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Proton transfer involving a photoacid in Langmuir–Blodgett films of octadecylamine by time-resolved fluorescence spectroscopy

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Abstract

Proton transfer in organized assembly has been investigated by steady-state and picosecond time-resolved fluorescence spectroscopy. Pyranine has been incorporated into the functionalized Langmuir–Blodgett (LB) films of octadecylamine. This paper is the first example of investigating proton transfer involving pyranine in the restricted geometry of functionalized LB films. Time-resolved fluorescence spectra of pyranine in LB film matrices show that as deprotonation occurs the $PyOH^*$ band decays and the PyO^{-*} band builds up. It is observed that the proton transfer reactions in restricted geometry can be monitored by choosing proper parameters.

Keywords: Pyranine; Proton transfer; Langmuir–Blodgett films; Time-resolved fluorescence

1. Introduction

The fluorescence of pyranine (8-hydroxy-1,3,6-pyrene-trisulphonic acid trisodium salt) has intrigued the scientific community for half a century [1–4] and used in scientific, medicinal and commercial applications. Pyranine has been used to study the binding of carbon monoxide to hemoglobin [5], as a pH probe of liposome interiors and surfaces [6] and in sensors of pH [7], carbon dioxide [8] and ammonia [9]. The study of reactions of acid and bases and the exact nature of the process and the role played by the surrounding medium is of paramount interest. In the first excited states, the aromatic alcohols are stronger acids than their ground state where the rate of deprotonation may increase by several orders of magnitude ($pK^* < pK^0$) [2]. One of the key features of pyranine molecule is the excitation of both acidic and basic forms in different environment resulting in the fluorescence of both forms. Steady-state fluorescence spectra of pyranine exhibit two fluorescence bands where the short wavelength is the emission of the neutral form ($PyOH^*$), while the other one, at the longer wavelength, is that of the excited anion (PyO^{-*}). The Langmuir–Blodgett (LB) films of octadecylamine provide a suitable microenvironment where the anionic dyes can be incorporated. The reactivity in any reaction medium depends not only on its chemical nature but also on its structure. One of the interesting features of the structure and reactivity is relevant to the efficiency of proton transfer. Photoinduced proton transfer from pyranine to water has been studied by picosecond [10] and ultrafast fluorescence spectroscopy [11]. Information on proton transfer efficiency and thus on acidity in the water pool of reversed micelles [12,13] provided the interesting aspects of the relation between structure and reactivity. Pyranine has also been used as a probe for charged miceller surfaces [14], vesicles [15] and binding sites of proteins [16].

The aim of the present work is to investigate, by means of picosecond time-resolved spectroscopy, the deprotonation and reprotonation processes of pyranine in the molecular organizates. Attention has been focused in the present work on the influence of positively charged surfaces on proton transfer

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mechanism. Cationic LB films of octadecylamine were used to provide the medium for proton transfer involving pyranine. Pyranine has been incorporated in the LB films of octadecylamine at different pH. The picosecond time-resolved fluorescence spectra of pyranine in LB film matrix shows that as deprotonation occurs the $PyOH^*$ band decays and the PyO^{-*} band grows. This molecule binds tightly to the cationic LB film owing to its trianionic character similar to its binding with the cationic surface of a membrane [15]. Moreover, the results allow us to examine the relation between structure and reactivity regarding proton transfer in the LB films. To the best of our knowledge, this is the first report on the incorporation of pyranine in LB films and the time-resolved fluorescence spectra in the picosecond time domain demonstrate the proton transfer in the functionalized organized assembly. Also we present the important role of microenvironment on the proton transfer process.

2. Experimental section

A Langmuir-type film balance (Lauda) was used to prepare the nine layers of LB films of octadecylamine on quartz substrate at a surface pressure of 45 mN/m and 20 °C, where the pH of the aqueous subphase was 10.3 [17]. Surface pressure–area isotherms at the air–water interface showed that the area occupied by the octadecylamine molecule increased on the pyranine aqueous subphase compared to that on the water subphase at the lower pressure region at different pHs. Distilled water (pH ∼ 5.8 at 20 °C) deionized by a Milli-Q water purification system was used. The pHs of the aqueous subphase were varied at about 10.3 and 3.1 with addition of $NaOH_{aq}$ and HCl_{aq}, respectively just before the measurements. The isotherms suggest that the octadecylamine molecule is interactive with the pyranine molecule. The octadecylamine LB films were immersed in the aqueous solution of pyranine at different pH for a given period of time. The pHs of the solution were adjusted with the addition of $NaOH_{aq}$ and HCl_{aq}, respectively. Fluorescence spectroscopic studies have been used to investigate the photophysical properties of pyranine in octadecylamine LB films. Steady-state fluorescence emission spectra of the LB films were recorded on a Hitachi MPF-3 fluorescence spectrophotometer. Picosecond time-resolved fluorescence spectroscopy was performed by a streak camera (Hamamatsu, C4334-01) operating at the photon counting mode. The fundamental output (775 nm, pulse width ≈ 130 fs, repetition rate 1 kHz) from a femtosecond Ti:Sapphire regenerative amplifier seeded by the second harmonic of a mode-locked Er-doped fiber laser (Clark-MXR, CPA-2000) was used to excite an optical parametric amplifier (Clark-MXR, IR-OPA). The second harmonic of the signal wave from the OPA was used for excitation. We used 400 and 450 nm as the excitation wavelength (λ_{ex}) for exciting the PyOH and PyO^- species, respectively. The laser beam was focused on the LB films in a quartz cell under a nitrogen atmosphere. Scattered light at 90° was focused onto the entrance slit of a single spectrograph (Acton Research, SpectraPro 150) equipped with the streak camera. Long-wavelength-pass filters (Sigma koki, SCF-38L) were placed between the collimate lens and the entrance slit. A synchronous delay generator (Hamamatsu, C4792-01) was used to compensate for the time delay in the electronic circuit of the streak camera. The FWHM of the instrument response function was ∼30 ps. The two-dimensional data from the streak camera were accumulated and analyzed with a personal computer. All measurements were performed with the photon counting mode at room temperature. The fluorescence decay curves at the respective emission maxima were fitted to the multiexponential function convoluted with the instrumental response function. The experimental set up for time-resolved spectroscopy has been described in detail elsewhere [18]. The measured fluorescence lifetimes of pyranine in aqueous solution with our experimental setup are in good agreement with the previously reported values [14].

3. Results and discussion

Fig. 1 shows the fluorescence spectra of pyranine in octadecylamine LB films after immersing in aqueous solution of pyranine (1×10^{-4} M, pH ≈ 6.2) for different periods of time. The emission spectrum of pyranine in aqueous solution (1×10^{-4} M) has also been included in Fig. 1 for comparison. In aqueous solution, the emission intensity of the neutral form of pyranine ($PyOH^*$) at 445 nm is very weak, while a strong emission with band maximum at 510 nm is observed from the anionic form of the pyranine (PyO^{-*}). In bulk water, with a pH between the ground and excited pK_a values, the emission arises mostly from

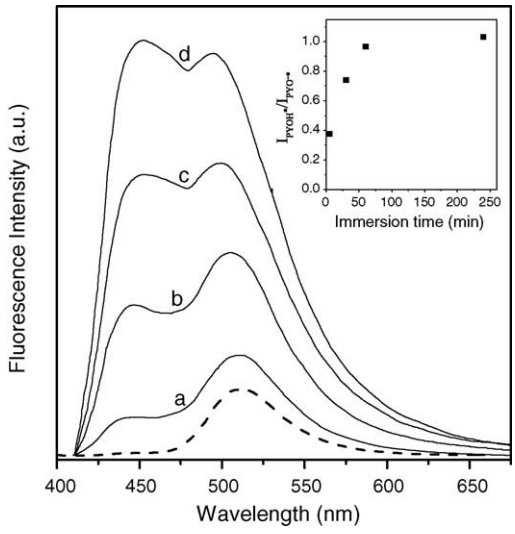
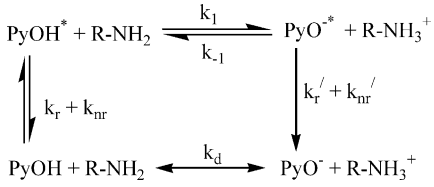


Fig. 1. Fluorescence spectra of octadecylamine LB film after immersing in aqueous solution of pyranine (1×10^{-4} M) for different period of time (a) 5, (b) 30, (c) 60 and (d) 240 min. Fluorescence spectra of pyranine in aqueous solution (- - - -) (λ_{ex} = 400 nm). Inset shows the ratio of fluorescence intensities of the $PyOH^*$ and PyO^{-*} species as a function of the immersion time of the LB films in aqueous solution of pyranine.

the prototropically formed excited state base. The peak emission intensities at 445 and 510 nm observed from pyranine incorporated in the LB film matrix varies as a function of immersion time as shown in Fig. 1. Suwaiyan et al. [19] earlier reported that the protonation/deprotonation kinetics of pyranine in water–organic solvent mixtures were controlled by the proton-acceptor character of the medium. With increase of immersion time of the LB film in aqueous solution of pyranine, both the intensities of the $PyOH^*$ (band maximum at 445 nm) and PyO^{-*} (peak intensity at 510 nm) emission bands increase. It is worth noting that the ratio of I_{PYOH*} and $I_{PYO^{-*}}$ increases in the LB film matrix with the increase of the immersion time as shown in the inset of Fig. 1. These results clearly indicate that the pyranine molecule is sensitive to the microenvironment. The high adsorbability is attributed to the presence of ionic interaction between the amino group of the octadecylamine LB film and the sulfonate groups of pyranine, similar to the LB films of long-chain alkylammonium salts. The ratio of intensities between the two peaks at 445 and 510 nm must be related to the factors known to significantly affect the fluorescence of pyranine, e.g., protonation/deprotonation events and the rate kinetics. The increase of fluorescence intensities of the peak at 445 nm must have been occurred due to the protonation of the pyranine molecule adsorbed in the octadecylamine LB films. The emission spectra reveals that the equilibrium of $PyOH^*$ and PyO^{-*} in the excited states becomes more and more competitive with fluorescence emission. In the present case, the extent of dissociation can be modified by the immersion time, which hinders the excited state prototropism and results in an increase in undissociated pyranine ($PyOH^*$) emission [14]. It is important to mention that pyranine, despite its polyanionic character, binds significantly to the zwitterionic micelles and lecithin vesicles [20,21]. In the present case, pyranine is a trianionic probe in aqueous solution, which is strongly attracted to the immersed cationic LB film of octadecylamine. A usual kinetic scheme has been used to describe the behavior of pyranine in LB films of octadecylamine ($R–NH_2$).



k_1 is the rate constant of proton transfer to the octadecylamine, k_{-1} is the recombination rate constant of the excited basic form and a proton, k_r and k_{nr} are the radiative and non-radiative rate constants of $PyOH^*$, respectively, and k'_r and k'_{nr} are the corresponding values for PyO^{-*}. The relative magnitude of k_1 and k ($1/k = 1/k_r + k_{nr}$) is a critical factor in determining the emission from $PyOH^*$ in a given matrix. In aqueous solution, the reported values of k_1 and k are 2.1×10^9 and $1.6 \times 10^8\ s^{-1}$, respectively, making the emission from $PyOH^*$ at 445 nm unobservable [12]. The strong emission observed at 445 nm from $PyOH^*$ in adsorbed LB films may be interpreted by two plausible explanations: (i) the decrease in the excited state lifetime ($\tau \equiv 1/k$) of pyranine in the LB film so that k exceeds k_1, (ii) the diminished rate of proton transfer (k_1). Politi and Fendler [14] earlier reported a 10-fold slower rate of proton dissociation for pyranine in micellar environment. Similar reduction in excited state deprotonation rate observed in case of 1-naphthol in many organized media has been ascribed to the lower polarity of the microenvironment and the lower accessibility of the fluorescent probes, encaged in the micelles, to the water molecules [22].

To investigate the details of the protonation–deprotonation processes, excited state dynamics of the pyranine incorporated in the LB films have been performed. Fluorescence decay curves are recorded for the LB films with different adsorption conditions and at different emission wavelength. In the present case, the fluorescence decay curves are analyzed as a sum of exponentials. Hence, the fluorescence decay profiles are fitted with the following equation

$$I(t) = \alpha_1 \exp^{-t/\tau_1} + \alpha_2 \exp^{-t/\tau_2} \quad (1)$$

where the contribution of the fast and slow components amount to $\alpha_1\tau_1/(\alpha_1\tau_1 + \alpha_2\tau_2)$ and $\alpha_2\tau_2/(\alpha_1\tau_1 + \alpha_2\tau_2)$. Fig. 2 presents the fluorescence decay of octadecylamine LB films after immersing in aqueous solution of pyranine for 5 min. The decay curves analyzed using Eq. (1) yields lifetimes of 35 and 235 ps for pyranine adsorbed in LB films of octadecylamine where the emission is monitored at the 445 nm (neutral emission) and the contributions of the fast and slow decay components are 51 and 49%, respectively (Fig. 2A). In this case, the value of k is determined as $7.5 \times 10^9\ s^{-1}$. When the decay is monitored at 510 nm (anion emission), lifetimes of 120 and 995 ps with the contribution of 60 and 40%, respectively, are obtained. The fluorescence lifetime of the protonated ($PyOH^*$) and deprotonated (PyO^{-*}) species in LB films are less than the lifetime observed in aqueous solution. However, the fluorescence decays of pyranine in water/alcohol mixtures are reported to be much faster than that of bulk water [19]. The reported fluorescence lifetimes of pyranine molecules in water/alcohol mixtures [19] are consistent with the measured lifetimes for pyranine adsorbed in octadecylamine LB films. Politi and Fendler [14] reported the difference in the excited state properties of pyranine in aqueous and micellar environments. The decrease in fluorescence lifetime of PyOH has been related to reprotonation and/or to the possibility that some protons could not escape the field of PyO^- in the micellar cage [23]. Fig. 2B illustrates the dependence of the fluorescence decay on the observation wavelength of octadecylamine LB film after immersing in aqueous solution of pyranine for 4 h. The fluorescence decay at the observed wavelength of 445 nm is dominated by an exponential decay with lifetime of 35 ps, whose contribution is higher (80%) where as the contribution of the slower component with a lifetime of 320 ps is 20% (Fig. 2B). The value of rate constant k is estimated as $1 \times 10^{10}\ s^{-1}$. On the other hand, lifetimes of 270 and 40 ps are obtained with contributions of

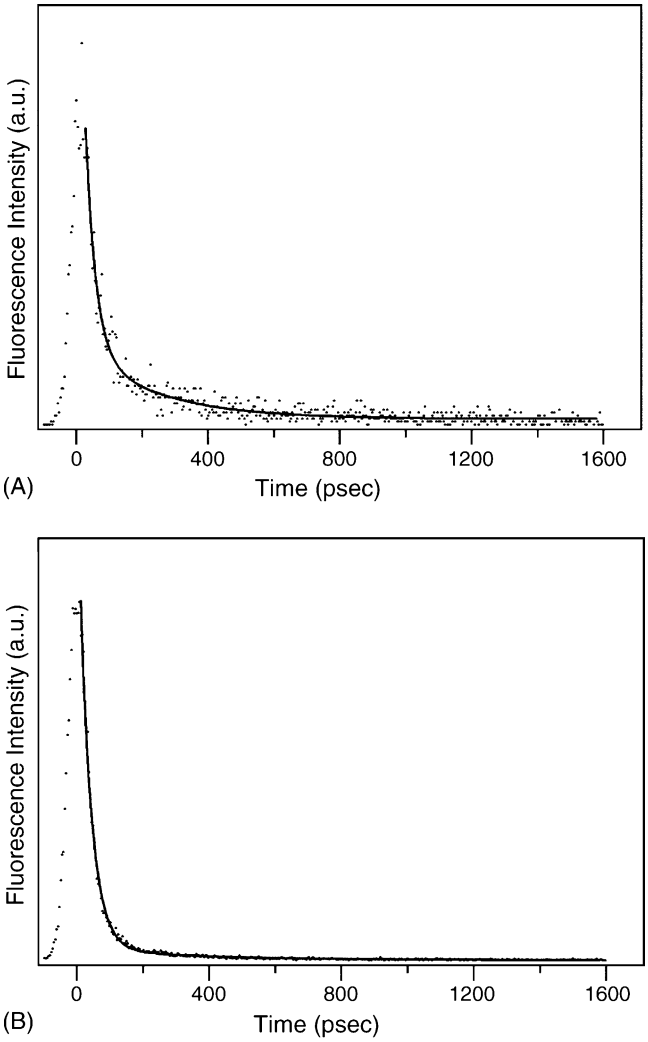


Fig. 2. Fluorescence decay (λ_{em} = 445 nm) of octadecylamine LB film after immersing in aqueous solution of pyranine (1×10^{-4} M) for 5 min (A) and 240 min (B).

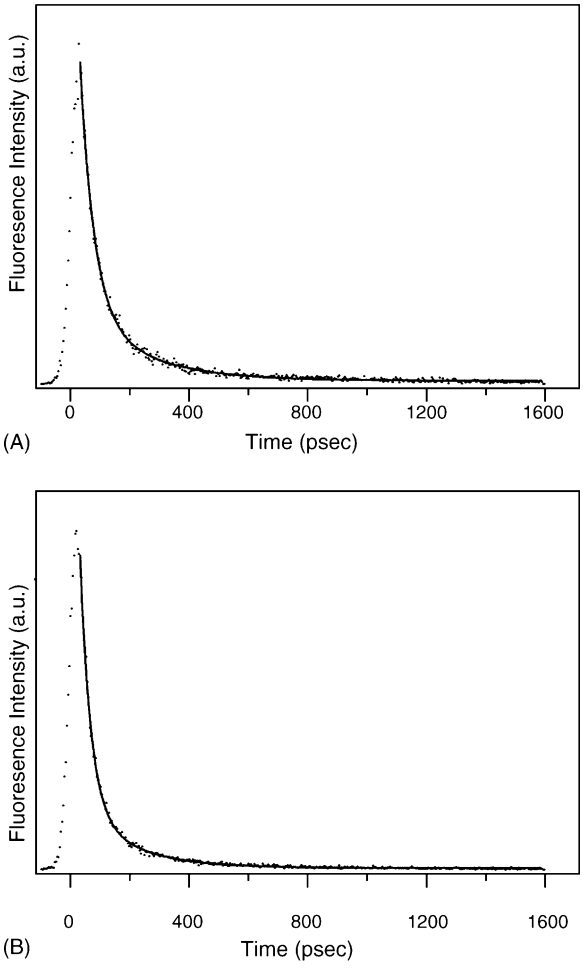


Fig. 3. Fluorescence decay of octadecylamine LB film after immersing in aqueous solution of pyranine (1×10^{-4} M) at (A) pH 2.0, (B) pH 9.0. Fluorescence decay curve measured at (A) 445 nm and (B) 510 nm, respectively.

45 and 55%, respectively, where the emission is monitored at 510 nm. Using the fluorescence lifetime of both species and the absolute fluorescence quantum yield of $PyOH^*$, the deprotonation rate (k_1) of $PyOH^*$ in LB films has been estimated [3]. From simple kinetic consideration, the analysis gives $k_1 \sim 3 \times 10^{10}\ s^{-1}$ for the pyranine molecules assembled in octadecylamine LB films. The increase of the value of k_1 in functionalized LB films compared to the aqueous solution, could be understood by considering that the $-NH_2$ group of the octadecylamine LB films has stronger affinity towards accepting proton than the bulk water. Thus, the deprotonation rate depends on the accessibility of the proton of the probe photoacid to the media and the nature of the microenvironment. The values of k_1 and k are 3×10^{10} and $1 \times 10^{10}\ s^{-1}$, respectively. As the relative magnitude of k_1 and k is comparable for pyranine molecules organized in octadecylamine LB films, the emission from $PyOH^*$ species at 445 nm is observed (as shown in Fig. 1) unlike pyranine in water.

Fig. 3A presents the fluorescence decay of octadecylamine LB film after immersing in aqueous solution of pyranine (1×10^{-4} M, pH ≈ 2.0) for 3 h. Lifetimes of 180 and 40 ps are obtained with the relative contributions of 35 and 65%, respectively, at the emission band at 445 nm (λ_{ex} = 400 nm). The fluorescence decay (Fig. 3B) of nine layer octadecylamine LB film after immersing in pyranine aqueous solution (1×10^{-4} M, pH ≈ 9.0) is fitted with a biexponential function and decay times of 45 and 215 ps with the contributions of the fast and slow components of 57 and 43%, respectively, where the decay has been monitored at 510 nm (λ_{ex} = 450 nm).

The time-resolved spectra of octadecylamine LB films after immersing in aqueous solution of pyranine (1×10^{-4} M, pH ≈ 6.2) for 5 min (Fig. 4A) and 240 min (Fig. 4B) are presented at different time domain. The time-resolved fluorescence spectra of the pyranine in LB films clearly demonstrate that as deprotonation occurs the directly excited acid band ($PyOH^*$, emission at 445 nm) decays and the indirectly formed base band (PyO^{-*}, emission at 510 nm) builds up. The rise of the fluorescence due to the formation of PyO^{-*} species is clearly evident in time-resolved spectra as shown

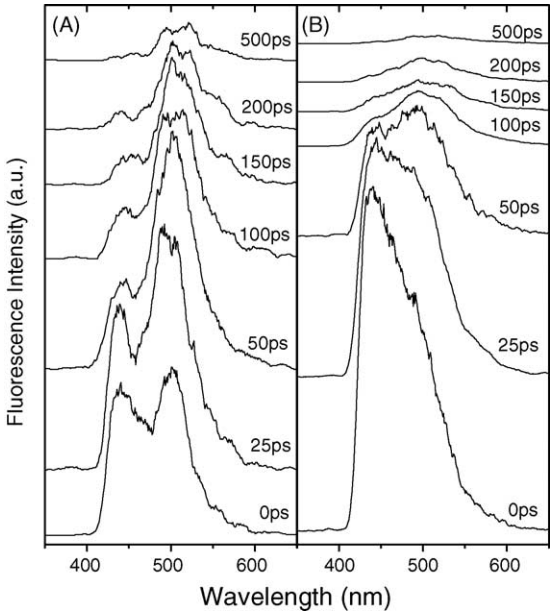


Fig. 4. Time-resolved fluorescence spectra of octadecylamine LB film after in immersing in the aqueous solution of pyranine (1×10^{-4} M) for (A) 5 min and (B) 240 min.

in Fig. 4, that justify the integrity of the kinetic scheme. Fig. 5A and B present the time-resolved fluorescence spectra of LB film of octadecylamine after immersing in aqueous solution of pyranine at acidic and basic pH, respectively. At acidic pH, the emission spectra exhibit a band at 445 nm arising from the blue fluorescence of the PyOH. As the pH increases, the excited PyOH molecules can be partially converted into excited PyO^- molecules before returning to the ground state; thus characteristic of green fluorescence

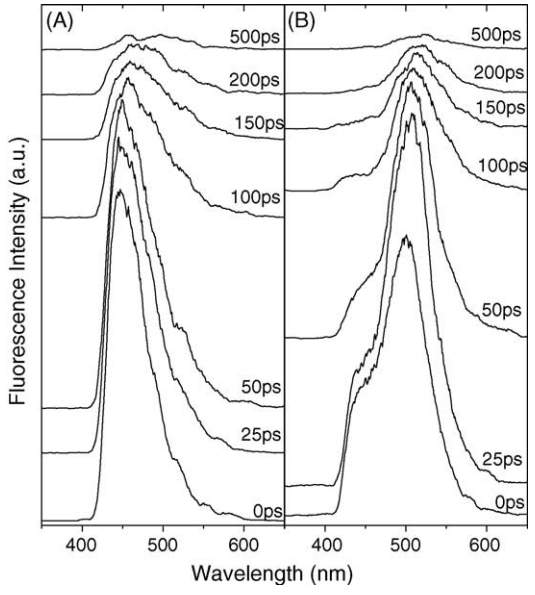


Fig. 5. Time-resolved fluorescence spectra of octadecylamine LB film after immersing in the aqueous of pyranine (1×10^{-4} M) at pH (A) 2.0 and (B) 9.0.

of PyO^{-*} at 510 nm appears. The rate of deprotonation of excited pyranine depicts the ability of the surrounding amine molecules to accept a proton with regard to structural consideration. The dynamics of pyranine has been established by observing the disappearance of the protonated species (PyOH) and the formation of the deprotonated form (PyO^-) by the fluorescence spectra in different time domain (Figs. 4 and 5).

The most significant result of the present work is the increase of the fluorescence intensities of $PyOH^*$ and PyO^{-*} peaks in picosecond time scale and the presence of the two species depend upon the excited state proton transfer in the organized assembly. Pyranine molecules are anchored in the LB films of octadecylamine by their anionic sulfonate group. Most importantly, the proton transfer reactions can be readily manipulated and functionalized by choosing proper parameters. Taken together, the present work also justifies pyranine as fluorescence and pH sensitive probe in organized assembly to study the proton transfer dynamics. Kinetics of proton transfer in LB films brings interesting information on the relation between structure and reactivity and permits a better understanding of the acidity in the molecular assembly.

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