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Thin Solid Films 476 (2005) 336–339

www.elsevier.com/locate/tsf

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

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Received 30 September 2004; accepted in revised form 15 October 2004
Available online 8 January 2005

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.

Keywords: Amphiphilic dye; Monolayers; Optical properties; Fluorescence

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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

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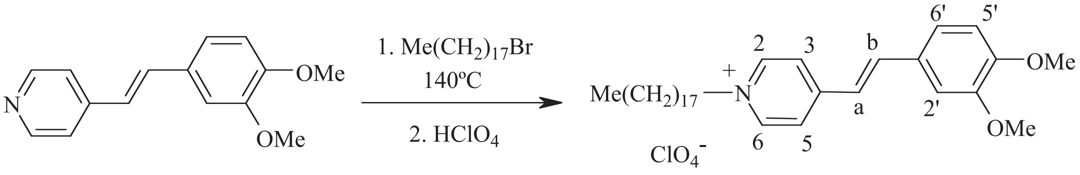
doi:10.1016/j.tsf.2004.10.052

solutions, crystals, micelles and Langmuir–Blodgett (LB) assemblies [12]. In other work [13], the structures of 1-octadecyl-4-styryl 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 spectrosopic 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-bromooctadecane followed by anion exchange with perchloric acid.



2 **1**

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-dimethoxy-phenyl)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%).

M.p.=164–166 °C. ^{1}H NMR (Bruker DRX500 spectrometer, CDCl$_3$, 30 °C) δ: 0.89 (t, 3 H, Me, *J* 6.7); 1.23–1.33 (m, 28 H, 14 CH$_2$); 1.37 (m, 2 H, CH$_2$CH$_2$CH$_2$N); 2.01 (m, 2 H, CH$_2$CH$_2$N); 3.96 (s, 3 H, MeO); 3.99 (s, 3 H, MeO); 4.50 (m, 2 H, CH$_2$N); 6.93 (d, 1 H, H(5′), *J* 8.2); 7.02 (d, 1 H, H(a), *J* 16.3); 7.19 (br.s, 1 H, H(2′)); 7.24 (br.d, 1 H, H(6′), *J* 8.2); 7.67 (d, 1 H, H(b), *J* 16.3); 7.97 (d, 2 H, H(3), H(5), *J* 4.8); 8.55 (d, 2 H, H(2), H(6), *J* 4.8). Anal. calcd. for $C_{33}H_{52}ClNO_6$ (594.2): C, 66.70; H, 8.82; N, 2.36. Found: C, 66.84; H, 8.87; N, 2.29%.

2.2. Methods

The surface pressure (π)–molecular area (A) and surface potential (ΔV)–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 π/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