
Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Jun 2010.

To cite this article: Mike I Sluch , Alexei G Vitukhnovsky , Julian G Warren & Michael C Petty (1993): Two-Dimensional Energy Transfer in Langmuir-Blodgett Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 37-45

To link to this article: http://dx.doi.org/10.1080/10587259308032173

*Mol. Cryst. Liq. Cryst.* 1993, Vol. 229, pp. 37–45
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Printed in the United States of America



# TWO-DIMENSIONAL ENERGY TRANSFER IN LANGMUIR-BLODGETT FILMS

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Abstract Multilayer mixed films of tricosanoic acid containing 1-pyrenebutanoicacid and 16-(anthroyloxy) palmitic acid have been prepared using the Langmuir-Blodgett technique. Evidence of two-dimensional energy transfer between the donor and acceptor molecules is presented.

## INTRODUCTION

The basic experimental and theoretical results for electronic energy transfer between donor and acceptor molecules have been obtained for both solutions and molecular crystals[1]. Recently, Leitner et al. and Yamazaki et al. have performed detailed investigations of chromophore distributions in mixed Langmuir-Blodgett (LB) films by means of picosecond fluorescence decay analysis[2,3]. In this work, special attention was paid to the quenching of donor fluorescence by means of fluorescent and non-fluorescent acceptors.

Energy transfer from a donor to an acceptor results in a shortened rate of decay for the donor. In addition, according to the calculations of Hauser et al., the resulting donor fluorescence decay function is no longer a single exponential decay[4]. In the two-dimensional

case it should be possible to apply the Forster formula

$$I(t) = A \exp\left(\frac{-t}{\tau_d} - 2\gamma_a\left(\frac{t}{\tau_d}\right)^{1/3}\right) \quad (1)$$

$$\gamma_a = \frac{2}{3} n_a R^2 \quad (2)$$

where $\tau_d$ is the mean lifetime of the donor without the acceptor; $n_a$ is the density of acceptor molecules per unit area and R is the Forster radius. Unfortunately the experimental data do not show a good fit to this theoretical curve. Yamazaki has proposed a modification to equation (1) involving a second exponential decay term.

$$I(t) = A \exp\left(\frac{-t}{\tau_d} - 2\gamma_a\left(\frac{t}{\tau_d}\right)^{1/3}\right) + B\exp\left(\frac{t}{\tau_d}\right) \quad (3)$$

However, in this case $\tau_d$ and R were used as fitting parameters to experimental data[3]. This is not correct, as both of these parameters are fixed and determined by the optical properties of donor and acceptor species.

In this work we use the Forster equation and a mean value of lifetime in order to investigate energy transfer in LB assemblies of donor and acceptor molecules.

## EXPERIMENTAL

Tricosanoic acid (TA) was obtained from Sigma while 1-pyrenebutanoic acid (PA) and 16-(9-anthroyloxy)palmitic acid (AA) were purchased from Molecular Probes. The LB film assemblies were fabricated at Durham. Mixed layers of the dyes were alternated with 22TA on quartz substrates which had been coated with six monolayers of TA in order to minimise the influence of the substrate on the energy transfer (figure 1). The total number of layers deposited was 36, giving an overall film thickness of approximately

900 Å. The concentration of PA in the films was kept constant at 1.5 molar %, whilst the concentration of AA was varied between 1.5 and 9 molar %. The distance between the mixed monolayers was 5 nm.

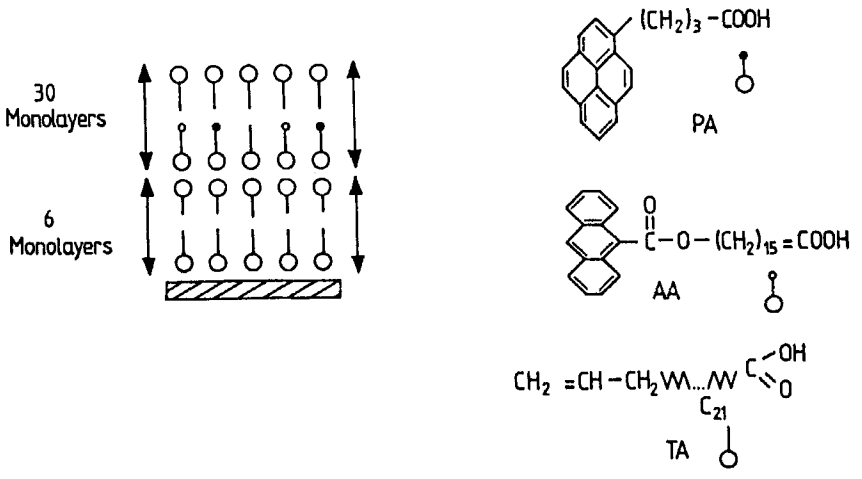


FIGURE 1: Structure of the LB multilayer used in this work. The chemical formulae of the materials used are given on the right.

Absorption and fluorescence spectra were recorded using a multichannel optical analyzer OMA-2 with a nitrogen laser source. Fluorescence decay curves were measured with an Edinburgh Instruments Spectrofluorimeter 199 by the time-correlated single photon counting technique. The flashlamp had a repetition rate of 20 kHz and a single pulse duration of 1.4 ns (fwhm), with excitation wavelengths of 316 nm and 380 nm. Fluorescence decay curve analysis and experimental control was performed by an LSI-11 computer. The experimental error in the values of lifetime was 0.3 ns. All measurements were undertaken at room temperature.

RESULTS AND DISCUSSION

Figure 2 shows the fluorescence and absorption spectra of PA and AA in benzene.

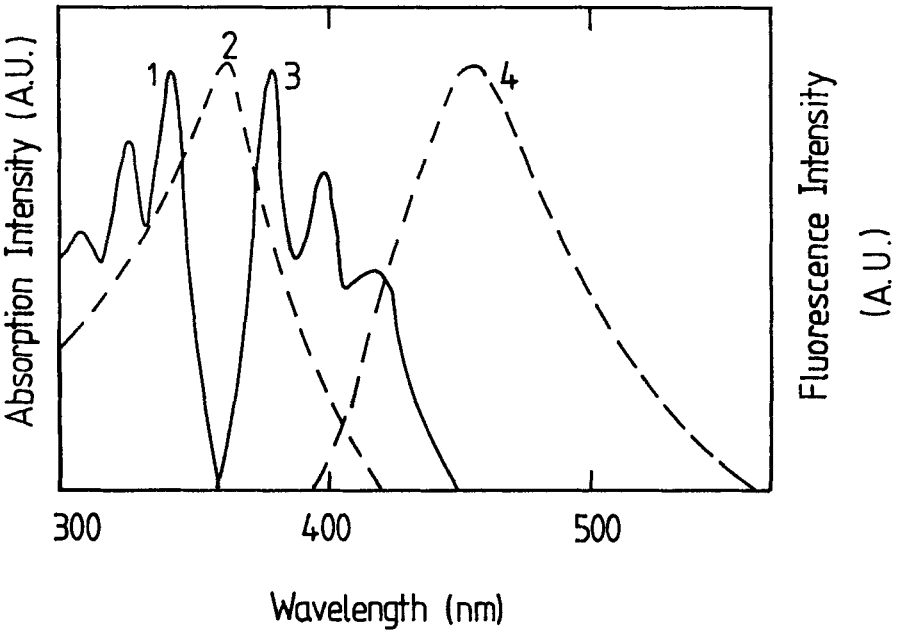


FIGURE 2: Absorption and fluorescence spectra of PA and AA in benzene (concentration $10^{-4}$ M): 1 and 2 - absorption spectra of PA (curve 1) and AA (curve 2); 3 and 4 - fluorescence spectra of PA (curve 3) and AA(curve 4).

The fluorescence spectrum of PA has a vibronic structure with bands at 377 nm, 397 nm and 420 nm and is characteristic of the PA monomer. The corresponding spectrum of AA has a broad fluorescence band centred around 453 nm. The optical absorption maxima for PA and AA are 339 nm and 359 nm, respectively.

The fluorescence spectra of the three LB film structures containing PA and AA are shown in figure 3. The film is selectively excited at a wavelength of 339 nm (the absorption band of PA). In addition to the emission from the donor, the sensitized emission from

the acceptor is also observed at 453 nm. Figure 3 reveals that as the acceptor concentration increases, the relative emission from the donors decreases. This indicates that energy transfer occurs between the PA and AA chromophores in the multilayer film.



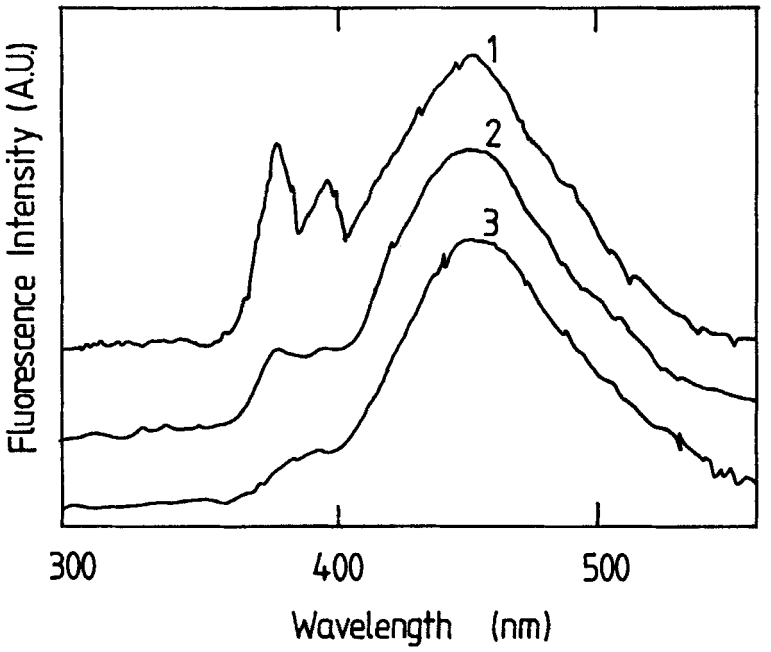


FIGURE 3: Fluorescence spectra of TA LB films containing 1.5 mol% PA: curve 1 - 1.5 mol% AA; curve 2 - 7 mol% AA; curve 3 - 9 mol% AA. The intensities have been normalised to the fluorescence band of AA at 453 nm and have been displaced along the ordinate for clarity.

The decay parameters derived from the experiment are summarised in Table 1, where the lifetime of PA was measured in benzene at a wavelength of 316 nm and the lifetime of AA was measured in LB film form at 380 nm. The shortening of the decay rate resulting from energy transfer from donor to acceptor can clearly be seen in Table 1.

| acceptor concentration mol% | $\tau_{PA}$(ns) ex.316nm | $\tau_{AA}$(ns) ex.316nm | $\tau_{AA}$(ns) ex.380nm |
|---|---|---|---|
| 1.5 | 12.4 | 10.2 | 9.7 |
| 7.0 | 11.4 | 10.9 | 9.8 |
| 9.0 | 9.6 | 10.6 | 9.6 |
| PA in benzene solution $10^{-4}$M | 19.0 | | |

TABLE 1: Fluorescence decay parameters for TA LB films containing PA and AA.

Mean Donor Lifetime

The decrease in the mean lifetime of donor molecules through energy transfer is usually referred to as resonance quenching. If the decay dependence for $\delta$-excitation is known, then the mean lifetime $<\tau>$ may be determined from equation (1).

$$<\tau>= \frac{\int_o^\infty tI(t)dt}{\int_o^\infty I(t)dt} \qquad (4)$$

Using equations (1) and (4), we have calculated the mean donor lifetime by numerical integration; the results are given in Table 2. We have used $\tau_d$ = 19 ns and R = 20 Å (evaluated from the absorption and fluorescence spectra of PA and AA). For three-dimensional energy transfer we

must use R>40 Å and the following expression

$$I_d(t) = \exp\left(\frac{t}{\tau_d} - 2q_a\left(\frac{t}{\tau_d}\right)^{1/2}\right) \quad (5)$$

$$q_a = 3.7\rho_a R^3 \quad (6)$$

where $\rho_a$ is the density of the acceptor molecules per unit volume. It should be remembered that $\gamma_a$ is proportional to the acceptor concentration and to the square of the characteristic distance R, in contrast to the three dimensional case, where it is the cube. Using equation (5) we have calculated the mean lifetime for the three-dimensional case (Table 3).

| acceptor concentration mol% | $n_a$ $10^{-4}$Å$^2$ | $\gamma_a$ | $\langle\tau_d\rangle$(ns) | $\langle\tau_a\rangle$(ns) |
|---|---|---|---|---|
| 1.5 | 7.2 | 0.19 | 16.9 | 14.0 |
| 7.0 | 33.6 | 0.89 | 10.9 | 12.0 |
| 9.0 | 43.6 | 1.15 | 9.2 | 11.9 |

TABLE 2: Fluorescence lifetime analysis for donors in LB films: 2-dimensional model (equation 1).

| acceptor concentration mol% | $\rho_a$ $10^{-5}$Å$^3$ | $q_a$ | $\langle\tau\rangle_d$(ns) |
|---|---|---|---|
| 1.5 | 1.44 | 3.4 | 1.9 |
| 7.0 | 6.72 | 15.9 | 0.1 |
| 9.0 | 8.72 | 20.6 | 0.06 |

TABLE 3: Fluorescence lifetime analysis for donors in LB films: 3-dimensional model (equation 5).

A comparison of the theoretical data in Tables 2 and 3 with the experimental results of Table 1 suggests that the Forster theory for the two-dimensional situation is the most appropriate for the case under study in this work.

Fluorescence Quenching of the Acceptor

We have the following equations for the number $n_d$ of excited donor and acceptor $n_a$ molecules in the two-dimensional case.

$$d_t n_d = -\frac{n_d}{\tau_d} - \left(\frac{2\gamma_a}{3\tau_d}\right)\left(\frac{t}{\tau_d}\right)^{-2/3} \quad (7)$$

$$d_t n_d = -\frac{n_a}{\tau_a} + \left(\frac{2\gamma_a}{3\tau_d}\right)\left(\frac{t}{\tau_d}\right)^{-2/3} n_d \quad (8)$$

Here we have $I_d \propto n_d$ and $I_a \propto n_a$. Equation (8) has a well-known solution

$$n_a(t) = \left(\frac{2\gamma_a}{3\tau_d}\right)\exp\left(-\frac{t}{\tau_a}\right)\int_o^t \exp\left(\frac{t}{\tau_a} - \frac{t}{\tau_d} - 2\gamma_a\left(\frac{t}{\tau_d}\right)^{1/3}\right)\left(\frac{t}{\tau_d}\right)^{-2/3} dt \quad (9)$$

Using equations (4) and (9) we have performed a numerical integration to obtain the values in Table 2 (using $\tau_d$ = 19 ns, $\tau_a$ = 9.7 ns and R = 20 Å). Under these conditions we have compared theoretical values of the acceptor lifetime

(Table 2) with the experimental data (Table 1). The differences may be attributed to the difficulties in determining accurately the contribution from the directly excited acceptor molecules.

## CONCLUSIONS

The observed fluorescence spectra and lifetimes of PA and AA confirm the existence of two-dimensional energy transfer between donor and acceptor molecules in LB films.

## Acknowledgement

We should like to thank Professor M.D.Galanin for helpful discussions.

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