Spectroscopic properties of an amphiphilic styryl pyridinium dye in Langmuir–Blodgett films


Abstract

Surface pressure–molecular area and surface potential–molecular area isotherms of the recently synthesized amphiphilic dye 1 indicate that it forms monolayers on distilled water. A shift of the fluorescence maximum from 505 up to 570 nm was measured upon increasing the surface pressure applied during the Langmuir–Blodgett transfer from 7 up to 20 mN/m, and a slight red shift in the absorption. The increase of the surface pressure also produces a new blue-shifted band only present in the p-polarized component of the absorption spectra under oblique incidence of light. The results were interpreted as reorientation and association of the chromophores in the monolayer, according to the extended dipole model.

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Keywords: Amphiphilic dye; Monolayers; Optical properties; Fluorescence

1. Introduction

Our recent studies [1–3] on monolayers of some amphiphilic styryl dyes demonstrated the possibility of preparing ultrathin films with particular photosensitive properties and the ability to selectively bind heavy metal cations. These monolayers can serve as unique models for the investigation of molecular recognition and interaction phenomena at interfaces, as well as for future applications like sensitive components for ion detection, and novel materials for recording, storage and processing of optical information, as well as for photo-controlled extraction of metal cations.

Styryl dyes are also of potential interest in the fabrication of nonlinear optical materials due to their large hyperpolarizability [4]. For the preparation of useful devices, the nonlinearity of the molecule must be transferred to the bulk so the chromophore must be assembled in a noncentrosymmetric arrangement [5] (i.e. crystals, monolayers, etc.). When the compound is amphiphilic, the Langmuir–Blodgett technique provides the means to prepare nanoscale devices with a better control of their properties. Understanding of the order and potential association of the chromophores in these films, as well as the influence that this has on the spectroscopic properties of the chromophores is thus of high interest.

During the past years, numerous studies of various dyes in supramolecular systems (for example, Refs. [6–11]) were conducted, but only a few of them were concerning photosensitive styryl pyridinium derivatives at interfaces. For example, the absorption and emission properties of 1-octadecyl-4-styryl pyridinium salts have been studied in
solutions, crystals, micelles and Langmuir–Blodgett (LB) assemblies [12]. In other work [13], the structures of 1-octadecyl-4-stryryl pyridinium bromide monolayers spread on water and those deposited on a solid substrate as LB multilayers were determined by grazing-incidence X-ray reflection and IR transmission.

In this paper, we report on the monolayer preparation and the unusual spectroscopic properties of a novel amphiphilic pyridinium compound (dye 1) of particular interest as a model compound for parent benzo crown-ether derivatives, with potential uses as supramolecular ion sensors.

2. Experimental details

The amphiphilic styryl dye (1) was prepared by N-alkylation of 4-[(E)-2-(3,4-dimethoxyphenyl)ethenyl]pyridine (2) with 1-bromoocatdecane followed by anion exchange with perchloric acid.

In the synthesis of the initial compound 2 has been previously described [14]. The new dye 1 was thoroughly characterized by $^1$H NMR spectroscopy and elemental analysis. According to the NMR spectrum, the dye was obtained in the $E$-configuration ($^3J_{H(a),H(b)}=16.3$ Hz).

2.1. Preparation

4-[(E)-2-(3,4-Dimethoxyphenyl)ethenyl]-1-octadecylpyridinium perchlorate (1). A mixture of 4-[(E)-2-(3,4-dimethoxyphenyl)ethenyl]pyridine (100 mg, 0.42 mmol) and 1-bromooctadecane (138 mg, 0.42 mmol) was heated at 140°C for 4 h and then cooled to room temperature. The resulting colored mass was treated with boiling ethyl acetate (~15 mL) for 10 min and cooled to $-15$ °C. The precipitate formed was filtered, washed with cold ethyl acetate (3 mL) and dried in air to yield the corresponding bromide salt of the dye (139 mg). This bromide (110 mg, 0.19 mmol) was dissolved in minimal quantity of boiling absolute ethanol (~10 mL) and 70% aq. HClO$_4$ (33 µL, 0.38 mmol) was added to the resulting dye solution. The solution was then cooled to $-15$ °C and the precipitate formed was filtered, washed with cold absolute ethanol (3 mL) and dried in air to yield dye 1 as a yellow powder (104 mg, total yield 53%).

2.2. Methods

The surface pressure ($p$)–molecular area ($A$) and surface potential ($D\text{V}$)–molecular area ($A$) isotherms of dye monolayers were recorded on a rectangular trough (11×38×0.8 cm) provided with a 2-cm-wide filter paper Wilhelmy balance and a vibrating plate condenser [15]. Chloroform solutions (1 mM) of dye 1 (50 µl) were spread onto water or different 1 mM aqueous salt solutions at 20°C. After ca. 10 min of relaxation to allow solvent evaporation, the monolayers were compressed by moving the barrier with a constant speed of about 10 cm$^2$/min. The dye 1 monolayers were transferred onto quartz plates by the Langmuir–Blodgett technique at various constant pressures (mainly between 7 and 20 mN/m). Fluorescence of LB films was measured at different excitation wavelengths (366, 400 and 436 nm) on a Varian Cary Eclipse fluorescence spectrophotometer, and absorption spectra were recorded in a self-made setup [16].

3. Results and discussion

The dye 1 forms relatively stable monolayers on distilled water, and various aqueous subphases containing different salts. Surface pressure–area and surface potential–area curves for monolayers spread on water subphase are shown in Fig. 1. The $\pi/A$ isotherm indicates a transition between liquid expanded and condensed states of the dye monolayer at a surface pressure in the range of 7.1–7.5 mN/m and molecular areas of 0.65–0.68 nm$^2$/molecule (Fig. 1, curve
1. The surface potential value for a dye monolayer on water increased gradually to about 570 mV along the whole range of compression (Fig. 1, curve 2).

Important information on the chromophore association and orientation was gained by measuring the transmission spectra of the dye monolayers transferred onto quartz. A strong absorption band was observed in the range 350–450 nm (Fig. 2). The intensity of the band depended strongly on the surface pressure during monolayer transfer (Fig. 2, curves 1 and 2), and there is a slight red shift of 5 nm in the absorption band for the monolayer transferred at high surface pressure. This is evidence for some reorganization of the chromophores produced by the compression of the dye monolayer. It was unexpected that the dye fluorescence properties of the monolayer on quartz strongly depended on the surface pressure during monolayer transfer. A shift in the fluorescence maximum from 505 to 570 nm was observed by just increasing the surface pressure from 7 up to 20 mN/m (Fig. 2, curves 3 and 4, respectively), while the position of the absorption maximum was almost unaffected. This fluorescence shift was observed for dye 1 LB monolayer independently of the excitation wavelength around the absorption maximum (for example, 360, 400, 430 nm).

Monolayers transferred from a pure water subphase at low and high pressure (7 and 20 mN, respectively) were also characterized by polarized absorption spectroscopy measured with light incident under 45° (Fig. 3). An orientation parameter \( p \) [17] of 0.09 was estimated from these measurements for the chromophores in monolayers transferred at 7 mN/m (Fig. 3a, curves 1 and 2). This value indicates that the transition moment of the chromophore must be oriented preferably in the plane of the monolayer. An unusual feature was found in case of monolayers transferred at 20 mN/m. The band maximum was blue shifted in the p-polarized spectrum (Fig. 3b, curve 2) as compared to that obtained with s-polarized light (Fig. 3b, curve 1). Deconvolution of the p-polarized spectrum (assuming Gaussian behaviour) results in a new band with maximum at 360 nm as well as the same band observed in the s-polarized component (402 nm). This is evidence for some chromophore association in monolayers transferred at high surface pressure. Considering all the experimental evidence, the behavior of the monolayers on quartz indicates a change to a non-homogenous system when increasing the surface pressure during transfer from 7 to 20 mN/m.

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Fig. 1. Surface pressure–area per molecule (curve 1) and surface potential–area per molecule (curve 2) of dye 1 monolayers spread onto distilled water.

Fig. 2. Absorption and fluorescence spectra of dye 1 monolayers transferred onto quartz plates (one monolayer on each side) from distilled water at 7 mN/m (absorption: curve 1; fluorescence: curve 3) and 20 mN/m (absorption: curve 2; fluorescence: curve 4).

Fig. 3. Absorption spectra of dye 1 monolayers transferred onto quartz plates (one monolayer on each side) from distilled water: (a) at 7 mN/m (curve 1: s-polarized; curve 2: p-polarized light) and (b) at 20 mN/m (curve 1: s-polarized; curve 2 p-polarized light); angle of incidence 45°.
model proposed is sketched in the upper part of Fig. 3 where a mixture of dimers [18] of different nature and orientations coexist in the monolayers transferred at high pressure, and only the monomer is present in the monolayers transferred at low pressure with an absorption peak at 397 nm, emission at 505 nm, and an in-plane preferred orientation.

According to the extended dipole model [19], the shift in the absorption band of a dimer can be calculated according to Eqs. (1) and (2):

\[
\Delta E_{\text{dimer}} = \Delta E_{\text{monomer}} + 2J_{12}
\]

\[
J_{12} = \frac{\delta^2}{4\varepsilon_0\varepsilon} \left( \frac{1}{a_1} + \frac{1}{a_2} - \frac{1}{a_3} - \frac{1}{a_4} \right)
\]

where \(J_{12}\) is the interaction integral, \(\delta\) is the dipole charge, \(\varepsilon\) and \(\varepsilon_0\) are the dielectric constants of the media and the vacuum, respectively, and the distances \(a_i\) are defined in Fig. 3 (upper right sketch).

From this model, the blue shifted band in the p-polarized absorption may be interpreted as a face to face dimer, with transition moment oriented perpendicular to the monolayer plane. Using the following values \(|\delta|=0.29\ \varepsilon, \varepsilon=2.5, a_1=a_2=0.3\ \text{nm} \text{ and } a_3=a_4=0.69\ \text{nm},\) a blue shift of 43 nm is calculated which is in a good agreement with the experimental value (42 nm). Using the same model, a red shift of 5 nm in the non-polarized absorption at high pressure may be interpreted as a slipped dimer oriented in the monolayer plane, with a slip angle of about 32° (intermonomer distance was assumed to be the same for both kind of dimers). This kind of dimers could be also responsible for the emission at 507 nm or either for the formation of excimers, previously described for similar styryl compounds [12]. From the polarized absorption spectra (after deconcolution), an orientation parameter of \(p \approx 0.09\) is estimated for this slipped dimers in the 402 nm band, which is also consistent with the model proposed (Fig. 2b).

These results are the first direct evidence for particular chromophore association and orientation in monolayers of the novel dye herein presented. Such monolayers may be useful for the construction of functional supramolecular systems and their further applications. The properties of monolayers on solid substrates, in particular the emission wavelength, may be shifted by selection of the surface pressure during monolayer transfer from water. We are currently extending the studies of monolayer organization to several different salt subphases in order to fully understand the phenomena observed.

Acknowledgements

Some parts of this work were supported by grants from the Russian Foundation for Basic Research and the Deutsche Forschungsgemeinschaft (project 436 RUS 113/686). D.M. thanks the Fonds der Chemischen Industrie, Germany, for financial support.

References

[18] We cannot exclude larger aggregates, but the absence of sharp absorption bands limits the size of such aggregates to a small size.