolecular charge transfer (non-fluorescent) states, whereas *E*–*Z* isomerization is unlikely to occur in the excited state.¹⁵ When two methoxy groups are introduced in the para and the meta positions of the phenyl ring (such as in DMPOP, Figure 1), reversible photoisomerization between the strongly fluorescent *E* isomer and the nonfluorescent *Z* isomer is observed in different solvents.¹⁶ This behavior is highly interesting for the design of devices for optical information storage by switching between the emitting and the non-emitting states.¹⁷ Although a large number of photochromic compounds have been reported in the literature,² only a few of them are

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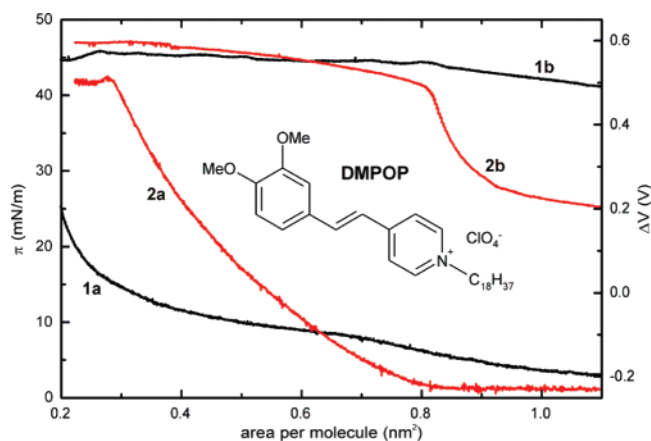


Figure 1. Isotherms of the pure *E* isomer of DMPOP on the air–water interface (black lines); (1a) surface pressure; (1b) surface potential) and of the photostationary state reached by irradiating the spreading solution with blue light (red lines; (2a) surface pressure; (2b) surface potential). The inset shows the structure of the amphiphilic dye (*E* isomer).

fluorescent and allow a modulation of their fluorescent properties.^{18–21}

The preparation of useful devices generally requires the dyes to be incorporated into a matrix such as, for example, a polymer film or a system prepared by the Langmuir–Blodgett (LB) technique.²² One of the advantages of the latter is that the anisotropic properties of the molecule may be transferred to the assembled device (i.e., the chromophores can be arranged in a noncentrosymmetric structure²³ to preserve a high second-order hyperpolarizability). The LB technique allows one to prepare nanoscale devices with an improved control of their properties as compared to self-assembly. The octadecyl substituent at the pyridinium nitrogen of DMPOP confers the molecule the amphiphilic properties necessary to prepare monolayers at the air–water interface and to transfer them to a solid substrate by the LB method.

Understanding the organization and association of the chromophores in LB films is of high interest, as well as the influence that these processes have on the spectroscopic properties of the chromophores, because it defines the performance of the potential devices. In a previous work, these orientation and association phenomena, as well as the surface-active properties of DMPOP at the air–water interface, were presented.²⁴ In the present work, we investigate the photochemical behavior of the amphiphilic styryl dye DMPOP (i.e., the changes of the spectroscopic properties) in monolayers, which are transferred to solid substrates, and the influence of the different conditions during the monolayer transfer on the properties of the resulting films including the switching behavior. Spectroscopic methods such as absorption, emission, and fluorescence excitation spectroscopy and polarized absorption spectroscopy provided information on the orientation

of the chromophores in the LB films and enabled the analysis of the photoinduced changes produced by irradiation with visible and ultraviolet radiation.

Materials and Methods

The synthesis of the amphiphilic dye has been previously described.²² Chloroform (Baker, 99.8% purity) was used as the solvent for preparing the dye monolayers. The instruments for performing the measurements of the surface pressure (π)–area (*A*) and surface potential (ΔV)–area (*A*) isotherms of dye monolayers have also been described previously.²⁴ Monolayers were formed by spreading 50 μ L of a 1 mM chloroform solution of DMPOP onto water at 20 °C, initial area 353 cm². Following a relaxation period of 10 min to allow solvent evaporation, the monolayers were compressed by moving the barrier with a constant speed of about 10 cm²/min, corresponding to 0.031 nm² molecule^{−1} min^{−1}. The monolayers were transferred onto both sides of quartz plates by the Langmuir–Blodgett technique in a wide range of constant surface pressure with a transfer speed of 0.5 mm/min. The transfer coefficient was about 0.95 for surface pressures in the range 7–20 mN/m and could not be determined for films transferred at lower surface pressure values in the usual way, because the surface pressure changes during transfer were too small for activating the feed-back system that reduces the monolayer area. However, the homogeneous appearance of the fluorescence on the solid substrate after monolayer transfer indicated the absence of a dye surface density gradient. The fluorescence of the LB films (excitation and emission spectra) was measured on a Varian Cary Eclipse fluorescence spectrophotometer in a self-made cell holder in a geometry of 60°/30° for the excitation and the emission detection, respectively. The absorption was measured in a Varian Cary 4000 UV–vis spectrophotometer under normal incidence, and the polarized absorption measurements were performed in a home-made single beam instrument of the type described earlier.²⁵ The absorption is plotted as the difference $\Delta T = T_{\text{reference}} - T_{\text{sample}}$ of the transmission of a reference section and the sample section of the plate. The samples were irradiated with a 200 W high-pressure mercury lamp. A monochromator (fwhm = 10 nm) was used to select the wavelength (λ), and the light was defocused to ensure homogeneous irradiation of a larger area than the observed one. The light intensities were 6 mW/cm² at 405 nm and 4 mW/cm² at 313 nm.

Results and Discussion

Monolayers at the Air–Water Interface. Monolayers of DMPOP were characterized at the air–water interface by surface pressure (π)–area (*A*) and surface potential (ΔV)–area isotherms prior to transfer to quartz plates. Figure 1 shows the π –*A* (a) and ΔV –*A* (b) isotherms of DMPOP by spreading a solution of the pure *E* isomer (black lines), and a solution previously irradiated with blue light ($\lambda = 405$ nm) until the photostationary state was reached (red lines). The monolayers of the initial form (*E* isomer) already have a surface pressure of $\pi = 3$ mN/m and a surface potential of $\Delta V = 0.5$ V at an area of *A* = 1.1 nm². After passing a phase transition as can be seen by Brewster angle microscopy (formation of small bright domains similar to those in ref 24, Figure 5a, images not shown here) from the liquid-expanded to liquid-condensed phase upon compression in the surface pressure range between 8.3 and 9 mN/m, the monolayer showed a strong surface pressure decrease with time at constant areas smaller than 0.25 nm², indicating monolayer relaxation. The surface potential increased slightly with compression from 0.5 V at 1.1 nm² to 0.55 V at 0.25 nm². In contrast to this behavior, the monolayer formed from the solution after reaching the photostationary state by irradiation with blue light (PSS-405) showed

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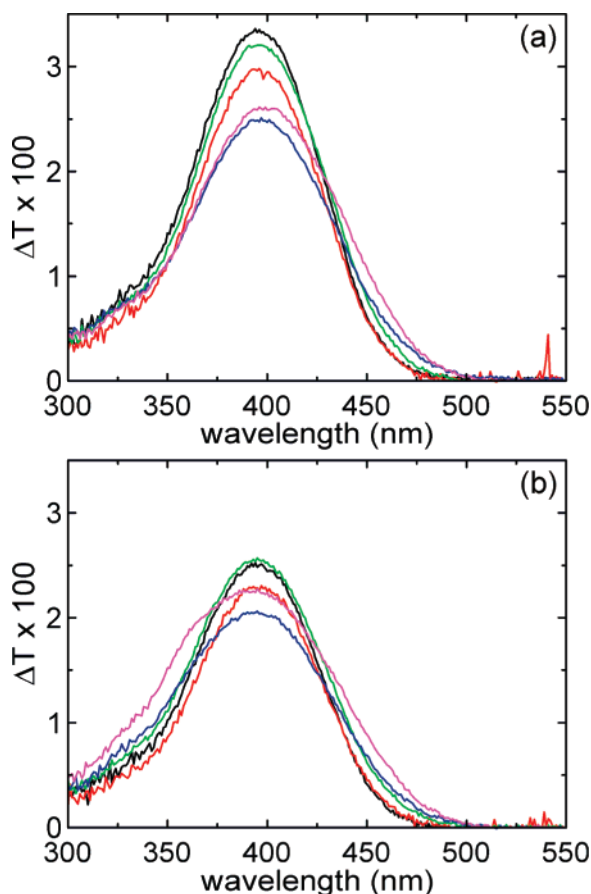


Figure 2. Polarized absorption spectra $\Delta T = T_{\text{reference}} - T_{\text{sample}}$, at an angle of incidence of 45° ((a) s-polarized light; (b) p-polarized light), for monolayers transferred from the air–water interface to quartz plates at different surface pressures. Color references: black lines, $\pi = 2.5$ mN/m; red lines, $\pi = 4.5$ mN/m; green lines, $\pi = 7.0$ mN/m; blue lines, $\pi = 15$ mN/m; purple lines, $\pi = 20$ mN/m.

a surface pressure of $\pi = 0$ mN/m upon compression to about 0.8 nm^2 . The surface pressure increased without detectable phase transition to collapse at $\pi = 43$ mN/m and $A = 0.3 \text{ nm}^2$. As compared to the initial form, curve 1a, the area per molecule is smaller for areas $A > 0.6 \text{ nm}^2$ and larger for $A < 0.6 \text{ nm}^2$. The surface potential was 0.2 V at 1.1 nm^2 and increased rather abruptly upon compression to about 0.5 V before the onset of the surface pressure at 0.8 nm^2 . This value was slightly more positive than that observed for the pure *E* isomer at areas smaller than 0.6 nm^2 . The similarity of the surface potentials observed in Figure 1 at low values of areas per molecule (below 0.7 nm^2) is somewhat puzzling, because a different orientation of the molecules or at least of the static dipole moments may be expected, due to the large difference in shape between DMPOP (*E* and *Z*) isomers.

Spectroscopic Properties of Monolayers Transferred onto Quartz Plates. The Langmuir–Blodgett films were transferred from a water subphase at surface pressures ranging from 1.7 to 20 mN/m. The wide range of surface pressures was selected to obtain films transferred from both phases. Indeed, a clearly different behavior was observed for the monolayers transferred from the liquid-expanded phase as compared to the liquid-condensed phase. The polarized absorption spectra (angle of incidence = 45°) of the transferred monolayers are presented in Figure 2, and fluorescence excitation and emission spectra are shown in Figure 3.

The polarized absorption spectra (s- and p-polarized) of the monolayers transferred from the liquid-expanded phase ($\pi \leq 7$

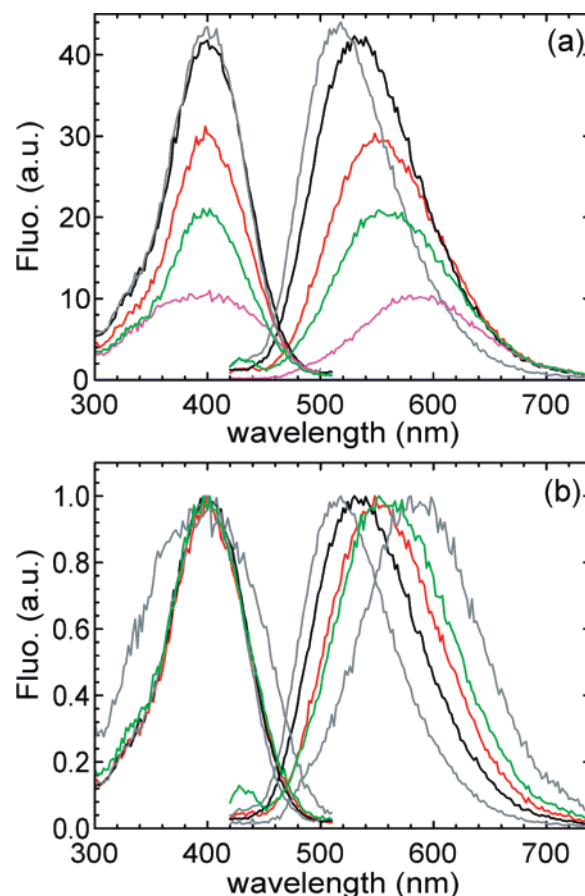


Figure 3. (a) Fluorescence spectra (excitation and emission, respectively) of monolayers transferred from the air–water interface to quartz plates at different surface pressures; (b) spectra normalized to unity at the maximum. Color references: gray lines, $\pi = 1.7$ mN/m; black lines, $\pi = 2.5$ mN/m; red lines, $\pi = 4.5$ mN/m; green lines, $\pi = 7.0$ mN/m; purple lines, $\pi = 20$ mN/m.

mN/m) could be fitted to two Gaussian peaks, centered at around 400 and 340 nm , respectively. We focused only on the first band because the second one is possibly a vibrational substructure. The average angle that the optical transition moment of the chromophores forms with respect to the normal to the substrate was $74 \pm 1^\circ$ for all of the films transferred from the liquid-expanded phase, calculated from the dichroic ratio ($\Delta T_s/\Delta T_p$) at 400 nm according to procedures described in the literature.²⁶ This indicates that the changes observed in the emission properties (see Figure 3) are not related to changes in the orientation of the chromophores. The monolayers transferred from the liquid-condensed phase ($\pi \geq 15$ mN/m) presented a third band at around 360 nm , which was only observed in the p-polarized component. The amplitude of this band increased upon compression, while the band centered at 400 nm was red-shifted to about 404 nm . The behavior observed for monolayers transferred from the liquid-condensed phase was interpreted²² as the presence of a non-homogeneous system composed of face to face dimers oriented perpendicular to the substrate surface, responsible for the band at 360 nm , and slipped dimers oriented preferably parallel to the substrate, with a small red-shifted absorption compared with the monomers, responsible for the band at 404 nm . The average angle between the chromophores and the normal to the substrate calculated from the band at 404 nm was $72 \pm 1^\circ$ for all of the films transferred from the liquid-condensed phase, indicating

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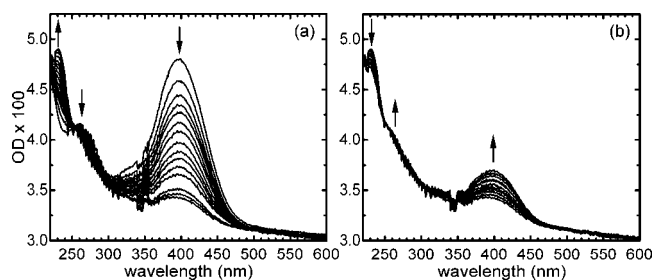


Figure 4. Absorption spectra after different irradiation times with 405 nm light (a) and posterior recovery with 313 nm radiation (b), for a monolayer transferred from the liquid-expanded phase ($\pi = 4.5$ mN/m). Irradiation times may be inferred from the abscissa in Figure 5 (circles). The arrows show the direction of change in the optical density (OD) at different wavelength ranges.

that the chromophores in the slipped dimers were preferably oriented forming a small angle with respect to the quartz substrate. The small difference as compared to the angle obtained for the same band (400 nm) in monolayers transferred at low pressures could be attributed to a slight change in the orientation of the remaining monomers or a difference in the orientation of the transition moment of the slipped dimers. With the exception of the face to face dimers present in the films transferred at high pressure, there is not a big difference in the chromophore's average orientation in the films transferred from both phases.

The fluorescence excitation spectra of the monolayers transferred from the liquid-expanded phase are invariant, within experimental error, as can be better appreciated from the spectra normalized to unity at the maximum (Figure 3b). An unusual red shift of 45 nm in the emission maxima (from 515 nm at 1.7 mN/m to 560 nm at 7 mN) was observed, considering that a maximum solvatochromic shift observed in solutions of DMPOP in organic solvents was less than 15 nm (i.e., from 532 nm in chloroform to 545 nm in acetonitrile solutions). When the monolayers are transferred from the liquid-condensed phase, a broadening of the fluorescence excitation spectrum (see the monolayer transferred at 20 mN/m in Figure 3b) and a further red shift in the emission maximum were observed. Considering that the fluorescence experiments were not performed with polarized light, the broadening in the excitation spectra is consistent with the changes in the polarized absorption experiments, while the shift in the emission spectra may be explained by the presence of aggregates (face to face and slipped dimers).

Photochemical Transformations. The monolayers of DMPOP are strongly light sensitive. Irradiation with blue light results in a modification of the luminescence properties. An analysis of the processes that occur during irradiation may provide useful information regarding the organization of the monolayers. We thus analyzed the effect of irradiation with 405 nm light on two films transferred from the water subphase, one in the liquid-expanded phase and the other in the liquid-condensed phase ($\pi = 4.5$ and 20 mN/m, respectively), and the subsequent recovery upon irradiation with UV radiation at 313 nm. The absorption spectra after several irradiation times with blue and UV radiation are shown in Figure 4a and b, respectively, for a sample transferred from the liquid-expanded phase. Upon irradiation with blue light, the absorption decreased at around 400 and 275 nm, and increased at around 232 nm. Two isosbestic points are observed at 253 and 213 nm. This change was reversed upon irradiation at 313 nm, however, with incomplete recovery to the photostationary state (PSS-313). Similar changes were observed for a film transferred from the liquid-condensed phase ($\pi = 20$ mN/m, spectra not shown here), but with different characteristic times. This suggests that the predominant photochemical process is *E*–*Z* isomerization.

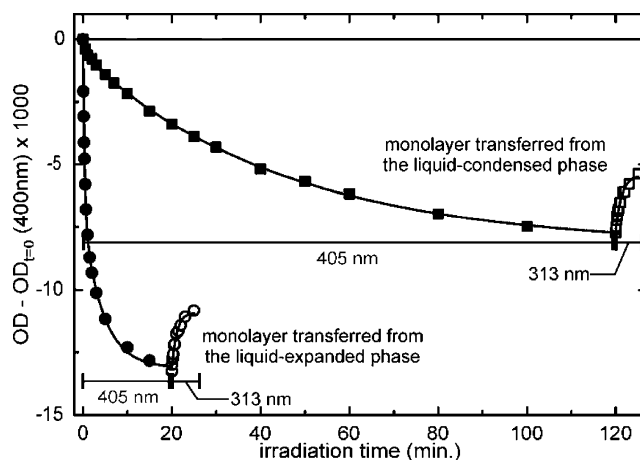


Figure 5. Absorption kinetics under irradiation with 405 nm light (filled symbols) and 313 nm radiation (hollow symbols) of monolayers transferred from the liquid-expanded phase ($\pi = 4.5$ mN/m; circles) and from the liquid-condensed phase ($\pi = 20$ mN/m; squares).

In Figure 5, the changes in the absorption at 400 nm as a function of irradiation time are presented for both films for a complete irradiation cycle (405 and 313 nm light).

The kinetic behavior was biexponential for both films under irradiation with blue light, and the recovering with UV radiation was monoexponential. The parameters for the fitting curves also shown in Figure 5 are listed in Table 1. Considering the initial absorption values, the conversion in the photostationary state under irradiation with blue light (PSS-405) was similar for both films within experimental errors and corresponds to a value of about 73–74%. However, the characteristic time was 1 order of magnitude larger for the monolayer of highly packed chromophores transferred at 20 mN/m than for that transferred at 4.5 mN/m. The biexponential behavior can be interpreted by the presence of two rotamers, one with the *meta*-methoxy group syn to the pyridine and the other in an anti orientation. While these two rotamers are expected to interconvert in a fast scale in solution, that may not be the case in a constrained media (such as LB films). Thus, one can expect to have a different proportion of each rotamer, depending on the packing of the film (i.e., the surface pressure). Because of the difference in stability and shape of each rotamer, the isomerization process should have a different activation barrier. The absence of facile rotamer interconversion resulted in the biexponential behavior observed, with each exponential component corresponding to each rotamer. The relative amplitude ($A_i/[A_1 + A_2]$) obtained in the fits reflects the fraction of each rotamer. The two amplitudes are similar in the case of the film transferred at low surface pressure (A_2/A_1 is close to unity, see Table 1), indicating a similar amount of each rotamer, but is larger than 10 for the film transferred at high surface pressure. This reflects the marked influence of the transfer conditions on the rotameric equilibria; one of the rotamers (probably syn) becomes highly favored in a close packed film. When the samples were then irradiated with 313 nm light, both films showed a fast recovering with very similar characteristic times and amplitudes. The two *Z*-rotamers may quickly interconvert (as compared to the *E*-rotamers), or the formation of the bent *Z* isomer produces a perturbation of the monolayer resulting in a local expansion. Three pieces of evidence support the second conclusion: (1) the larger area per molecule at ca. 20 mN/m observed in the isotherm obtained in the case of the irradiated sample, as compared to the pure *E* isomer of DMPOP, (2) the photoinduced reverse reaction (*Z*→*E*) with 313 nm radiation has the same characteristic time (τ_1) in both cases, and (3) the blue

Table 1. Parameters for the Irradiation Kinetics Shown in Figure 5, Fitted to a Single ($A_1 \cdot \exp[-t/\tau_1]$) or a Double ($A_1 \cdot \exp[-t/\tau_1] + A_2 \cdot \exp[-t/\tau_2]$) Exponential Function^a

irradiation light	surface pressure	A_1	τ_1 [min]	A_2	τ_2 [min]	A_1/A_{TOT}	A_2/A_{TOT}
405 nm	4.5 mN/m	$6.8 \times 10^{-3} \pm 4 \times 10^{-4}$	0.36 ± 0.03	$6.1 \times 10^{-3} \pm 3 \times 10^{-4}$	4.4 ± 0.6	0.53	0.47
	20 mN/m	$6.0 \times 10^{-4} \pm 1 \times 10^{-4}$	1.2 ± 0.3	$7.6 \times 10^{-3} \pm 1 \times 10^{-4}$	46 ± 1	0.07	0.93
313 nm	4.5 mN/m	$-2.3 \times 10^{-3} \pm 1 \times 10^{-4}$	1.1 ± 0.1				
	20 mN/m	$-2.1 \times 10^{-3} \pm 1 \times 10^{-4}$	1.4 ± 0.2				

^a Amplitudes (A_i) and characteristic times (τ_i) are presented, as well as the relative amplitude of each component ($A_i/A_{TOT} = A_i/[A_1 + A_2]$).

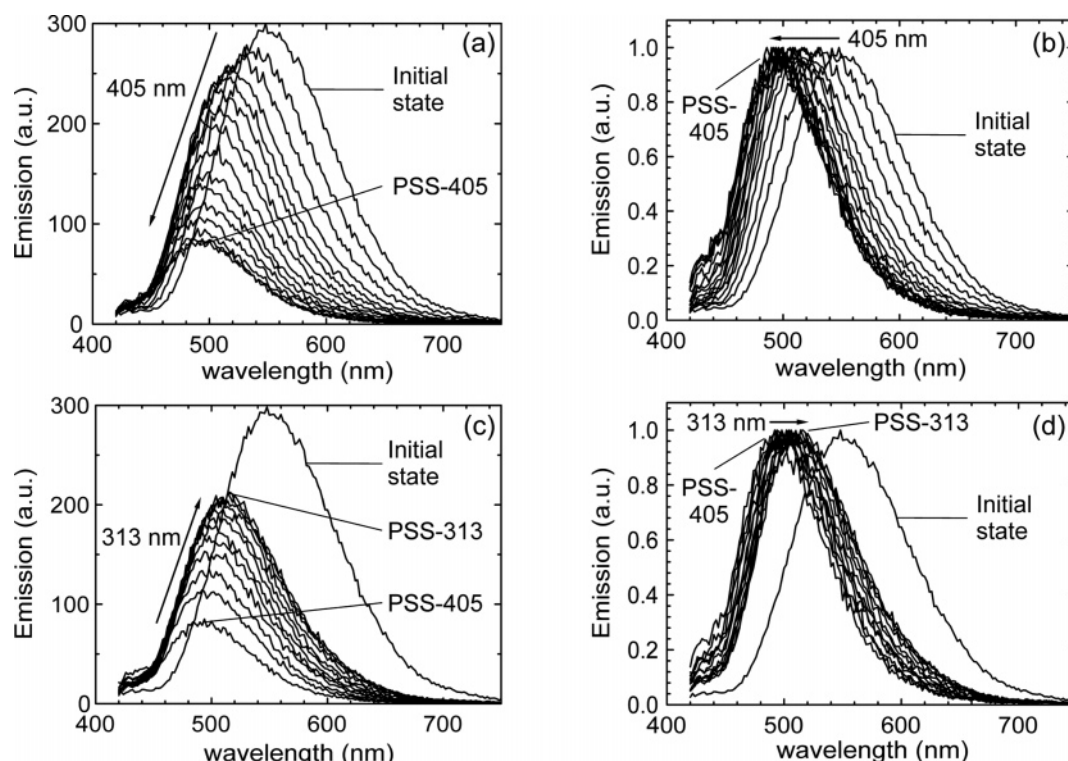


Figure 6. Emission spectra from a monolayer transferred from the liquid-expanded phase ($\pi = 4.5$ mN/m) after different irradiation times with 405 nm light (a, absolute values; b, normalized data) from the initial state to the PSS-405, and recovery under irradiation with 313 nm radiation (c, absolute values; d, normalized data). Irradiation times are the same as for the absorption experiments in Figure 5. The arrows show the direction of change in the spectra with increasing irradiation times.

shift of the emission maximum with increasing irradiation time with 405 nm light (see below and Figure 6). The latter also suggests that excimers or aggregates responsible for the emission at longer wavelengths are either not formed with the *Z* isomer (*Z*-*Z* or *Z*-*E*) or that the orientation of the *Z* isomer is not the correct one to form such aggregates. When the samples were submitted to irradiation with blue or UV radiation for longer times, irreversible diminution of the absorbance at 400 nm was observed. Among the possible photodegradation reactions, the formation of cyclobutane adducts should also be considered.²⁷

The presence of the rotameric equilibrium discussed above is not expected to play an important role in the other experiments performed in this work, because absorption and emission properties of both rotamers should be identical. However, when examined with polarized light, as in the absorption experiments, the equilibrium may be taken into account because both rotamers have a different angle between the absorption transition moment and the long molecular axis. The small difference in the dichroic ratio of the blue band (Table A1) resulting in a change in the chromophore's orientation angle from 74° to 72° when going from the liquid-expanded to the liquid-condensed phase (vide supra), which we attributed to a possible change in the orientations

of the remaining monomers in the condensed phase, may be also interpreted as a result of a different proportion of rotamers in each phase.

The irradiation with blue light reduced the intensity of the absorption band at 400 nm, but no chromatic shifts were observed; that is, the shape and the center of the band remained unaltered. More interesting is the behavior observed in the luminescence properties. In Figure 6, the changes in the emission spectra under similar irradiation conditions for a monolayer transferred at 4.5 mN/m are shown. A reduction in the fluorescence signal after irradiation at 405 nm was expected, due to the conversion from the fluorescent *E* isomer to the nonfluorescent *Z* isomer (Figure 6a). This change was accompanied by a large blue shift of about 60 nm in the emission (Figure 6a and b), from the initial state to the photostationary state under irradiation with blue light, PSS-405. When the film was further irradiated at 313 nm, an increase of the signal was observed together with a red shift of 25 nm from the PSS-405 to the PSS-313 (Figure 6c and d). The irradiation times were exactly the same as those used in the absorption experiments. A similar behavior was observed for the monolayer transferred at 20 mN/m (data not shown), obtaining a blue shift in the emission maximum of about 70 nm from the initial to the PSS-405, and a red shift of about 25 nm from this state to the PSS-313 (see Table 2).

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Table 2. Wavelengths of Emission Maxima for Monolayers Transferred at Different Surface Pressures in the Initial State, and in the Photostationary State under Irradiation with Blue Light (PSS-405) and UV Radiation (PSS-313), Respectively^a

phase	transfer condition		emission maxima [nm]			blue shift [nm] initial→PSS-405	red shift [nm] PSS-405→PSS-313
	A [nm ²]	π [mN/m]	initial state	PSS-405	PSS-313		
liquid-expanded	2.5	1.7	515	497	505	18	8
	1.3	2.5	535	495	510	40	15
	0.90	4.5	552	496	518	56	22
	0.69	7.0	560	495	521	65	26
liquid-condensed	0.22	20	587	515	541	72	26

^a The last two columns show the chromatic shifts between the states.

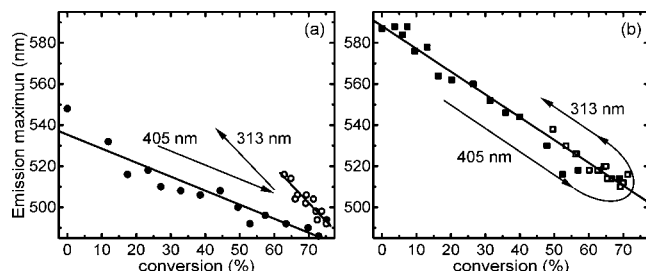


Figure 7. Wavelength of fluorescence emission maximum as a function of the conversion for monolayers transferred from (a) the liquid-expanded phase ($\pi = 4.5$ mN/m, circles), and (b) the liquid-condensed phase ($\pi = 20$ mN/m, squares), upon irradiation with blue (full symbols) and UV (open symbols) radiation, respectively.

Further analysis of the data obtained from irradiation experiments indicates that there is an apparent correlation between the wavelength of the emission maxima and the conversion at low and high surface pressure (see Figure 7). Thus, the properties of the monolayer are strongly dependent on the fraction of each isomer in the monolayer. However, this correlation is different after irradiation with blue and UV radiation in the case of the monolayer transferred at low pressure ($\pi = 4.5$ mN/m), indicating, first, that not only the fraction of each isomer determines the properties of the monolayer and, second, that the photoisomerization produces a modification in the order of the monolayer, which is not recovered after achieving the PSS-313. This was unexpected because the monolayer was transferred from a liquid-expanded phase at a large area of 0.9 nm^2 , and the chromophores were found to be oriented preferably parallel to the monolayer plane (vide supra). The chromatic shift of the fluorescence emission should be attributed to changes in the properties of the surrounding media (i.e., polarity, refractive index, etc.), rather than to changes in the chromophore association because there is no evidence of any kind of aggregates from polarized absorption spectroscopy (see Figure 2) or Brewster angle microscopy (data not shown). In the case of the film transferred at $\pi = 20$ mN/m, with evidence of aggregation in the initial state (e.g., the presence of an additional band in the polarized absorption spectra), it is surprising to observe a similar correlation between emission maximum and conversion and particularly that the data obtained under irradiation with blue and UV radiation, respectively, fall on the same line. The latter indicates that the emission wavelength of *E*-DMPOP only depends on the proportional amount of each isomer in the films transferred from the liquid-condensed phase and that there is no hysteresis effect in a complete irradiation cycle (compare Figure 7a and b).

Considering all of the evidence, we conclude that in the highly packed monolayer transferred from the liquid-condensed phase, *E*–*Z* photoisomerization is also the predominant photochemical process, whose speed is highly reduced with respect to that observed in the films transferred from the liquid-expanded phase, due to steric constraints. We also conclude that reorientation of

the chromophores after irradiation in this monolayer is considerably smaller than that in the monolayer transferred at low pressure (liquid-expanded phase). This conclusion is based on the following results: (1) the kinetics of the transformation by irradiation with blue light is 1 order of magnitude slower in the case of the monolayer transferred at high surface pressure than for the one transferred at low surface pressure, (2) the difference in the contribution of the two components to the mentioned kinetics (i.e., the amplitude for the slow component is 1 order of magnitude larger than the amplitude for the fast component in the monolayer transferred at high surface pressure, while these amplitudes are of the same order in the monolayer transferred at low surface pressure), indicating that chromophore reorientation is marginal as compared to the photoisomerization process in the monolayer transferred from the liquid-condensed phase, and (3) the result observed in Figure 7b, where the same correlation is observed for the fluorescence maxima as a function of the conversion for the film transferred at high pressure in the forward and back conversion between *E* and *Z* isomers.

To support these conclusions, a LB film was prepared consisting of 11 monolayers of a mixture of DMPOP and arachidic acid (AA), in a molar ratio DMPOP:AA = 1:40 (several monolayers had to be transferred to obtain an absorption at 405 nm similar to that presented by films of pure DMPOP). Because the properties at the air–water interface (i.e., the isotherms) of the mixtures with large ratio AA/DMPOP are governed by the main component (AA), the monolayers were transferred at a surface pressure of 40 mN/m. The films were irradiated under identical conditions to the experiments presented in Figure 4 and Table 1. The kinetics of the photoisomerization by irradiation with 405 nm light fitted to two exponential functions with lifetimes of 2 and 28 s, respectively, and the recovery under irradiation with 313 nm radiation was fast with a lifetime of 1 s. Because of the fact that the fraction of DMPOP in the two-component monolayer was very small, the formation of cyclobutane adducts was disregarded in this case. Moreover, a small blue shift of 12 nm in the emission maximum upon irradiation with blue light was observed (from 514 to 502 nm), and a red shift of 6 nm was observed upon irradiation with UV radiation (compare with the values in Table 2).

The particular photochemical behavior observed for the monolayers of DMPOP transferred from the liquid-expanded phase (i.e., the large blue shift of the emission maximum after irradiation with 405 nm light) motivated us to investigate the photochemical response of monolayers transferred at much larger areas (lower surface pressures). The monolayers transferred at areas of 0.22, 0.69, 0.9, 1.3, and $2.5 \text{ nm}^2/\text{molecule}$ (surface pressures of 20, 7, 4.5, 2.5, and 1.7 mN/m, respectively) were irradiated first with blue light to the PSS-405, and then with UV radiation to the PSS-313. The wavelengths of emission maxima in the initial state, in the PSS-405, and in the PSS-313, together with the calculated chromatic shifts, are summarized in Table 2. For a better comparison, the results for all transferred

monolayers from pure water subphase are also presented in the same table. The spectra recorded in the PSS-405 were very similar for all of the films, while those in the PSS-313 presented a red shift upon increasing the surface pressure. Considering that the area calculated for the chromophores lying flat on the surface²⁴ is 0.72 nm², it is unusual that the film transferred at the largest area per molecule (2.5 nm²/molecule) showed a relatively large blue shift of about 20 nm upon irradiation with blue light and that the emission of the monolayer in the initial state (pure *E* isomer) is blue-shifted upon expansion, that is, from 1.3 to 2.5 nm²/molecule (see Figure 3).

Conclusion

Langmuir–Blodgett films of DMPOP present interesting properties toward their utilization in molecular photonic devices. Stable films could be transferred from a very large range of conditions (surface pressure or area per molecule) with fluorescence emission spectra covering the green and yellow regions of the visible spectra. Irradiation with blue and UV radiation, respectively, allowed a reversible modulation of the intensity and the emission wavelength. A control of the conditions during the transfer of the films allowed an adjustment of the initial emission wavelength and the modulations upon irradiation. Larger modulations were obtained from films transferred from the liquid-condensed phase, but with a slower response. When using low surface pressures (i.e., transferring films from the liquid-expanded phase), the response of the films to irradiation with blue light was rather fast. The speed of this response was reduced by 1

order of magnitude when the film was transferred at high surface pressure. This distinct behavior may be an advantage for the preparation of complex devices, if more than one monolayer is transferred under different conditions in one film. The response to irradiation with UV is not drastically altered by changing the mentioned conditions. In the case of a mixed multilayer system, modulation of different layers can be performed with the same wavelengths due to the small change in the absorption spectra.

This particular behavior of the monolayers of DMPOP transferred onto quartz substrates under different conditions during the transfer was interpreted as a function of the physical conditions in the film and the orientation of the chromophores with respect to the substrate. The changes produced in the film upon irradiation with visible and UV radiation, and the rate at which these changes take place, were found to be exclusively produced by reversible *E–Z* isomerization and were also influenced by the physical conditions in the film.

Acknowledgment. M.L.B. and S.W.H. acknowledge the European Commission for a Marie Curie Fellowship and support through the SPOTLITE project (NEST-Adventure). D.M. gratefully acknowledges financial support by the Fonds der Chemischen Industrie, Germany.

Supporting Information Available: Details on the fitting procedure of the polarized absorption spectra and extended results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA0630460