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Immobilization of a fluorescent dye in Langmuir-Blodgett films

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Abstract

We immobilized a hemicyanine dye, Di-8-ANEPPS, in ordered thin films of an organic matrix, dihexadecyl phosphate (DHP), and we transferred the mixed monolayers onto solid support by the Langmuir-Blodgett technique. We used gold and quartz slides and indium tin oxide (ITO) evaporated on glass slides as substrates. The multilayers formation was confirmed by ellipsometric and contact angle measurements. The optical response of the nanostructures was investigated collecting UV–Vis absorption and fluorescence emission intensity profiles.

Keywords: Fluorescent dye; Langmuir-Blodgett films; Immobilization

1. Introduction

In recent years, many efforts have been devoted to build electronic devices using ultrathin organic films with the aim of observing new electrical and optical properties [1,2].

In this regard, our attention has been focused on a fluorescent molecule, Di-8-ANEPPS, which responds to changes of the surrounding medium modifying its electronic structure [3,4] (see Fig. 1). Such properties allow the use of this potential sensitive molecule for chemical sensors, biosensors, electrochromic displays and other microelectronic devices. An attempt to obtain an electro-optic device was carried out immobilizing the dye in ordered thin films of an anionic amphiphile (see Fig. 1), dihexadecyl phosphate (DHP), on solid support by the Langmuir-Blodgett technique. The optical properties of the fluorescent dye in the LB film were evaluated.

2. Experimental

2.1. Materials

The hemicyanine dye pyridinium, 4-[2-[6-(dioctylamino)-2-naphthalenyl]ethenyl]-1-(3-sulfopropyl)-, inner salt, Di-8-ANEPPS, was obtained from Molecular Probes (assay > 99%, $M = 592.88$) and dihexadecyl phosphate, DHP (assay > 98%, $M = 546.86$), was purchased from Fluka. Water was obtained from a Milli-RO coupled with a Milli-Q set-up (Millipore): resistivity 18.2 MΩ cm, pH 5.6 at 20 °C. Gold 99.9% slides, quartz slides (Hellma) and indium tin oxide, ITO, sputtered onto glass slides (Thin Film Devices, CA) were used as solid supports. The quartz slides were cleaned with chromic acid for a night, then rinsed with water and immersed in ultrasonic bath of $CHCl_3$ for 10 min. Gold substrates were pre-treated by the flame annealing method according to a procedure previously reported [5] and further immersed in a piranha solution (30:70 v/v H_2O_2 30%/H_2SO_4) at room temperature, then rinsed thoroughly with Milli-Q and finally dried. ITO slides were cleaned following a procedure described by Hillebrandt and Tanaka [6] consisting of an ultrasonic bath with acetone and ethanol for 10 min followed by immersion in a solution of 30% H_2O_2/25% NH_4OH/H_2O (1:1:5 v/v/v) for an hour at a temperature of 60°.

2.2. Methods

Mono- and multilayers of Di-8-ANEPPS/DHP mixtures were prepared using a KSV 5000 film balance (KSV Instruments); the experimental conditions were previously reported [7]. The temperature, controlled by a Haake thermostat, was 20 °C for all the experiments. Transfer surface pressures of the monolayers were 20 and 35 mN

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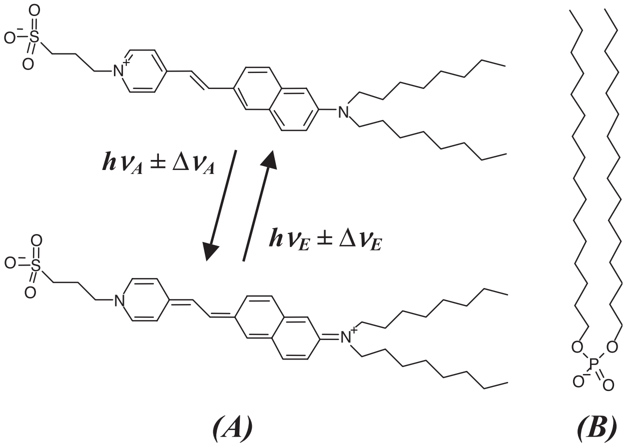

Fig. 1. Chemical structures of Di-8-ANEPPS (A) and of DHP (B).

m^{-1}: the transfer rates were 3 mm min^{-1} both for the upstroke and for the downstroke. The transfer ratio obtained [8] was 1.0 ± 0.1 in all cases. Ellipsometric measurements were performed with a Rudolph Research Ellipsometer (Mod. 437-02) equipped with a He–Ne laser. Contact angle values, $\theta°$, were determined using an automated goniometric apparatus (Ramé-Hart, USA): Milli-Q water was used as a probe liquid. UV–Vis absorption and fluorescence emission spectra were recorded using a Perkin-Elmer Lambda 900 and LS50B instruments, respectively.

3. Results and discussion

Surface pressure vs. molecular area, π–A, isotherms of Di-8-ANEPPS/DHP mixtures were characterized in a previous paper [7]; the results indicated that the association of the dye with the amphiphilic matrix depends on the surface density of the monolayer and on the mixing ratio used. In particular, spreading isotherms of the mixed monolayers containing a small quantity of Di-8-ANEPPS show the presence of three regions separated by two transition surface pressures, i.e. 28 and 40 mN m^{-1}. In Fig. 2, we reported the spreading isotherms of the 1:4 and of the 2:3 Di-8-ANEPPS/DHP monolayers on water subphase. We optimised the transfer of the selected mixtures onto solid supports at 20 and at 35 mN m^{-1}, that is to say before and after the first transition.

Contact angle values obtained for the multilayers on quartz slides show different wettability properties (see Table 1). LB films of 2:3 Di-8-ANEPPS/DHP mixtures show low and scarcely reproducible $\theta°$ values, indicating a slight hydrophobicity and a poor compactness of the multilayers. On the contrary, 1:4 Di-8-ANEPPS/DHP LB layers show higher contact angle values, in particular the monolayers transferred at 35 mN m^{-1} exhibit a marked stability over time, confirmed also by their relaxation behavior at water–air interface at constant π (data not reported).

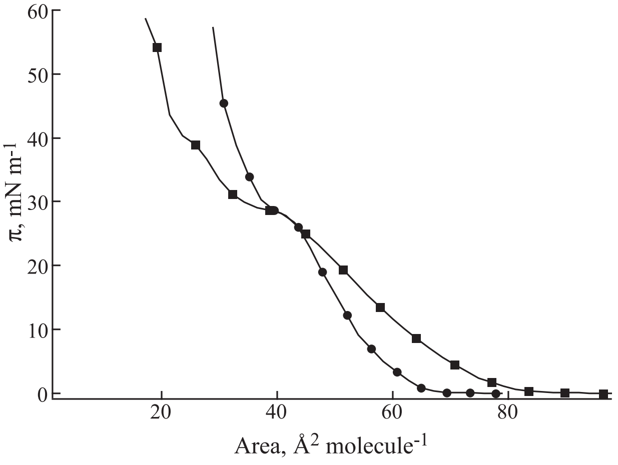

Fig. 2. Surface pressure vs. molecular area of monolayers of 1:4 Di-8-ANEPPS/DHP (circles) and of 2:3 Di-8-ANEPPS/DHP (squares) on water subphase, pH 5.60.

The hydrophobicity of the latter system on metallic supports is a bit higher than that on quartz, because of the different morphology of the pure substrates or of the different orientation of the LB layers. The ellipsometric thickness of LB films obtained on gold substrates was measured as a function of the number of layers. The experimental data show a linear behavior with an average thickness of 17.4 Å for each layer. If we ascribe the ellipsometric thickness totally to the DHP molecules, we obtain an angle of 38° with respect to the normal to the surface plane, a value consistent with the literature reports [9]. However, the incorporation of Di-8-ANEPPS in Langmuir-Blodgett films is clearly evidenced by the electronic spectra of the LB layers. Fig. 3A and B shows the UV–Vis absorption and fluorescence emission spectra of 5 LB layers on quartz and on ITO slides together with the electronic spectra of the 1:4 Di-8-ANEPPS/DHP in $CHCl_3$ solution. Table 2 reports the characteristic absorption and emission intensity maxima. Although the absorption profile of the multilayers on quartz slides is very different from that shown in solution, the fluorescence emission intensity curves are quite similar. In chloroform solution, the dye exhibits two absorption bands centred at 330 and at 550 nm. The bands are ascribed to the isolated transition of the pyridinium and naphthyl moieties and to the π–π* transition over the entire chromophore in the trans-configuration, respectively [10–13]. In the case of LB

Table 1
Static contact angle values, θ, of Di-8-ANEPPS/DHP LB films on solid supports

Support	Di-8-ANEPPS/DHP	π, mN m^{-1}	θ, °
Quartz	2/3	20	< 60
	2/3	35	< 60
	1/4	20	83 ± 1
	1/4	35	90 ± 1
ITO	1/4	35	96 ± 1
Au	1/4	35	95 ± 3

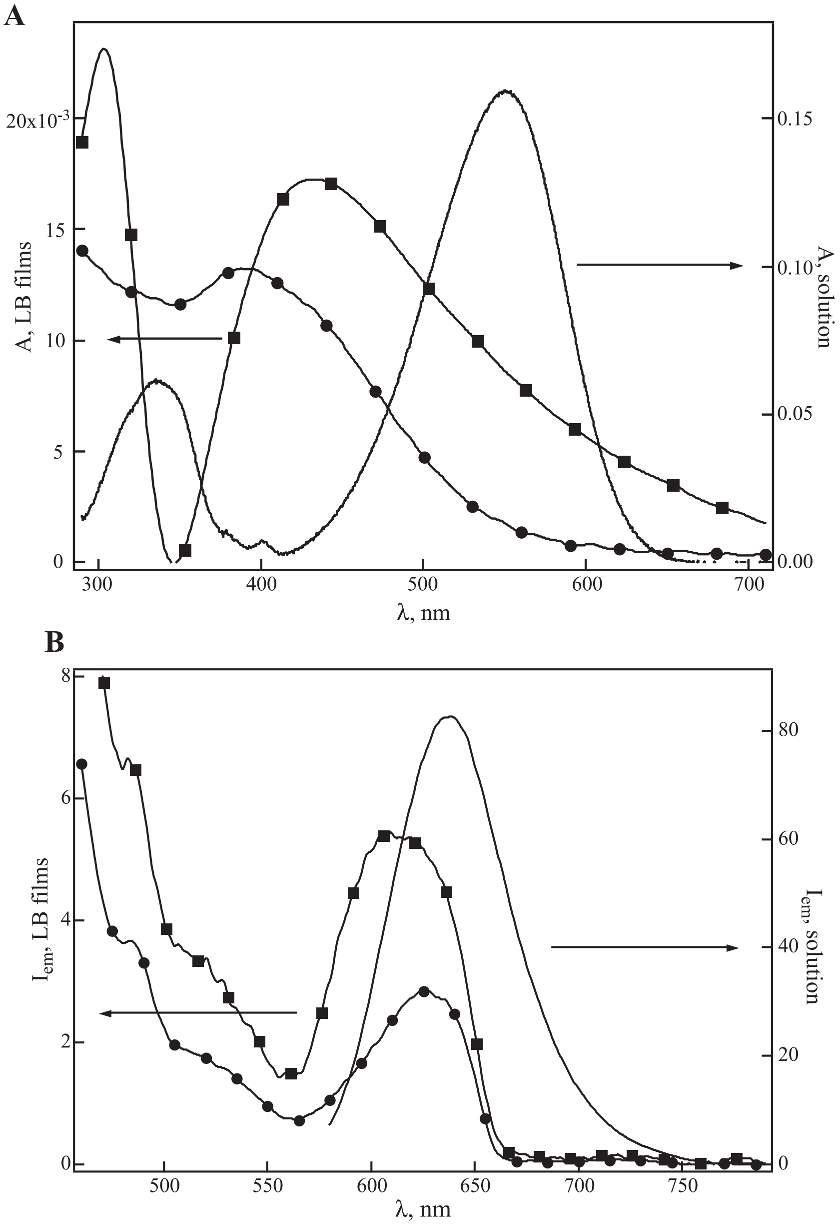

Fig. 3. (A) Left axis: UV–Vis spectra of 5 LB films of 1:4 Di-8-ANEPPS/DHP on quartz (circles) and on ITO (squares); $\pi = 35$ mN m^{-1}. Right axis: UV–Vis spectra of solutions of Di-8-ANEPPS/DHP 1:4 (no symbols) in CHCl$_3$; [Di-8-ANEPPS] = 3.98 10^{-6} M. (B) Left axis: Fluorescence emission intensity profiles of 5 LB films of 1:4 Di-8-ANEPPS/DHP on quartz (circles) and on ITO (squares); $\pi = 35$ mN m^{-1}, $\lambda_{exc} = 430$ nm. Right axis: Fluorescence emission intensity profiles of solutions of 1:4 Di-8-ANEPPS/DHP (no symbols) in CHCl$_3$; [Di-8-ANEPPS] = 3.98 10^{-6} M, $\lambda_{exc} = 550$ nm.

multilayers, the transition at 550 nm is shifted to lower wavelengths, according to the hypothesis that the chromophore remains anchored in a polar zone of the monolayer. The emission spectrum shows a band centred at 627 nm, ascribed to the chromophore in the monomer form. The slight shift of the emission band reflects the stronger polarity of the environment sensed by the chromophore in LB films with respect to the solution.

Table 2
UV–Vis absorption and fluorescence emission intensity maxima

Di-8-ANEPPS/DHP 1:4	λ_{abs}, nm	λ_{em}, nm
CHCl$_3$ solution	335, 550	638
5 LB layers on quartz, $\pi = 35$ mN m^{-1}	388, 430 (sh)	485, 526, 627
5 LB layers on ITO, $\pi = 35$ mN m^{-1}	303, 430	482, 519, 610

The electronic spectra on ITO surfaces are quite different from those on quartz slides (see Table 2); this finding may be due to a different orientation of the dye on the metal surface or, more probably, to a change in the electrical properties of the ITO layer. In fact, it is known from the literature [14] that the presence of a monolayer on conductive or semiconductive materials modifies their energy bands and their optical properties.

4. Conclusions

Di-8-ANEPPS molecules have been successfully incorporated in multilayers of DHP by the Langmuir-Blodgett technique. The compactness and the stability of the resulted nanostructures were analysed by contact angle and ellipsometric measurements. In particular, LB films obtained transferring 1:4 Di-8-ANEPPS/DHP monolayers at $\pi = 35$ mN m^{-1} resulted the most hydrophobic and the most stable system.

The analysis of the UV–Vis spectra of the LB films on quartz showed a displacement to lower wavelengths with respect to the solution, indicating the presence of the chromophore in a rather polar environment. The possibility to obtain stable and reproducible multilayers of 1:4 Di-8-ANEPPS/DHP mixture is of a great interest: Di-8-ANEPPS could be used as an active material for organic light emitting diodes (OLEDs) or as a filter for traditional electro-optical device.

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