Characterization of hemicyanine Langmuir–Blodgett films by picosecond time-resolved fluorescence

Emmanuel Abraham [a,*], Christine Grauby-Heywang [a], Sophia Selector [b], Gediminas Jonusauskas [a]

[a] Centre de Physique Moléculaire Optique et Hertzienne, UMR 5798, Université Bordeaux I, 351 Cours de la Libération, 33405 Talence, France
[b] Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Leninsky pr., 31-4, GSP-1, 119991 Moscow, Russia

ARTICLE INFO

ABSTRACT

Hemicyanine Langmuir–Blodgett films have been elaborated and characterized using stationary and time-resolved spectroscopic techniques. Depending on the experimental conditions, especially the pH of the water subphase, the absorption spectra of the films indicate the presence of non-fluorescent H-aggregates in the monolayer. Time-resolved fluorescence measurements revealed three mono-exponential decay times: a very short one (20–23 ps) attributed to an excited intramolecular charge transfer state and two longer ones (100–120 ps and 400–590 ps) attributed to the photoisomerization of the chromophores.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Monolayer or multilayer systems have been the subject of substantial investigations in recent years, motivated by the possibility to functionalize the corresponding films with various active chemical groups [1,2]. Functionalization includes for instance capabilities of energy transfer, charge transfer, molecular recognition, information processing, etc. To improve the functionalization of these complex systems, it is essential to investigate the photophysical properties of the organic molecules incorporated into these films [3].

Particularly, for the past decade, hemicyanine LB films and Langmuir monolayers have been the subject of numerous investigations [4–9]. These films exhibit an efficient second harmonic generation and several studies report on the relationship between the non-linear optical properties and the chromophore structure [10–12]. Particularly, the role of the donor group and acceptor group of electrons has been under debate [13].

In this paper, 4-[4-(dimethylamino)styryl]-1-docosylpyrimidium bromide (DMA-R, Fig. 1a) has been used for the formation of the hemicyanine LB films and we will focus on the photophysical characterization of the films using steady-state and time-resolved spectroscopic methods. DMA-R is composed by a photosensitive chromophore and a long hydrophobic chain. The chromophore is composed by a donor group of electrons (dimethylamino group)

and an acceptor group of electrons (pyridinium moiety) connected by an ethylene chain with delocalized π-electrons. Especially, the central double bond can lead to trans–cis photoisomerization. More generally, the photophysics of DMA-R in solution can be compared with the photophysics of the similar molecule DASPMI (trans-4-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide) or more generally push–pull stilbenes [14–18].

Photoinduced intramolecular charge transfer (ICT) processes in aromatic systems with strong electron donor and acceptor groups have been extensively studied over the past 20 years [19–21]. In solutions, these processes are known to be strongly dependent on solvent–solute interactions, and the existence of twisted intramolecular charge transfer (TICT) excited states has been under debate [22,23]. In push–pull dyes, the presence of single bonds linking the donor group and the acceptor group of electrons makes TICT state formation possible and could lead to increase the coupling between the excited state and the vibrational levels of the ground state. This effect will facilitate the effective non-radiative decay according to the loose bolt theory [19,24].

To explain the photophysics of push–pull stilbenes in solutions, Rettig et al. proposed a kinetic model that implies both intramolecular charge transfer and photoisomerization [25]. For DMA-R, as the compound is ionic, the situation is a little bit different. The charge transfer does not lead to a complete charge separation but to a simple charge shift. Nevertheless, we can assume that Rettig's model can be applied. The corresponding kinetic scheme is depicted in Fig. 2 and can be explained as follows. Before excitation, the molecule has a planar geometry and a high dipole

---

* Corresponding author. Tel.: +33 54000 3122; fax: +33 54000 6970.
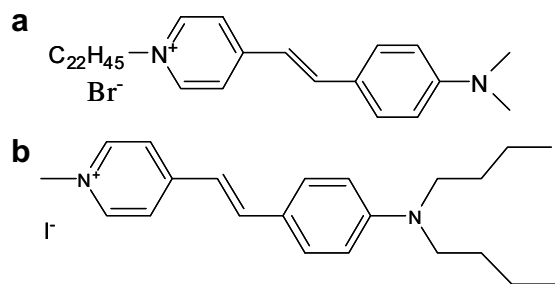E-mail address: em.abraham@cpmoh.u-bordeaux1.fr (E. Abraham).

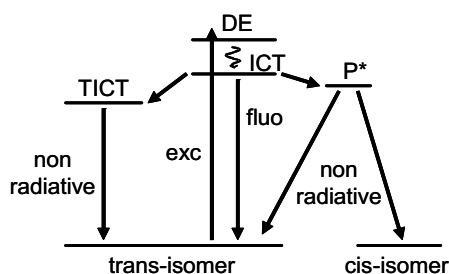**Fig. 1.** Molecular structure of (a) DMA-R and (b) DBA-CH₃.

Fig. 2. Conventional three-state kinetic scheme used as a basis for the interpretation of the photophysical behavior of donor–acceptor dyes.

moment owing to the ionic character. Just after excitation, by vertical transition, the initial Franck–Condon state (DE for delocalized state) evolves on a 1 ps timescale towards an ICT state without any deviation from the initial conformation. Owing to the charge redistribution after excitation, the ICT state has a smaller dipole moment than the initial ground state and the molecular relaxation is possible by direct radiative recombination from the ICT state to the ground state on a nanosecond timescale.

From this state, *trans–cis* isomerization can occur in non-polar solvents by population of the intermediate phantom state P*. However, in polar solvents, the new TICT state, which is highly polar, can be populated because the energy barrier between the ICT and the TICT states decreases and the route for isomerization is strongly quenched. The formation of the TICT state, on a picosecond timescale, is controlled by the solvent properties (polarity, viscosity, relaxation time) and also by conformational changes between the donor group and the acceptor group of electrons of the dye, owing to internal single bond twistings.

For DMA-R, it seems that, if a TICT state can be formed, it should be mainly formed by twisting the aniline ring (rotation of the dimethylanilino group around the C–C single bond) [26]. It has also been confirmed by several studies that the relaxation from the TICT state to the ground state should be non-radiative, in agreement with TICT state formation theory (perpendicular conformation between donor and acceptor groups) [27].

In solutions, all these considerations could certainly be applied to the DMA-R molecule. However, very few information have been collected concerning the photophysics of LB films composed with DMA-R. This may be due to the low absorbance of the films (in the order of 10^{-3}) making it difficult to measure the time-resolved emission. For the functionalization of the films, such as light-harvesting, energy transfer, sensor capabilities, it is of primary importance to understand the photodynamics of the films after photoexcitation.

In this paper, absorption and fluorescence measurements were used to characterize the photophysics and photodynamics of DMA-R LB films. Especially, a time-resolved fluorescence technique was adopted to determine quantitatively, with a picosecond resolution time, the emission lifetimes of the films transferred under different experimental conditions. Especially, the influence of the pH of the water subphase will be discussed.

2. Materials and methods

2.1. Materials

trans-4-[4-(Dimethylamino)styryl]-1-docosylpyridinium bromide (DMA-R, Fig. 1a) was purchased from Sigma Aldrich (95% pure) and was used without further purification. Chloroform (HPLC grade) was also purchased from Sigma (France). Ultrapure Millipore water (pH 5.6, resistivity > 18 MΩ cm) was used as subphase. Its pH was increased to 10 or decreased to 4 by adding a concentrated solution of NaOH or HCl, respectively.

As DMA-R is spread onto a water surface before the LB transfer, the chromophore is supposed to interact with water molecules. Therefore it should be important to understand the photophysics of DMA-R in water solution. However, the solubility of the molecule is very poor into water solution due to the long hydrophobic chain. To understand the photophysics of the dye in the presence of water molecules, we also studied *trans*-4-[4-(dibuthylamino)styryl]-1-methylpyridinium iodide (DBA-CH₃, Fig. 1b) which is similar to DMA-R except that there is no long hydrophobic chain. The molecule was 98% pure and purchased from Sigma Aldrich. DBA-CH₃ cannot be used for monolayer formation but can be dissolved into water (pH 4–10). In water solution, for pH < 6–7, the dibutylamino group is able to protonate.

2.2. Methods

To characterize the photophysics of DMA-R films, we used different experimental systems to measure the absorption and fluorescence properties of the samples. All preparations and measurements were made at room temperature.

2.2.1. Langmuir–Blodgett transfer
Surface pressure measurements were carried out in air by using a 601M Nima Langmuir through (approximately 19 cm × 12 cm × 0.5 cm) equipped with a Wilhelmy balance (Nima). Molecules were dissolved in chloroform at a concentration in the 0.5–1 mM range. After spreading of the solution and evaporation of solvent (15 min), molecules were compressed continuously at a rate of 15 cm² min⁻¹ until the suitable surface pressure was reached. Monolayers were then kept at constant surface pressure during 10–15 min, thanks to a pressure-control system which maintained the surface pressure at the required value by decreasing the monolayer surface. They were finally transferred from the air–water interface onto quartz plates by the Langmuir–Blodgett (LB) method, at a speed of 20 mm/min. This transfer was also carried out under constant surface pressure. The temperature of the subphase was kept constant to 20 ± 1 °C, and all these experiments were performed under red light, in order to limit non-desired photoreactions.

2.2.2. Absorption spectra of monolayers at the air–water interface (Langmuir monolayers)
UV–visible absorption spectra of Langmuir monolayers were acquired with a home-built spectrophotometer. A Deuterium lamp was guided to the water surface by an optical fiber. The trough is equipped with a transparent quartz window so that the light transmitted through the monolayer can be collected by another optical fiber and imaged into a dual channel fiber optic spectrometer (Avantes, AvaSpec-2048-2). To determine the optical density of