

Photoinduced Electron Transfer between 16-(9-Anthroyloxy)palmitic Acid and Fullerene C₆₀ in Langmuir–Blodgett Films

M. I. Sluch,^{†,‡} I. D. W. Samuel,[§] A. Beeby,^{||} and M. C. Petty^{*,‡}

School of Engineering, Centre for Molecular Electronics, Department of Physics, Department of Chemistry, and Centre for Time-Resolved Spectroscopy, University of Durham, Durham DH1 3LE, U.K.

Received November 28, 1997. In Final Form: March 6, 1998

Langmuir–Blodgett (LB) layers of 16-(9-anthroyloxy)palmitic acid (AA) and C₆₀ mixed with tricosanoic acid have been studied as a model system for photoinduced electron transfer (PET). The PET has been investigated by monitoring the quenching of AA fluorescence in mixed LB films containing different concentrations of C₆₀. Perrin's hard-sphere model adapted for the two-dimensional case provides a good fit to the experimental results, confirming the two-dimensional nature of the system. The critical radius is found to be 11 Å.

Introduction

Photoinduced electron transfer (PET) between excited donor and acceptor molecules is currently the subject of considerable research interest. Investigation of the PET process in organized molecular assemblies is particularly attractive, as the position and orientation of the donor and acceptor moieties can be varied. The use of pyrene derivatives as donors has been reported for a range of molecular systems, including monolayers at an air/water interface, Langmuir–Blodgett (LB) films, and vesicles.^{1–5} Ultrafast and efficient PET from a conjugated polymer to C₆₀ has also been reported.^{6,9}

The LB technique offers an elegant means of organizing donor and acceptor compounds at the molecular level. PET from excited molecules in monolayer assemblies and LB films has usually been studied through the quenching of the fluorescence of photoexcited donor molecules.^{1–5,10} Most LB film studies have concentrated on the fluorescence quenching of photoexcited pyrene-labeled phospholipid donors with viologen^{2–4} or TCNQ acceptors.⁵ 16-(9-Anthroyloxy)palmitic acid (AA) has also been used as an acceptor to investigate energy transfer in LB films.^{11,12} It

was found that AA and tricosanoic¹¹ or stearic¹² acid form good-quality mixed films.

We have previously shown that C₆₀ can form a condensed layer at the air/water interface and that reproducible Y-type LB films (up to 50 layers in thickness) can be built-up.^{13–15} We have reported on PET between monomers and excimers of pyrene and C₆₀.¹⁶ However, we needed to use different equations to describe the fluorescence quenching of the monomer and the excimer bands. In addition, excimer formation resulted in a nonexponential fluorescence decay.¹⁷ In this work we attempt to avoid aggregate formation and to simplify the model system in order to investigate two-dimensional PET in LB films. We report a study of the quenching of AA donor fluorescence in LB films containing C₆₀ using measurements of absorption, steady-state luminescence, and time-resolved luminescence.

Experimental Section

LB film assemblies were built-up using a constant perimeter trough located in a microelectronics clean room. Tricosanoic acid (TA) and 16-(9-anthroyloxy)palmitic acid were obtained from Sigma and Molecular Probes, respectively (Figure 1). C₆₀ was purchased from the Texas Fullerene Corporation. The molar ratio of AA/TA was 1:2. The molar ratios of AA/TA/C₆₀ were 1:2:0.04, 1:2:0.08, 1:2:0.125, 1:2:0.175, 1:2:0.25, and 1:2:0.32. The materials were dissolved separately in benzene, the solutions were mixed, and the resulting solution was spread onto an ultrapure water subphase obtained by reverse osmosis, deionization, and UV sterilization. After evaporation of the solvent (~20 min), the floating monolayer was carefully compressed at a speed of approximately 10⁻² nm² molecule⁻¹ s⁻¹ to a surface pressure of 27 mN m⁻¹. The AA/TA/C₆₀ layers were built-up on

* To whom correspondence should be addressed.

[†] Permanent address: P. N. Lebedev Physical Institute, Russian Academy of Science, Leninsky Pr. 53, 11 7924 Moscow, Russia.

[‡] School of Engineering and Centre for Molecular Electronics.

[§] Department of Physics and Centre for Time-Resolved Spectroscopy.

^{||} Department of Chemistry and Centre for Time-Resolved Spectroscopy.

(1) Huesmann, H.; Striker, G.; Möbius, D. *Langmuir* **1997**, *13*, 4929.
(2) Caminati, G.; Gabrielli, G.; Ricceri, R.; Turro, C.; Turro, N. J. *Thin Solid Films* **1996**, *284–285*, 718.

(3) Li, L.; Patterson, L. K. *J. Phys. Chem.* **1995**, *99*, 16149.
(4) Caminati, G.; Ahuja, R. C.; Möbius, D. *Thin Solid Films* **1994**, *243*, 651.

(5) Choi, J. W.; Jung, G. Y.; Oh, S. Y.; Shin, D. M. *Thin Solid Films* **1996**, *284–285*, 876.

(6) Kohler, A.; Wittmann, H. F.; Friend, R. H.; Khan, M. S.; Lewis, J. *Synth. Met.* **1996**, *77*, 147.

(7) Kraabel, B.; McBranch, D.; Sariciftci, N. S.; Moses, D.; Heeger, A. J. *Phys. Rev. B* **1994**, *50*, 18543.

(8) Halls, J. M.; Pichler, K.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Appl. Phys. Lett.* **1996**, *68*, 3120.

(9) Gao, J.; Hide, F.; Wang, H. L. *Synth. Met.* **1997**, *84*, 979.

(10) Vuorimaa, E.; Ikonen, M.; Lemmetyinen, H. *Thin Solid Films* **1992**, *214*, 243.

(11) Sluch, M. I.; Vitukhnovsky, A. G.; Petty, M. C. *Phys. Lett. A* **1995**, *200*, 61.

(12) Yamazaki, I.; Tamai, N.; Yamazaki, Y. *J. Phys. Chem.* **1987**, *91*, 841.

(13) Williams, G.; Pearson, C.; Bryce, M. R.; Petty, M. C. *Thin Solid Films* **1992**, *209*, 150.

(14) Williams, G.; Soi, A.; Hirsch, A.; Bryce, M. R.; Petty, M. C. *Thin Solid Films* **1993**, *230*, 73.

(15) Petty, M. C. *Langmuir Blodgett Films*; Cambridge University Press: Cambridge, 1996.

(16) Sluch, M. I.; Samuel, I. D. W.; Petty, M. C. *Chem. Phys. Lett.* **1997**, *280*, 315.

(17) Sluch, M. I.; Vitukhnovsky, A. G.; Petty, M. C. *Thin Solid Films* **1996**, *284–285*, 622.

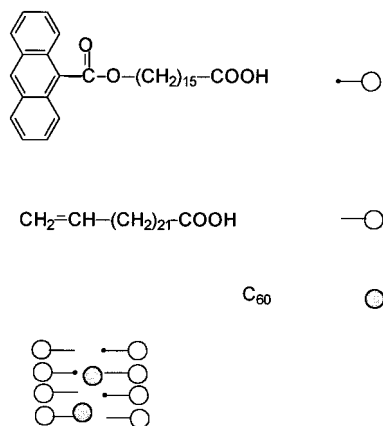


Figure 1. Chemical formulas of 16-(9-antroyloxy)palmitic acid and tricosanoic acid used in this work. The probable structure of the LB films used is also given.

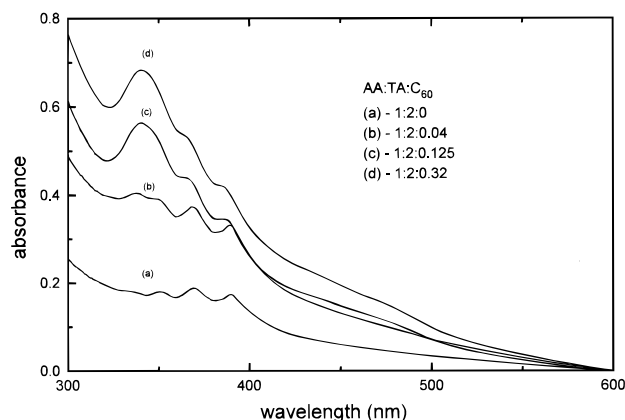


Figure 2. Absorption spectra of tricosanoic acid LB films containing (a) AA and (b–d) AA + C₆₀ deposited on both sides of the quartz substrates.

quartz (Y-type deposition with transfer ratio of 1.0 ± 0.1). Films of 40 monolayers (approximate total thickness 100 nm, estimated from the length of the TA molecule) were used for the fluorescence measurements.

The absorption spectra of the LB films were measured using a Perkin-Elmer Lambda 19 spectrophotometer, and fluorescence spectra were obtained with a Perkin-Elmer 50B luminescence spectrometer with xenon lamp excitation (330 nm). To decrease the experimental error in the measured fluorescence intensity of AA due to absorption in the C₆₀, we excited and detected the fluorescence from the front of the sample (i.e., in contrast to excitation at the front and fluorescence measurement from the back). The angle between the excitation beam and the detection direction was 30°. Time-resolved fluorescence was investigated by the time-correlated single-photon counting technique following excitation by a nanosecond flash lamp. The flash lamp was a pulsed source with a repetition rate of 20 kHz. The fwhm of the instrument response function was 2.8 ns. The excitation wavelength was 337 nm, and emission was detected at 450 nm. Fluorescence decay curve analysis was undertaken on a PC using a least-squares iterative convolution method based on the Marquardt algorithm. The experimental error (after reconvolution) in the value of the fluorescence lifetime was 300 ps. All measurements were undertaken at room temperature and in air.

Results

Figure 2 shows the absorption spectra for LB films of AA/TA, deposited on both sides of the quartz substrates, and a mixture of AA/TA/C₆₀ for different concentrations of C₆₀. The absorption spectra of the AA-containing films have a structure with maxima at 334, 351, 370, and 390

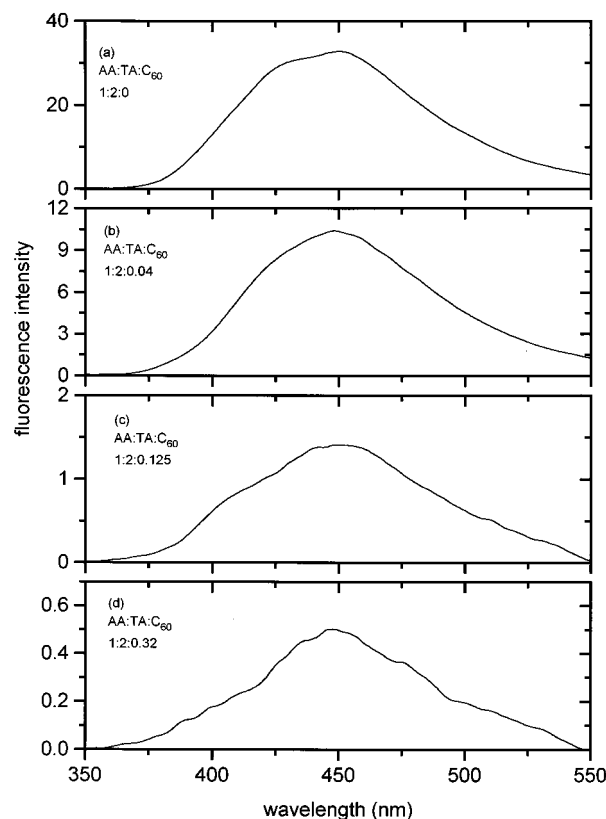


Figure 3. Fluorescence spectra of AA in mixed LB films (a) without C₆₀ and (b–d) with C₆₀ for different AA/TA/C₆₀ molar ratios.

nm (Figure 2a and b). This corresponds to that of AA monomers and coincides with data in the literature.¹² The absorption band at 340 nm in Figure 1c and d is due to C₆₀ and coincides with that published previously for LB films.^{13,14} The absorption spectrum of the mixed LB film is simply a superposition of the spectra of AA and C₆₀. The position of the absorption maximum was found to be independent of the AA and C₆₀ concentration over the range studied.

Figure 3 shows the fluorescence spectra of AA in LB films for the different C₆₀ concentrations. The fluorescence spectrum of AA has one broad structureless band at approximately 450 nm, similar to that reported for previous measurements of AA in LB films.^{11,12} Figure 3 shows that, for all C₆₀ concentrations studied, the wavelength of the fluorescence maximum does not change on addition of C₆₀. However, the fluorescence intensity decreases by nearly 2 orders of magnitude as the C₆₀ concentration increases.

Figure 4 shows the fluorescence decay for the AA/TA/C₆₀ ratio 1:2:0.175. This can be described by a single exponential, with a lifetime of approximately 9.0 ± 0.3 ns, in agreement with previous work.¹¹ The observation of a single fluorescence band with a monoexponential decay shows that there is only one emitting species in the LB films. The results for a range of C₆₀ concentrations are shown in Table 1. As the C₆₀ concentration increases, the fluorescence intensity decreases, but the lifetime stays the same.

Discussion

The distance between donor and acceptor molecules and the energetic match of their molecular orbitals are important factors in determining the efficiency of PET. It has been shown that molecules of C₆₀ in mixed fullerene/

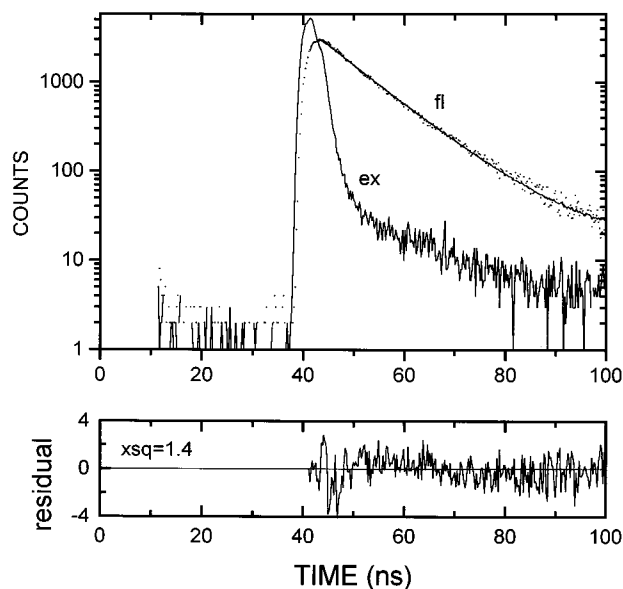


Figure 4. Fluorescence decay curve of 1:2:0.175 AA/TA/C₆₀ in a mixed LB film with C₆₀: (points) experimental data; (solid line at 450 nm) model. The excitation pulse at 337 nm is also given. The residuals are also shown.

Table 1. Fluorescence Intensities and Lifetimes for AA-Containing LB Films in the Presence of C₆₀

molar ratio AA/TA/C ₆₀	concn of C ₆₀ , (molecule Å ⁻²)	I ^a /I ₀ ^b	τ ^c (ns)	χ ²
1:2:0	0	1	9.3	1.2
1:2:0.04	0.0007	0.33	8.7	1.4
1:2:0.08	0.001	0.11	9.2	1.5
1:2:0.125	0.0021	0.051	9.0	1.45
1:2:0.175	0.003	0.045	8.9	1.4
1:2:0.25	0.004	0.026	9.2	1.5
1:2:0.32	0.005	0.017	9.1	1.47

^a I is the fluorescence intensity of a film. ^b I₀ is the fluorescence intensity of a film without C₆₀, τ is the fluorescence lifetime of AA in LB films.

fatty acid LB films are located within the hydrophobic fatty acid hydrocarbon chains.¹³ We suggest that the molecules of AA are also positioned in this region.^{11,12} Therefore, it is probable that both the AA head group and the C₆₀ molecules are in the same plane within a bilayer. This makes mixed LB films containing AA and C₆₀ molecules an ideal two-dimensional system for investigating PET. We have calculated the average distance between doped molecules within the plane by using the molecular areas of TA and AA and the molar ratio AA/TA, and by assuming a random two-dimensional distribution. The mean distance between AA molecules is 7.7 Å for the AA/TA concentration 1:2 used in our experiments. The average distances between molecules of C₆₀ vary from 14 to 37 Å for the range of concentrations studied. Hence, we estimate that the average distance between molecules of AA and C₆₀ is in the range 7–30 Å for the films studied. This small distance is favorable for electron transfer.

The electron transfer between a donor and an acceptor molecule is possible when the ionization potential I_d of the donor, the electron affinity of the acceptor A_a , and the Coulombic energy U of the separate ions are related by¹⁸

$$I_d - A_a < U \quad (1)$$

However, if either the donor or the acceptor becomes electronically excited, then the expression given by inequality 1 must be modified to reflect the increasing redox activity that results from photoexcitation.¹⁹ For example, if the donor molecule has an electron excited into the LUMO (lowest unoccupied molecular orbital), then the electron can be subsequently transferred to the vacuum level with less energy than required to excite directly a ground-state electron to the vacuum level. The magnitude of this energy enhancement is simply given by the LUMO–HOMO (highest occupied molecular orbital) gap. For anthracene, I_d is 7.55 eV,²⁰ the HOMO–LUMO gap is 3.2 eV, so the ionization potential for an excited electron is 4.35 eV. We assume that the value of I_d for AA is similar. The electron affinity of C₆₀ is 2.8 eV,²¹ which is similar to that for TCNQ.¹⁹ For the latter material, the Coulombic energy between the excited donor and the reduced acceptor is about 3 eV.²² If we assume a similar value of U for C₆₀, then eq 1 shows that charge transfer is favored. In view of the weak overlap between the emission of the donor and the electronic absorption spectrum of the acceptor, we propose that the observed fluorescence quenching is due mainly to photoinduced electron transfer from AA to C₆₀.

The quenching of the fluorescence intensity in the monomer peak of pyrene LB films has been analyzed using both the Stern–Volmer model and the Perrin model adapted for the two-dimensional case.^{1,2}

The Stern–Volmer model assumes that (a) the rate constant for transfer is independent of the concentrations of excited donors and acceptors and that (b) “statistical mixing” of donor and acceptor is completely achieved during the fluorescence donor lifetime.

The relevant equations for fluorescence quenching are¹⁹

$$I_0/I = 1 + KC\tau_0 \quad (2)$$

$$1/\tau = 1/\tau_0 + KC \quad (3)$$

where K is a rate constant, τ and τ_0 are the fluorescence lifetimes in the presence and absence of the acceptor, respectively, C is the acceptor concentration, and I and I_0 are the fluorescence intensities in the presence and absence of the acceptor, respectively.

In contrast, the Perrin model is based on the following assumptions: (a) there is no molecular diffusion, and (b) around each of the excited donors is an “active sphere”. If an acceptor molecule is inside the sphere, the transfer efficiency to the acceptor is equal to unity. However, if an acceptor molecule is outside the sphere, then there is no charge transfer. The radius of the sphere is known as the critical radius R . In the case of the LB films studied here, assumption (a) will be valid, since statistical mixing and material diffusion of AA are very unlikely in rigid fatty acid LB films.

The two-dimensional modification of the Perrin model assumes that quenching occurs if the acceptor is located inside a disk of critical radius R , with the donor at the center of the disk. According to Inokuchi–Hirayama, the Perrin decay of fluorescence intensity is described by a single-exponential decay.²³ In our films there will, of course, be a distribution of the distances between the AA

(19) Fox, M. A.; Chanon, M. *Photoinduced Electron Transfer*; Elsevier: New York, 1988.

(20) *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1978.

(21) Curl, R. F.; Smalley, R. E. *Science* **1988**, *242*, 1017.

(22) Dringenberg, B. J.; Budach, W.; Ahuja, R. C.; Möbius, D. *Thin Solid Films* **1994**, *243*, 569.

(23) Inokuchi, M.; Hirayama, F. *J. Chem. Phys.* **1965**, *43*, 1978.

(18) Zhang, G. P.; Fu, R. T.; Sun, X.; Zong, X. F. *J. Phys. Chem.* **1995**, *99*, 12301.

and C_{60} molecules. This may be expected to result in a more complex model with a deviation from the single-exponential decay.¹² However, we do not observe this in the work here. We adopt a Perrin model as an approximation and obtain adequate fits to a single-exponential decay. A two-exponential decay has previously been reported in a pyrene/viologen system and has been assigned to monomer and excimer emission.¹ This was also explained by a two-dimensional Perrin mode. It should be noted that in the Perrin model the donor fluorescence lifetime is independent of acceptor concentration and equals the lifetime when no acceptor is present. However, the fluorescence intensity depends on acceptor concentration, and it is described by the Perrin equation^{2,23}

$$I = I_0 \exp(-C/C_0) \quad (4)$$

In three dimensions, C is the concentration of the acceptor and C_0 is the reciprocal volume of the Perrin sphere. In two dimensions, C is the surface acceptor concentration and C_0 is the reciprocal of the area of the Perrin disk for the two-dimensional case.

PET and exchange energy transfer will compete with each other and cannot be distinguished by the measurement of fluorescence quenching. However, the efficiency of exchange energy transfer depends on the fluorescence-absorption overlap integral. The overlap of the absorption in C_{60} and the fluorescence of AA is less than the overlap of viologen and pyrene^{1-4,24} and that of C_{60} and pyrene.¹⁶ The latter system is a well-known example of PET. We therefore consider that the fluorescence quenching observed in our study is also due to PET.

Table 1 shows that the donor fluorescence lifetimes are independent of acceptor concentration. This is incompatible with the Stern-Volmer model (eq 3) but as expected for the Perrin model. Figure 5 shows a plot of $\ln(\text{intensity})$ versus concentration of C_{60} . Note the experimental points at high C_{60} concentration, with large errors in the measured fluorescence intensity, fall outside the range of the graph. These data points will also be more affected by absorption in C_{60} , which results in a decreasing fraction of excitation light for AA and an increasing experimental error of the fluorescence intensity of AA at the concentration ratio 1:2:0.32. Therefore, to estimate the critical

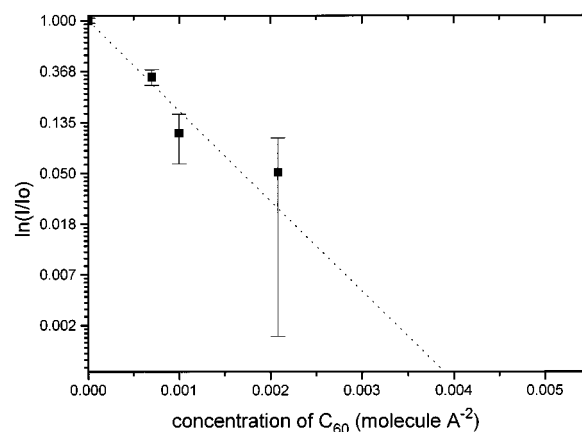


Figure 5. Fluorescence intensity of AA at different concentrations of C_{60} . The dashed line shows a fit to the two-dimensional Perrin model. The points represent the experimental data.

radius, we used the data points corresponding to low C_{60} concentrations. There is good agreement between the experimental data (points) and two-dimensional eq 4 (dashed line). The critical radius of photoinduced electron transfer was found to be 11 Å. This is comparable to the previously reported value of 10 Å for pyrene and viologen.²

Conclusions

Mixed LB films containing 16-(9-anthroyloxy)palmitic acid (donor) and C_{60} (acceptor) provide an ideal model system for the study of photoinduced electron transfer in two dimensions. Strong quenching of the fluorescence due to photoinduced electron transfer was observed for films containing C_{60} . The Stern-Volmer model does not fit the data. However, Perrin's hard-sphere model modified for the two-dimensional case provides a good fit to the experimental results, confirming the two-dimensional nature of the system. The critical radius was found to be 11 Å.

Acknowledgment. M.I.S. acknowledges the support of a Royal Society/NATO Postdoctoral Fellowship Award. I.D.W.S. is a Royal Society University Research Fellow. We are grateful to the University of Durham and the Royal Society for financial support.

LA9712956

(24) Penner, T. L.; Möbius, D. *J. Am. Chem. Soc.* **1982**, *104*, 7407.