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Energy Transfer between Anthracene Chromophore and Sexithiophene in Langmuir–Blodgett Assemblies

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Excellent Langmuir–Blodgett (LB) films of 9,10-diphenylanthracene (DPA) and α,α-linked sexithiophene (6T) with arachidic acid (AA) can be formed on water subphase and can be transferred on to quartz substrates. Electronic absorption and emission spectra of these films have been studied and compared with those in solution. Results suggest formation of aggregates of DPA and 6T in LB films. 6T has been used as a quencher for the DPA donor fluorescence. It is shown that the efficiency of energy transfer from the donor to the acceptor decreases with the quadratic power of the distance separating them. Such quadratic dependence confirms that the donor excitation is delocalized.

The energy transfer between two parallel Langmuir–Blodgett (LB) layers of donors and acceptors is itself of interest because of the uniqueness of the method where spacer distance between them can be tailored. This aspect of LB films has been used by several authors[1—6] who followed Kuhn[7] to examine the distance dependence of energy transfer between an excited donor and an unexcited acceptor where both of them are in the form of LB monomolecular layers. While most of the works concentrate on energy transfer between fluorescent dyes in LB films, a very few groups have studied the traditional aromatic hydrocarbons.[5,6] In this article, we report the spectroscopic properties of LB layers of 9,10-diphenylanthracene (DPA), a chromophore of anthracene and use this as an energy donor. α,α-Linked thiophene oligomer, sexithiophene (6T), is used as an energy acceptor or quencher. We have used 6T as the acceptor molecule because of its immense current interest.[8,9] It is a good model compound for polythiophene and has the potential application in molecular electronic devices such as field effect transistors.[10] Distance dependence of energy transfer from DPA donor to 6T acceptor is discussed in this article.

Experimental

9,10-Diphenylanthracene purchased from Aldrich Chemical Co., U.S.A., was sublimed three times and then recrystallized twice from spectroscopy grade ethanol before use. α,α'-Linked sexithiophene was obtained as a gift from the Institute of Molecular Spectroscopy, Bologna, Italy. Chemical synthesis of 6T was done as proposed by Kagan et al.[11] The melting point of the sample is 302—304 °C. Arachidic acid (AA) purchased from Sigma Chemical Company, U. S. A., was used without further purification. All solvents used were of spectroscopic grade. A Langmuir–Blodgett alternate layer trough made of poly(tetrafluoroethylene) (PTFE) (Model 4 Joyce Loebl U. K.) was used for deposition of the monolayers. A filter paper Wilhelmy plate attached to a microbalance which in turn was interfaced to a microcomputer, maintained constant pressure with an accuracy of 1 $\mathrm{mN\,m^{-1}}$ over a very long time. Triple distilled water further purified by a milli-Q plus water purification system was used as a subphase. The resistivity of water used was 18.2 $\mathrm{M\Omega}$ cm. Fluorescence grade quartz slides were treated with chromium trioxide and boiling nitric acid to ensure that no traces of organic contaminants remained on the substrates. After acid treatment the slides were repeatedly washed with deionized water and sonicated for about ten minutes in spectroscopic grade chloroform. The slides were finally dried in a hot air oven and stored in a dust free chamber.

About 20 μL of a solution of DPA and AA mixed in a 1 : 2 molar ratio was dissolved in spectroscopic grade chloroform and spread on the clean water surface of the Langmuir trough. After waiting for about 20 min for the solvent to evaporate, the film was slowly compressed at the rate of 2 $\mathrm{cm^2}$ per minute. The isotherm data of surface pressure versus area per molecule was collected by an IBM PC and analyzed with software from Joyce Loebl (U. K.). Deposition of mono- and multilayers were achieved by allowing the substrate to dip with a speed of 5 mm $\mathrm{min^{-1}}$ and drying time allowed was approximately 40 min. Transfer ratio was found to be almost equal to unity. Mono- and multilayer LB films of 6T mixed with AA were similarly made.

Absorption spectra were recorded by a Shimadzu 210 UV-vis spectrophotometer and emission spectra were recorded by a Perkin Elmer MPF-44A spectrofluorimeter. For energy transfer study, a monolayer of DPA and AA mixture (1 : 2 molar ratio) was first deposited on to a substrate. Specific number of AA layers were deposited subsequently to act as spacers between the DPA and the final monolayers of 6T-AA mixed in 1 : 2 molar ratio.

Results and Discussion

Characterisation of LB Films. Figure 1 shows the surface pressure versus area per molecule isotherms of DPA and 6T mixed with arachidic acid (AA), the molar ratio being 1 : 2 in both the cases. The samples were mixed with AA in order to increase the surface pressure and to facilitate Y-type deposition on the quartz substrates. The areas of 0.25 and 0.26 $\mathrm{nm^2}$ per molecule for DPA and 6T respectively were maintained at 30 $\mathrm{mN\,m^{-1}}$ surface pressure at which the films were transferred from the subphase. As AA has completely different structure from those of DPA and 6T molecules, it is unlikely that DPA or 6T will form homogeneous

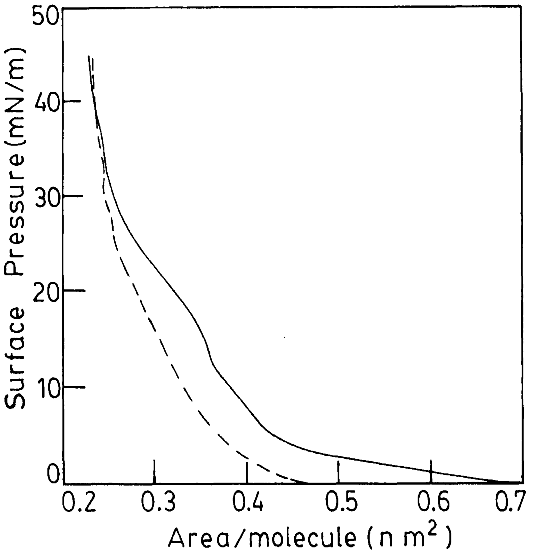

Fig. 1. Surface pressure vs. area per molecule isotherm of DPA : arachidic acid (---) and 6T : arachidic acid (—) molar ratio being 1 : 2 in both the cases.

mixture with AA. Instead, they may separate out to form small clusters or aggregates.

The absorption and emission spectra of DPA in chloroform solution have sharp features which are characteristics of the parent anthracene molecules. In the LB films, the bands are significantly broadened (Fig. 2) suggesting aggregation of the molecules. Such a behavior has also been observed in perylene LB films.[12] Nakahara et al.[13] have reported the successful incorporation of thiophene oligomers mixed with fatty acids in LB films. Polarized absorption spectra and space filling model have indicated that the molecules are oriented with their long axis perpendicular to the substrate.

Absorption spectra of 6T has been investigated by several groups.[14,15] While the solution absorption spectra show a single broad band with its maxima at 432 nm, LB films show a strong band at 368 nm (Fig. 3). In addition, a number of weak bands are observed in the 350—600 nm spectral region. This blue-shifted intense absorption maxima may represent H-aggregation of most of the 6T molecules. The additional weak bands appeared in the longer wavelength region is similar to that observed in the vapour deposited films of 6T. These bands may indicate the presence of rotational conformers[14] which are indeed possible in a rigid rod-like molecule like 6T.

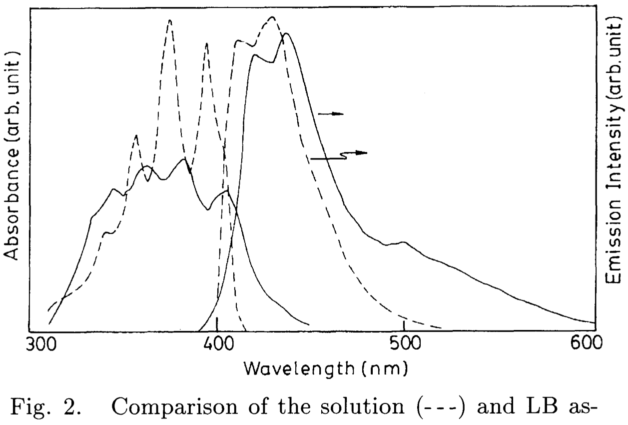

Fig. 2. Comparison of the solution (---) and LB assembly (—) absorption and emission spectra of DPA.

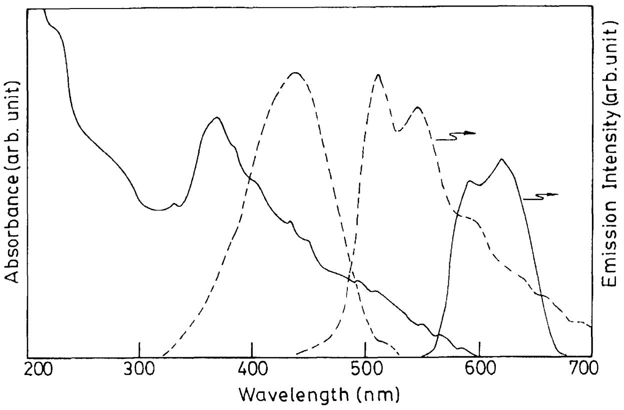

Fig. 3. Comparison of the solution (---) and LB assembly (—) absorption and emission spectra of 6T.

Emission spectrum of 6T in chloroform is well-structured with band maxima at 510, 551, and a shoulder at 600 nm, which can be analyzed by considering two vibronic progression involving C=C stretching at 1459 cm^{-1}. Excitation spectrum monitored at these bands show one band system with its origin at 498 nm, which add support to the fact that these emission bands originate from the same species.

In LB films on the other hand, excitation spectra (Fig. 4) clearly show four distinct band systems with origins at 582, 503.5, 442, and 398 nm. The origins of the band systems have one to one correspondence with the weak bands that appear in the longer wavelength region of the absorption spectra. Moreover, each group of bands may be analyzed (Table 1) in terms of fundamental frequencies like 863, 1219, and 1459 cm^{-1} which are the well-known fundamental frequencies of 6T.[16] This further implies the existence of four different species or rotational conformers of 6T with different energies in the LB film.

The correspondence between the lowest rotameric state and the origin of the emission spectra in LB film (Fig. 3) suggests that the energy cascades from the highest rotameric state to the lowest one and radiative relaxation therefrom to the ground state results in a large red-shifted emission with band maxima at 595 and 625 nm.

As the singlet of the DPA is located at a higher energy than that of 6T, and there is a large overlap between the emission spectra of DPA and absorption spectra of 6T, there remains a good possibility of energy transfer from the donor (DPA) to the acceptor (6T) in a suitably designed molecular assembly. In the following section, the quenching of fluorescence of DPA monomolecular

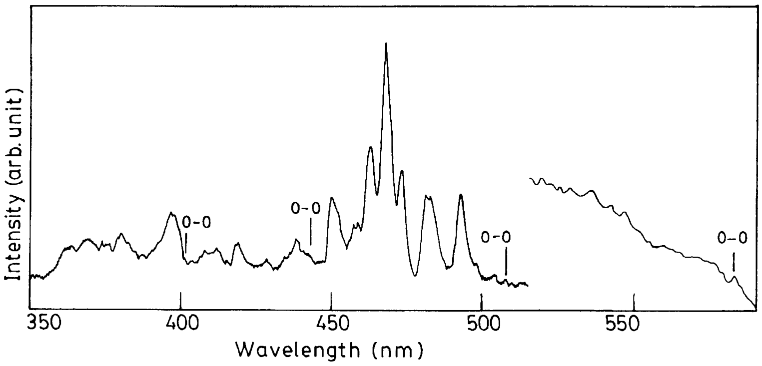

Fig. 4. Excitation spectra of 6T LB film monitored at $\lambda_{em}=595$ nm. The 515 to 590 nm region has been monitored at $\lambda_{em}=617$ nm.

Table 1. Vibrational Analysis of Excitation Spectra of 6T Langmuir–Blodgett Films Monitored at 595 nm

Position nm (cm^{-1})	Difference	Assignment	
582.0 (17182)	0	O–O	Species 1
503.5 (19861)	0	O–O	Species 2
493.0 (20284)	423	O+423	
482.5 (20725)	864	O+863	Ring stretching
474.0 (21097)	1236	O+1219	Ring breathing
469.0 (21322)	1461	O+1459	C=C Stretching
463.5 (21575)	1714	O+2×863	
450.5 (22196)	2335	O+1459+863	
442.0 (22396)	0	O–O	Species 3
438.5 (22805)	409	O+423	
426.0 (23474)	850	O+863	Ring stretching
420.0 (23809)	1185	O+1219	Ring breathing
416.0 (24038)	1414	O+1459	C=C Stretching
412.0 (24272)	1648	O+2×863	
408.0 (24509)	1885	O+1459+423	
404.5 (24722)	2326	O+863+1459	
398.0 (25126)	0	O–O	Species 4
385.0 (25974)	848	O+863	Ring stretching
380.0 (26316)	1190	O+1219	Ring breathing
375.5 (26631)	1505	O+1459	C=C Stretching
368.0 (27174)	2048	O+863+1219	
362.0 (27624)	2498	O+2×1219	

layer by a monomolecular layer of 6T will be described.

Distance Dependence of Energy Transfer. In an example that elegantly demonstrated the distance dependence of energy transfer in LB assemblies, Kuhn[7] used monolayer technique to vary the distance between the donor and acceptor layers. A monolayer of donors was separated from a monolayer of acceptors by varying number of AA spacers where each AA monolayer represents a distance of approximately 2.7 nm. The distance dependence was found to follow Förster theory of dipole–dipole energy transfer using a modified two-dimensional model as expressed by the following equation.

$$1-\phi_{et}=\phi_D/\phi_D^0=1/[1+(d_0/d)^4]$$

where ϕ_{et} is the efficiency of energy transfer, ϕ_D and ϕ_D^0 are the donor fluorescence quantum yields in presence and in absence of acceptor respectively, d is the separation distance between the layers and d_0 is the critical transfer distance at which the rate of energy transfer equals the rate of donor deexcitation by all other processes. In other words, it is a measure of quenching of donor fluorescence on introduction of an acceptor layer.

The above equation has been derived by considering the donor excitation to be localized. On the other hand, if the excitations in the donor layer are delocalized over distances large relative to interlayer spacing, the dependence of energy transfer with distance is predicted to be quadratic.

$$1-\phi_{et}=\phi_D/\phi_D^0=1/[1+(d_0/d)^2]$$

Both the equations have been verified by several workers for energy transfer between dyes[1,2,7] or from pure to photochemically oxidized LB layers,[4] while deviation from the quadratic or fourth power relationship has also been observed in certain dyes.[3]

In the present study, we have used DPA as donors and 6T as acceptors. The schematic representation of the two monolayer combination used to study the distance dependence of energy transfer has been shown in the inset of Fig. 5. Multilayers with the first layer containing DPA and the final layer containing 6T were prepared with $m=1$, 2, 3, 4, and 5 where m is the number of interposed bilayers of arachidic acid. Each value of m adds 5.4 nm to the separation distance between the donor and acceptor.

Electron transfer is the other channel for excitation transfer. Since the rate constant of the electron transfer decreases exponentially with distance, no electron transfer can be observed when the donor and acceptor layers are separated by two layers of AA.[17] In the present study, we have used minimum two and generally more AA layers as spacers between donor and acceptor monolayers. Excitation dissipation due to electron transfer can thus be ruled out in our study. Moreover, a strong overlap between donor fluorescence and accep-

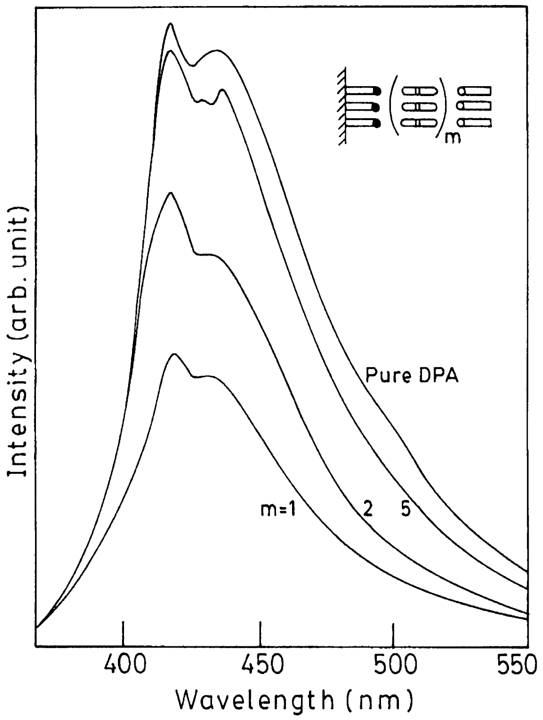

Fig. 5. Emission spectra of DPA spaced by different values of interlayer spacers of AA from 6T monolayer. Inset shows the schematic representation of the DPA-6T combination used to study the distance dependence of energy transfer.

tor absorption suggests that the energy transfer, not electron transfer, is more likely to occur.

The emission spectra of DPA-6T combination at different values of interlayer spacers of AA is shown in Fig. 5. It clearly demonstrates that the DPA fluorescence intensity increases with the number of spacer monolayers suggesting quenching by the acceptor. Similar quenching has also been observed in 1-hexadecylpyrene-DPA combination.[18] A plot I/I_0 versus number of spacers is shown in Fig. 6. This plot is in good agreement with the calculated curve according to Förster-type energy transfer quenching expressed by the quadratic behavior. No reasonable fit was found for the fourth power dependence. That the quadratic law is applicable here suggests formation of molecular aggregation in the LB film and delocalization of donor excitation. By fitting the above quadratic law, the critical transfer distance is found to be 7.0 nm.

To ensure that the quenching of DPA fluorescence occurs due to 6T was confirmed by a separate set of experiment where a single layer of DPA was coated with layers of AA of varied thicknesses. In all the cases no quenching of DPA fluorescence is observed in the absence of 6T monolayer.

Our experimental results thus suggest that the efficiency of energy transfer from DPA donor monolayer to 6T acceptor monolayer increases with the decrease in the distance separating them in a quadratic manner. This behavior is due to the formation of aggregates and delocalization of excitation energy with a critical transfer distance of 7.0 nm.

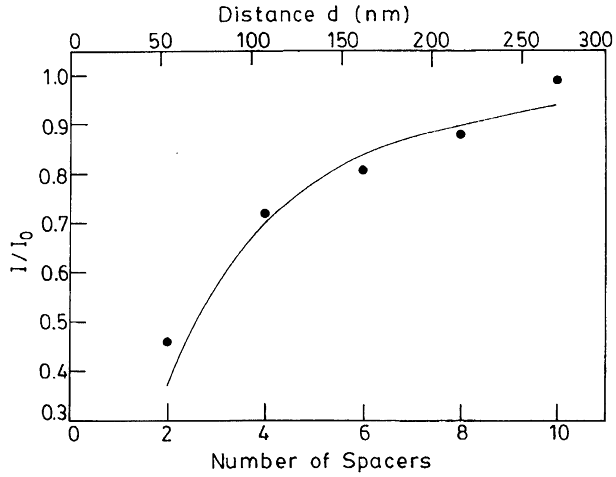

Fig. 6. Fluorescence quenching of DPA as a function of the number of spacer layers. The continuous line represents the calculated graph considering delocalized donor excitations. Here I/I_0 ($=\phi/\phi_D^0$) represents donor fluorescence quenching, where I and I_0 are the fluorescence intensities of the donor in presence and in absence of the quencher.

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