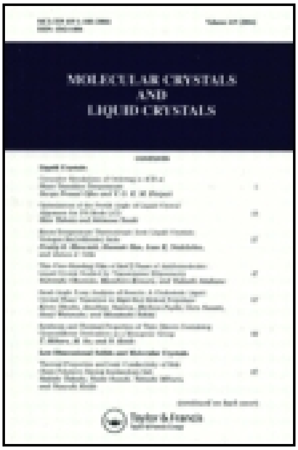

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Ultrafast Light-Induced Electron-Hole Pair Separation Along Oriented Molecular Clusters in a Langmuir-Blodgett Film†

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(*Received October 20, 1988*)

Supermolecules TA(4)P, i.e. 4-[*p*-*N*-methyl-*N*-[4-(3-perylenyl)-butyl]amino-phenyl]-2,6-diphenylthiopyrylium perchlorate, of elongated shape were synthesized consisting of a hydrophilic aromatic head unit and two consecutive hydrophobic aromatic moeities. Light-induced electron-hole pair separation was started from the lowest excited singlet state delocalized over the elongated TA subunits. Aligned clusters of the TA(4)P supermolecules were formed in a Langmuir-Blodgett film with their long axes pointing in about the direction of the desired unidirectional charge transfer across the LB film. Ultrafast hole transfer was measured as fluorescence decay from room temperature to 80 K. Hole transfer was measured directly at room temperature as hole injection from the perylene part of the TA(4)P clusters into an α-perylene single crystal. The observed signals suggest an adiabatic activation free reaction path for light-induced electron-hole pair separation in the TA(4)P clusters, though a case at the borderline to a non-adiabatic reaction path cannot be ruled out completely.

INTRODUCTION

In this paper we describe a new experimental approach to the realization of light-induced spatial separation of electron-hole pairs in a system of molecular dimensions. As photo-active units we have synthesized supermolecules where three different aromatic groups are linked together via short chemical bonds. Supermolecules consisting of three molecular subunits bound together via chemical bonds have been introduced several years ago by Moore and coworkers[1] who called their supermolecules triads.

Light-induced electron-hole pair separation in these triads was described as two consecutive charge transfer reactions. The first reaction starts from an excited singlet state that is localized on one of the three subunits. The consecutive reactions appear to be well separated on the ps time scale in this system and are thus of the

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†Dedicated to Prof. Martin Pope on the occasion of his 70th birthday.

hopping type. Variations of the latter hopping-type reactions appear to be also the most accepted models for light-induced electron-hole pair separation in the reaction centers of photosynthetic bacteria.[2] In a two step electron transfer process the second step has been discussed also as adiabatic for the bacterial reaction center.[3] In the activation free adiabatic situation the hopping time for the charge carrier is controlled by the frequency of a characteristic vibration or phonon in the system[4,5] whereas in the activation free non-adiabatic case the transfer is slower due to poorer electronic interaction.

We sought for a stronger electronic coupling between the subunits in our supermolecules and in particular in clusters built with the supermolecules. For the first charge separating step we sought for a strong optical transition along the axis joining the first and second subunit to extend the excited state spatially into the desired charge transfer direction. The second charge transfer step occurring between the second and the third subunit has been realized firstly as a non-adiabatic reaction in isolated supermolecules and secondly as adiabatic reaction path in oriented clusters of the supermolecules.

This concept for the realization of ultrafast light-induced electron-hole pair separation with the help of stronger electronic coupling between the subunits is inspired partially for the first step by the observations of direct optical electron-hole pair separation in suitable weak donor-acceptor pairs in solution[6] and in donor-acceptor type van der Waals single crystals of the anthracene-PMDA type.[7] The possibility of charge transfer to the third subunit via stronger electronic coupling is suggested by recent results on charge carrier transport in molecular crystals of the anthracene type in the presence of a strong potential gradient.[8,9]

The latter results give strong support to the notion of polaron type band transport of charge carriers in van der Waals crystals of the anthracene type. When an increasingly steep potential gradient was set up by an applied electric field the change carriers reached a saturation drift velocity of the order of 6×10^5 cm s^{-1} in these crystals even at room temperature.[9] This value is only about 20 times smaller than observed in GaAs.[10] The saturation drift velocity remains in the same order of magnitude also at liquid He temperatures.[8] For a typical molecular spacing between 5 and 10 Å (center to center) the saturation velocity corresponds to a downhill transfer time of the order of several 100 fs between nearest neighbor sites. It appeared very promising to explore whether we could realize a similar adiabatic coupling case also along the supermolecules or at least in clusters of such supermolecules when there is a downhill staircase in the electron affinities for electron transport or in the ionization energies for hole transport in place of the drop in the applied potential in the transport measurements in van der Waals single crystals of the anthracene-type.

Our supermolecules consist of one aromatic hydrophilic subunit that was linked via a C—C bond to the second hydrophobic subunit and this again via a chemical bridge of a variable length (2 or 4 CH_2 units) to the third hydrophobic subunit. With only one hydrophilic head unit and the rest hydrophobic the supermolecules were incorported tightly into a Langmuir-Blodgett film that contained arachidic acid molecules as supporting units. We obtained in this way a membrane-like structure with an average alignment of the supermolecules. It turned out that greater reorientational movements of the large subunits were suppressed in this fairly rigid environment.

The functionalized Langmuir-Blodgett film was deposited on a perylene single crystal electrode. This allowed for the measurement of the excitation spectrum of the corresponding injection current passing through the external circuit. The rise time of this injection current was measured with 70 ps time resolution. The supermolecule was chosen such that there should be a difference in the oxidation potentials of about 0.2 eV for the hole when residing on the second and third subunit of the supermolecule respectively. The main time-resolved information on hole transfer was obtained from charge transfer controlled decay of the fluorescence that was emitted when the hole resided on the first two subunits. A reference signal was measured with preparations of supermolecules that did not contain the third subunit. The measurements were carried out at individual functionalized LB films transferred onto various substrates and also at multilayers of these LB films, both between room temperature and 80 K.

The experimental results suggest that we have realized a new type of unidirectional light-induced electron-hole pair separation in clusters of the supermolecules incorporated into a supporting LB film. In the present system electron-hole pair separation follows an adiabatic reaction path with medium strong electronic coupling and does not proceed via two consecutive non-adiabatic hopping reactions.

EXPERIMENTAL

Synthesis of the main compound, i.e. dye 7 below, is outlined in the reaction scheme shown in Figure 1. All the intermediates were characterized by elemental analysis and by spectroscopic methods (IR, NMR, UV-VIS). The acylation of perylene(**1**) with succinic acid monomethylesterchloride yielded the 3-(3-perylenoyl)propionic acid methylester(**2**). The latter was converted with hydrazine hydrate to 4-(3-perylenyl)butyric acid(**3**). The amide **4** was prepared from **3** and *N*-methyl aniline using 2-chloro-*N*-methylpyridinum iodide,[11] and was reduced with borane dimethylsulfide reagent[12] yielding the amine **5** and the alcohol **6**. Condensation of **6** with 2,6-diphenyl-thiopyrylium perchlorate[13] formed compound **7**. This molecule **7** will be called TA(4)P in the following text, where P stands for perylene and 4 indicates four CH_2 units in the bridge linking the TA unit with P. The compound was purified extensively by repeated column and preparative thin layer chromatography on silica.

Langmuir-Blodgett (LB) films were assembled in a Lauda Film Waage. The compounds under study such as TA(4)P were diluted in arachidic acid (Fluka) (>99.9%). Subphase water was first refluxed over $KMnO_4$/KOH and then triply distilled in a quartz distillation apparatus. It contained in the trough 5×10^{-4} M $Cd(ClO_4)_2$ (Ventron) (99.9%) and the pH was adjusted to 5.5 by addition of dilute $HClO_4$. The temperature was kept at 15°C. Preparation of hydrophobic quartz slides has been described elsewhere.[14] The substances were spread from 3×10^{-3} M $CHCl_3$ or CH_2Cl_2 applying a Hamilton syringe. The film was compressed at a barrier speed of 3.3 cm/min to a film pressure of 30 mN/m for transfer. Complete

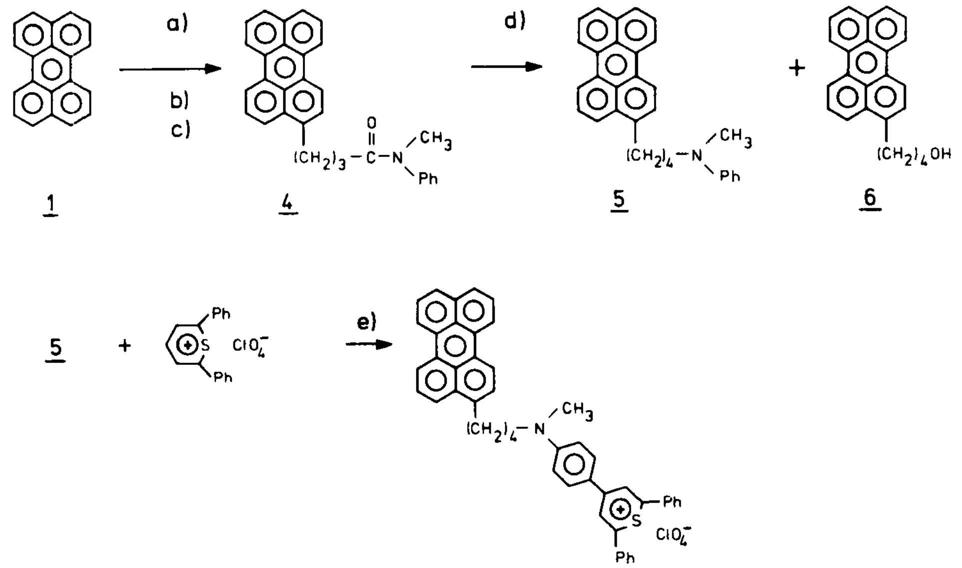

FIGURE 1 Reaction sequence leading to the supermolecule TA(4)P, i.e. 7 in the scheme. (a) $MeOCO(CH_2)_2COOCl/PhCl/AlCl_3$; 0°C. (b) NH_2NH_2, H_2O/KOH/triethylenegylcol; 180°C. (c) Ph-$NHCH_3$/2-chloro-*N*-methylpyridinium iodide/CH_2Cl_2, room temperature. (d) $H_3B{\cdot}SMe_2/THF$; 60–70°C. (e) NaOAc/HOAc; 120°C.

surface pressure versus area diagrams were recorded for all substances in preliminary experiments. They were well behaved in all cases with the above compound yielding a surface area of about 31 $Å^2$/molecule in the compressed film (mixing ratio of 0.3). Before transfer at a speed of 10 mm/min the compressed films were allowed to relax for 15 min on the water surface.

Absorption spectra were recorded with a Perkin Elmer spectrometer Lambda 9, fluorescence spectra with a triple ISA spectrometer consisting of a double monochromator mounted as filter stage (DHR 320) followed by a monochromator (0.64 m HR640). Fluorescence decay curves were measured with a synchroscan streak camera (Imacon 500, Hadland) in conjunction with a linear array detector (1420 PAR), an OMA II with controller 1218 and data transfer to a Cyber 830 host computer. The samples were mounted on the cold finger of a home-built He-cryostat equipped with 3 quartz windows. Laser pulses were produced by a Spectra Physics cavity dumped (344 S) dye laser (375) driven by a mode locked Ar ion laser (171). The autocorrelator (409) showed a pulse width of 5 ps whereas apparent averaged pulsewidths of the laser between 13 and 25 ps were measured with the streak camera for different integration times and signal heights. Home-built electronic[15] and commercial mechanical (Newport table) stabilization measures ensured a very stable performance of the system. Perhaps the most important stability factor was contributed by the temperature control to 0.1 K achieved with a laminar flow outlet over the whole length of the laser system and stabilized against convection with an antistatic curtain reaching from the laminar flow outlet down to 10 cm above the surface of the laser table. A schematic diagram of the set-up for fluorescence decay measurements is shown in Figure 2. The laser pulse was blocked off with a set of appropriate filters, at least 3 OG 630 and 1 OG 610 (Schott). Additional decay measurements with higher dynamic range but an apparent laser pulse halfwidth of 40 ps were carried out with time resolved single photon counting applying a microchannelplate photomultiplier (Hamamatsu R 1564 U-01) with a multichannel analyser (Norland IT 5400) and data transfer to the Cyber 830 computer. Excitation spectra of the injection current were measured in a conventional set-up,[16] and 70 ps time resolved measurements in a set-up as described before.[17] Ultrapure α-perylene crystals were grown[15] to function as electrodes for the injection current from the functionalized LB films that were deposited on the crystal as on a hydrophobized quartz slide.

EXPERIMENTAL RESULTS

Spectroscopic and photoelectrochemical measurements were carried out to clarify whether the supermolecules TA(4)P (Figure 1) and particularly whether oriented clusters of these supermolecules facilitate light-induced spatial electron-hole pair separation. It is helpful to remember first the standard redox energy (half wave potential) for the oxidation of a TA unit with two ethyl groups bound to the N atom, i.e. 1.23 V (SCE)[18] and also the estimate of the oxidation potential in the excited state[19] as the standard reduction potential, i.e. half wave potential of −0.46

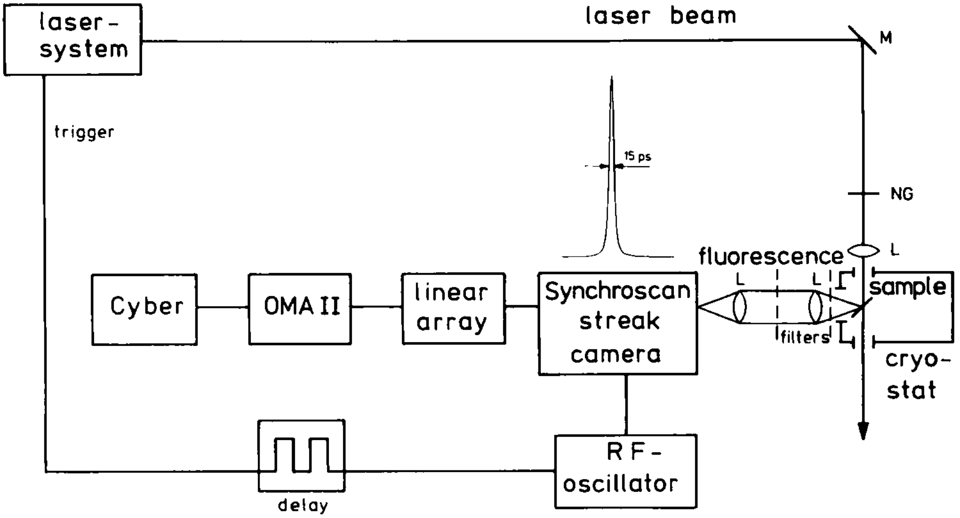

FIGURE 2 Block diagram for the measurement of fluorescence decay with a synchronously triggered streak camera. The apparent halfwidth (jitterspread) of the laser pulse is indicated above the streak camera. It depends on the integration time. The halfwidth of the individual laser pulse is 5 ps.

V (SCE)[18] plus the 0–0 excitation energy estimated at 1.99 eV (see below), i.e. 1.53 V (SCE), and finally the somewhat smaller standard redox energy (half wave potential) for oxidation of the perylene moeity in the same solvent acetonitrile, i.e. 0.85[20] to 0.89[21] V (SCE). With this in mind we had the expectation that electronic overlap between the wave functions of the excited singlet state of the TA subunit and of the perylene subunit could lead to partial or even complete hole transfer.

I ISOLATED SUPERMOLECULES TA(4)P

a) Absorption and fluorescence spectra

Figure 3 shows the absorption spectrum of the supermolecule TA(4)P at a concentration of 1×10^{-6} M in CH_2Cl_2 and also the fluorescence spectrum of the same solution when excited with a Krypton Laser line at 568 nm. The absorption spectrum in Figure 3 is essentially the superposition of the absorption spectrum of the perylene moiety with that of the TA moeity (dashed curve) as can be seen from a comparison of the solid and dashed curves. Absorption of the perylene moeity occurs only at wavelengths <470 nm. Superposition of the spectra of the

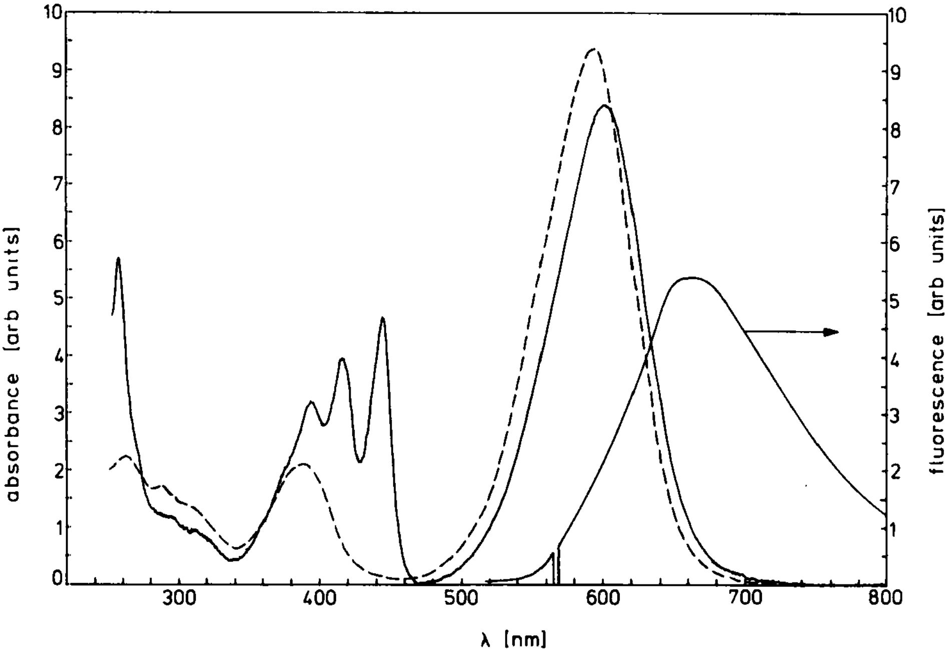

FIGURE 3 Absorption and fluorescene spectra of TA(4)P in CH_2Cl_2 (see Figure 1). The dashed curve is the absorption curve of TA where two alkane chains $C_{12}H_{25}$ have been attached to the N atom instead. The absorption coefficient at the maximum is 5.5×10^4 M^{-1} cm^{-1}.

TA unit and of the perylene unit in the Ta(4)P molecule is not surprising since the electronic coupling between the TA unit and the perylene unit is expected to be weak through the four CH_2 units of the bridge.[22] We would like to mention here that this coupling is already stronger and noticeable in the spectra when the bridge between TA and perylene contains only two CH_2 units and much stronger when the two units are coupled directly together. The latter two cases will be described elsewhere. The most interesting feature in the absorption spectrum of Figure 3 is the structureless band with a peak at 600 nm corresponding to an absorption coefficient of $5.5 \times 10^4\ M^{-1}\ cm^{-1}$. This band is not seen in the absorption spectra of the T and of the A units alone (not shown). A significant contribution of charge transfer character has been ascribed to this transition but this is not an essential point in the present context. A second interesting feature in Figure 3 is the fairly small Stokes' shift of $1389\ cm^{-1}$ between the maxima of absorption and fluorescence spectra for this transition. The origin (0–0 transition) is expected halfway between the energies of the maxima of fluorescence and absorption, i.e. around 624 nm.

b) *Fluorescence decay.* Figure 4 curve d gives the decay of the broadband fluorescence of the same solution measured with a synchroscan streak camera for excitation at 600 nm with a repetitive 6 ps laser pulse of less than 1 n Joule. Cut-off filters eliminated all the light at wavelengths < 640 nm. The width of the decay curve is in its upper part identical to the jitter-spread apparent width of the laser pulse measured with the synchroscan streak camera. A cautious estimate shows that the initial decay of the fluorescence is faster than 10 ps in CH_2Cl_2 at room temperature. As can be seen already in curve *d* of Figure 4 and is exposed more clearly with time-resolved single photon counting (not shown) this decay curve is non-exponential with smaller slower contributions showing up at later times. The fluorescence decay slowed down when the supermolecules were dissolved at a very small concentration in glycerol at room temperature (curve *c* in Figure 4), and it slowed down further (curve *b* in Figure 4) when this latter solution was brought to -10°C in a refrigerator.

Finally, further slow down in the fluorescence decay was observed (curve *a* in Figure 4) when the supermolecules were incorporated at high dilution (relative concentration of 10^{-3}) into a host matrix of a Langmuir-Blodgett film consisting of arachidic acid molecules. This same qualitative behavior, i.e. slow down in the fluorescence decay in the above different environments (curves *d* to *a*) was also observed for a supermolecule with identical chromophores (TA) but the perylene and the methyl group at the N atom exchanged for two alkane tails with 11 CH_2 and a methyl group each. The solution behavior (curves *b* to *c*) was also observed when the long alkane tails were exchanged for two methyl groups and remained identical when the two phenyl groups in the chromophore T were exchanged for two H atoms. The above signals show that the fluorescence decay became slower the more rigid the environment had been made for the supermolecule. This is a well known effect for molecules that show fluorescence quenching mediated by the rotation of subunits.[23,24]

The important point to notice here is the very similar decay curve in this time window for the TA moeity with the perylene moeity attached via four CH_2 groups

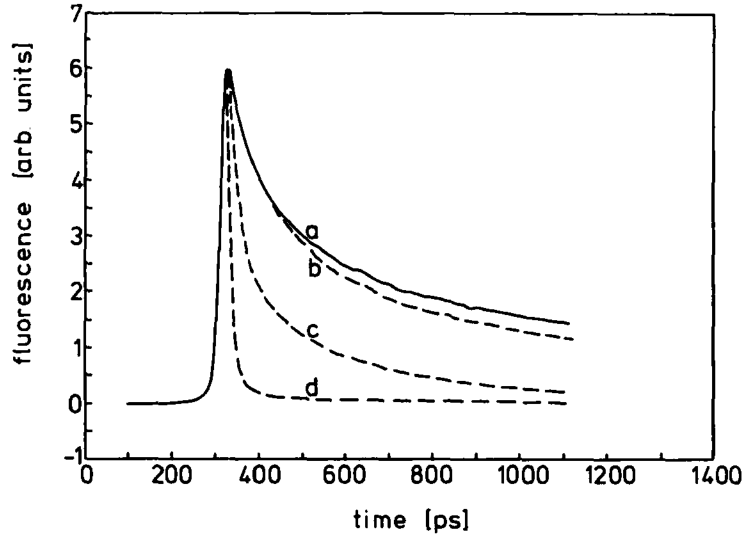

FIGURE 4 Fluorescence decay of isolated TA(4)P molecules: (a) in an LB film of arachidic acid with molar ratio $x = 10^{-3}$ at room temperature; (b) in glycerol at − 10°C; (c) in glycerol at room temperature; (d) in CH_2Cl_2 at room temperature. The upper part of the latter curve is of the same shape as that measured for the apparent laser pulse. Excitation at 600 nm.

and of the TA moeity with only alkane chains attached to the N atoms. Overlap of the excited state in the TA subunit with the wavefunctions in the perylene subunit through the bridge of four CH_2 units is apparently not effective at least in this time window of about 1 ns. Correspondingly, hole transfer through this bridge is negligible in this time window.

We like to mention here that the fluorescence decay is drastically shortened in the LB film matrix when the perylene moeity is attached via a shorter bridge of only two CH_2 groups instead of four CH_2 groups (not shown here).

II. ORIENTED CLUSTERS OF SUPERMOLECULES

a) Absorption and fluorescence spectra

Figure 5 shows the absorption spectrum (solid) curve of oriented clusters of the supermolecules TA(4)P formed in an LB film with relative concentration 0.3 of supermolecules TA(4)P to host arachidic acid molecules. The main features of the TA(4)P molecule absorption spectrum in CH_2Cl_2 (Figure 3) are essentially retained though all the peaks are wider in Figure 5 which is to some extent attributable to inhomogeneous broadening. There was a shift into a red shoulder of the long wavelength transition with peak at 600 nm when the concentration x was varied in the range from 0.2 to 0.3. There are also some further important differences from the absorption of the TA(4)P molecule. We expect that characteristic changes

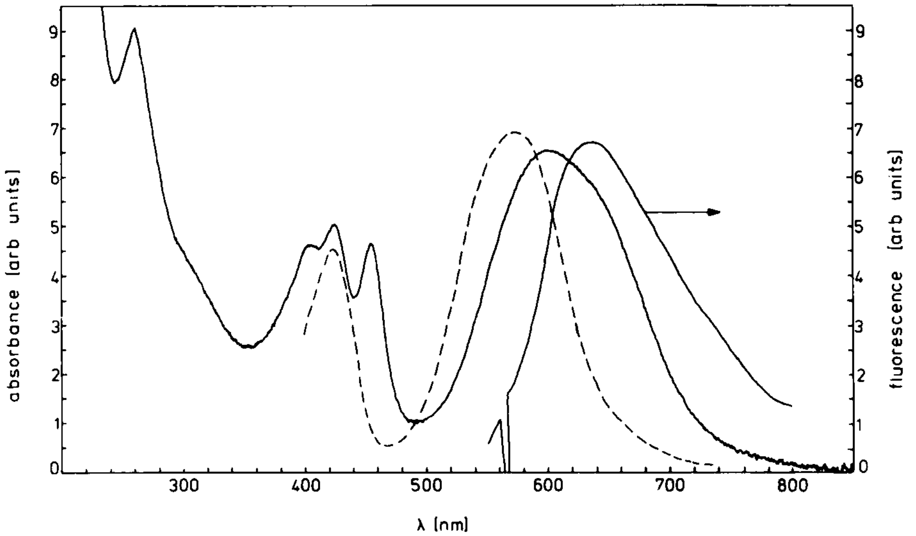

FIGURE 5 Absorption (normal incidence, unpolarized light) and fluorescence spectra of TA(4)P clusters in an LB film of arachidic acid, (molar radio $x = 0.3$). The dashed curve is the absorption curve of TA clusters (compare caption to Figure 3) also with $x = 0.3$ in an LB film of arachidic acid.

should arise in the spectrum of the clusters in the LB film compared to the molecules in solution already from the fact that the TA(4)P molecules are incorporated into the LB film with a preferential mean orientation since there is a hydrophilic subunit at one end and the other subunits are hydrophobic. The hydrophilic part is represented by the charged subunit T with its counter ion, here ClO_4^- (Figure 1). This part will remain close to the hydrophilic side of the LB film whereas the hydrophobic subunits A and P will be incorporated into the hydrophobic bulk of the LB film and will stretch towards the opposite hydrophobic surface of the LB film.

This alignment effect was seen very clearly for example in the absorption spectrum of perylene clusters that were formed in an LB film when the perylene moeities were attached to fatty acid chains and incorporated into the LB film together with long chain fatty acids at a concentration of $x = 0.3$.[25] Normal incidence unpolarized light was strongly absorbed by the short axis polarized transition at around 255 nm, 13 times stronger than for the long axis polarized transition with peak at around 445 nm. In contrast both these peaks were of similar height in the solution spectrum of the same randomly oriented perylene moeities. This change in relative peak heights from the solution to the LB film is indicative of an almost perpendicular alignment of the long axis of the perylene moeities to the surface of the LB film.[25] A qualitative indication of such an alignment is also noticeable in the absorption spectrum of the TA(4)P clusters (compare Figures 3 and 5). In Figure 5 the long axis polarized transitions, i.e. along the long axis of the perylene moeity[26] with a peak at about 455 nm in the cluster and in the direction linking the S and N atoms in the TA chromophore[27] with a peak at about 600 nm in the clusters, are decreased by a factor of about 2 and 3 respectively with respect to the short axis polarized peaks, i.e. for the perylene moeities at about 260 nm and at about 400 nm for the T moeities[26] in the cluster. From this decrease in the height of the long axis polarized transitions with respect to the short axis polarized transitions we can infer that the long axis has a preferred orientation towards the surface normal of the LB film. The electron density distribution[29] (not shown here) across this film of TA(4)P clusters with $x = 0.3$ did not reveal any maximum in addition to that of the carboxy groups. The same experiment gave a thickness of 54.2 Å for a double layer of this LB film. The observed even electron density across the LB film with TA(4)P clusters at $x = 0.3$ is strong evidence against the assumption of any significant back bending of the perylene moeities since it is established that e.g. clusters of anthracene moeities or perylene moeities when concentrated on one side of the LB film with arachidic acid as supporting molecules show up in the electron density distribution as a pronounced maximum.[29] The fluorescence decay curves (see below) for the TA(4)P clusters in the LB film suggest that the position of nearest neighbor TA(4)P molecules is alternating in the TA(4)P clusters such that each TA unit (most likely the N atom) comes very close to the perylene moeity of a nearest neighbor TA(4)P molecule. The shoulder at 640 nm in the absorption band of Figure 5 may indicate a corresponding optical transition involving stronger electronic interaction of the TA unit with a nearest neighbor perylene moeity. This is suggested by the occurrence of a band in this spectral range already for the TAP molecule when the length of the bridge is decreased between the TA and the perylene subunits (not shown here). Alternatively the same shoulder could be ascribed also to the interaction between the TA units in the 2-dimensional TA(4)P cluster since a peak at about 700 nm was observed for TA clusters formed in Lexan.[30] However, the following piece of evidence speaks against the latter assumption. The dashed absorption curve in Figure 5 was measured when clusters of TA subunits ($x = 0.3$) attached to $C_{12}H_{25}$ alkane chains were formed in another LB film. The TA cluster peak in the LB film was even blue shifted with respect to the same transition for the TA molecule in solution (compare the dashed curve in Figure 5 with the dashed curve in Figure 3). This suggests a totally different geometry for the 2-dimensional TA clusters formed in the LB film than for the TA clusters formed in Lexan. We see the reason for this in the different TA cluster geometries in the different environments due to the hydrophilic-hydrophobic constraints imposed on the alignment in the LB film. The latter do not allow for alternate positions e.g. of the hydrophilic part but only for an alignment with all the hydrophilic units pointing in the same direction. The TAP(4) and TA clusters for $x > 0.2$ are predominantly 2-dimensional. For concentrations $x > 0.2$ of either TA with alkane chains or of TA(4)P in an arachidic acid LB film there was no difference in the absorption spectrum between a single LB film and that of multilayers of the respective LB film.

It should be noticed in Figure 5 that the apparent Stokes' shift between the maxima of absorption and fluorescence curves of the TA(4)P clusters in the LB film was about 794 cm^{-1} and clearly smaller than in the solution spectrum of the TA(4)P molecules (Figure 3).

b) Fluorescence decay

The crucial result of our present investigation is shown as the solid curve in Figure 6. The fluorescence from the TA(4)P clusters ($x = 0.3$) shown in curve *a* of Figure 6 decayed rapidly with the same apparent half width as was measured under the same conditions for the jitter-broadened apparent laser pulse. A long integration period was necessary for the measurement of this weak signal leading to the significant jitter-broadening in spite of our careful stabilisation of the apparatus described above. Inserting different cut-off filters into the path of the fluorescence signal we obtained a crude fluorescence spectrum for the peak of the solid decay curve in Figure 6 which is shown as an insert in Figure 6. It agrees satisfactorily with the stationary fluorescence spectrum shown in Figure 5. The shape of the solid decay curve in Figure 6 remained identical when the signal was measured either for one LB film only or for a multilayer sample as long as the concentration of TA(4)P molecules was kept high, $x = 0.3$. The relative height of the long small tail in the decay signal varied somewhat for different samples reflecting variations in the local cluster geometries. The fast signal remained the same in these cases.

The much slower fluorescence decay of TA cluster excitation with $x = 0.3$ in the LB film is shown for comparison as the dashed curve in Figure 6. The faster decay of this curve compared to that for isolated TA molecules (identical with the solid curve in Figure 4) is due to the very often observed concentration quenching.[15,31]

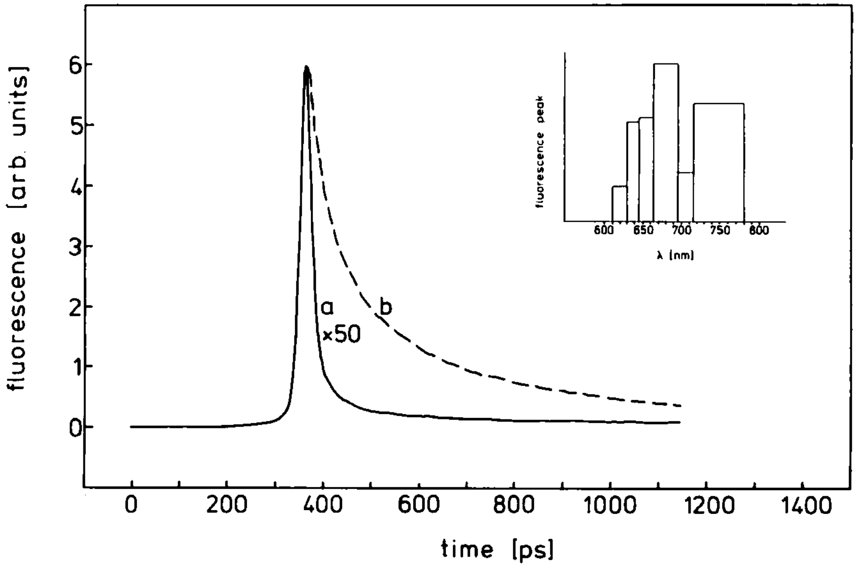

FIGURE 6 Fluorescence decay of TA(4)P clusters (molar ratio $x = 0.3$) in an LB film of arachidic acid. The upper part is identical with the apparent laser pulse shape. The dashed curve is 50 times higher at the peak and corresponds to fluorescence from TA clusters (molar ratio $x = 0.3$) in an LB film of arachidic acid. The insert is a crude spectrum determined for the peak emission with several cut-off filters. Excitation at 600 nm.

The peak of the fast decaying fluorescence signal from the TA(4)P clusters was 50 times smaller than that from the TA clusters with the same relative concentration $x = 0.3$ in the LB film. The half width of 25 ps for the fast decaying signal in Figure 6 is identical with the apparent halfwidth of the laser pulse. The peak height of a Gaussian with 25 ps half-width is reduced by a factor of 50 for the convolution of the Gaussian with an exponential having a decay time of 0.5 ps. The latter corresponds to the hole transfer time. A corresponding fit of a rate constants model to the initial fast part of the fluorescence signal is shown in the discussion. In this context we would like to mention that the decay of the isolated TA molecules in the LB films, $x = 10^{-3}$, was greatly accelerated when clusters of perylene moeities with fatty acid chains attached, $x = 0.3$, were incorporated simultaneously into the LB film. The very fast fluorescence decay of the solid curve in Figure 6 was also observed for the isolated TA(2)P molecule, i.e. when the TAP supermolecule was built with a bridge of only two CH_2 units inserted between the perylene and the A subunits. All these observations suggest that the extremely fast fluorescence quenching of the TA moeities in the TA(4)P clusters in Figure 6 is due to the presence of a perylene moeity in the immediate vicinity of the TA moeity.

Careful examination of the solid curve in Figure 6 reveals a small long tail as was already pointed out above. This long lived weak fluorescence tail is shown in Figure 7 over a wider dynamic range obtained with time resolved single photon counting. It is obviously non-exponential with leading decay times in the range of 1 to 2 ns.

The extremely fast decay of the fluorescence signal from the TA(4)P clusters

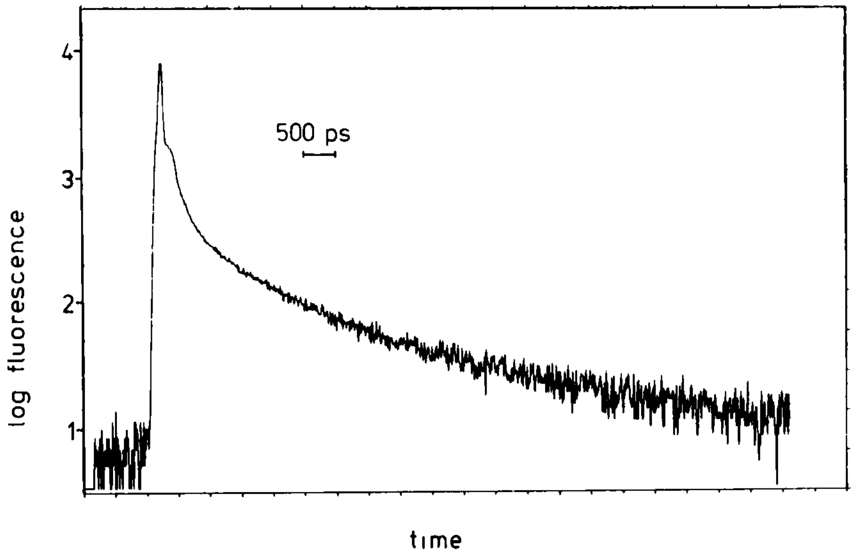

FIGURE 7 Small long-lived tail in the signal of Figure 6 measured with time-resolved single photon counting. Excitation at 600 nm.

remained unchanged when measured in a He cryostat with the LB film on top of a 2 mm quartz slide that was mounted on the cold finger. Temperature calibration was achieved via a sensor placed in the center of a quartz slide through a central bore and fixed there with conducting glue. According to this calibration the LB film reached 80 K on the quartz slide. The shape of the fast decaying solid curve in Figure 6 remained the same as also the reduction in peak height by a factor of 50 in comparison to the sample containing only the TA clusters with identical concentration $x = 0.3$. Both samples were measured at the same time under identical conditions in the cryostat. The decay of the fluorescence from the TA clusters slowed down with decreasing temperature as is expected for thermally activated energy migration to sinks in the disordered TA clusters. The latter is a well known quenching mechanisms that we have observed for various 2-dimensional dye systems.[15] The reaction kinetics in the TA(4)P clusters giving rise to the extremely fast fluorescence quenching does not involve such energy migration to sinks. It is controlled by hole transfer from the excited state of the TA unit to nearest neighbor perylene moeities as will be shown in the following section.

c) Charge carrier injection

Hole transfer from the excited singlet state of the TA moeity to the perylene moeity of a neighboring molecule in the TA(4)P cluster is a plausible cause for the initial ultrafast fluorescence decay shown in Figure 6. The oxidation potential of perylene and the reduction potential of the excited singlet state of the TA moeity for both the molecules in acetonitrile as given above suggest that such a downhill hole transfer is feasible even though there will be unknown shifts of these levels in the TA(4)P clusters of the LB film. To observe this reaction we have employed a direct measurement of the photogeneration of holes as injection current into an electrode. A suitable electrode for this purpose is an ultrapure vapor grown organic crystal with an appropriate position of the valence band,[16,17] in this case obviously an α-perylene crystal. For the present purpose there is the additional requirement of transferring the LB film containing the TA(4)P clusters from the surface of the Langmuir trough onto the surface of the perylene crystal without causing any greater damage to the film. The usually successful technique of preparing the surface by depositing first LB films of pure arachidic acid and then the LB film of interest is obviously not possible for this injection experiment. Deposition of the hydrophobic surface of the LB film onto the hydrophobic naturally grown even surface of a vapor grown plate-shaped α-perylene crystal occurred with very good match of the area disappearing from the trough and the area covered on the crystal surface. This does not exclude however the occurrence of damage in the submicron range. We have also tried to transfer the hydrophilic surface of the functionalized LB films directly onto polycrystalline n-SnO_2 electrodes that were produced in our institute.[32] Here the transfer was not so perfect as in the case of the perylene crystal. To avoid a discussion of an unclear preparation we show for the latter case only an injection current of electrons into n-SnO_2 arising when adsorbed TA(4)P molecules are excited with light. The TA(4)P molecules were adsorbed first from a 10^{-4} M solution in CH_2Cl_2. The solution was soaked off after 20 minutes and the n-SnO_2 electrode was contacted in the conventional way[16] with 1 M KCl containing 10^{-5} hydroquinone as regenerator for measuring the excitation spectrum of the electron injection current due to electron transfer from the excited singlet state of TA(4)P into the n-SnO_2 electrode with a conduction band edge in the range of about 0 V SCE.[32] Figure 8 shows that the shape of the excitation spectrum of the electron injection current is due to TA(4)P aggregates since it is somewhere between that of the TA(4)P monomer absorption (Figure 3) and that of the TA(4)P cluster absorption (Figure 5) in the LB film. It is an interesting point that we observed also electron injection from the excited perylene moeities as well (Figure 8) but this will not be discussed further in the present context.

The excitation spectrum of the hole injection current from the LB film containing TA(4)P clusters (x = 0.3) into the perylene crystal is shown in Figure 9. We employed here the conventional electrolytic contacts containing 1 M KCl where regeneration of the reduced dye, here the TA(4)P clusters, occurs through O_2 in the aqueous solution.[16] The long wavelength side of the excitation spectrum followed the absorption of TA(4)P clusters. The spectrum in Figure 9 was recorded with a high pressure Xenon arc light source and was left uncorrected. There is a hole photocurrent in the α-perylene crystal with an electrolytic contact also in the absence of dye molecules.[33,34] The latter is due to electron transfer from singlet excitons to O_2 at the interface. Its excitation spectrum follows the absorption spectrum of the α-perylene crystal. When the light is passing first through the perylene crystal before reaching the electrolytic contact as in our experiment the

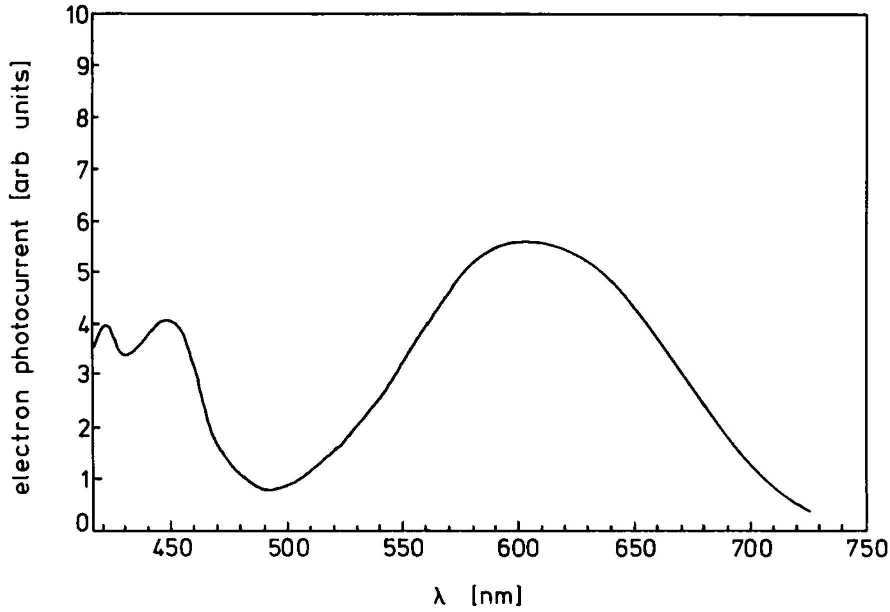

FIGURE 8 Excitation spectrum for electron injection current from adsorbed TA(4)P molecules into n-SnO_2 electrode.

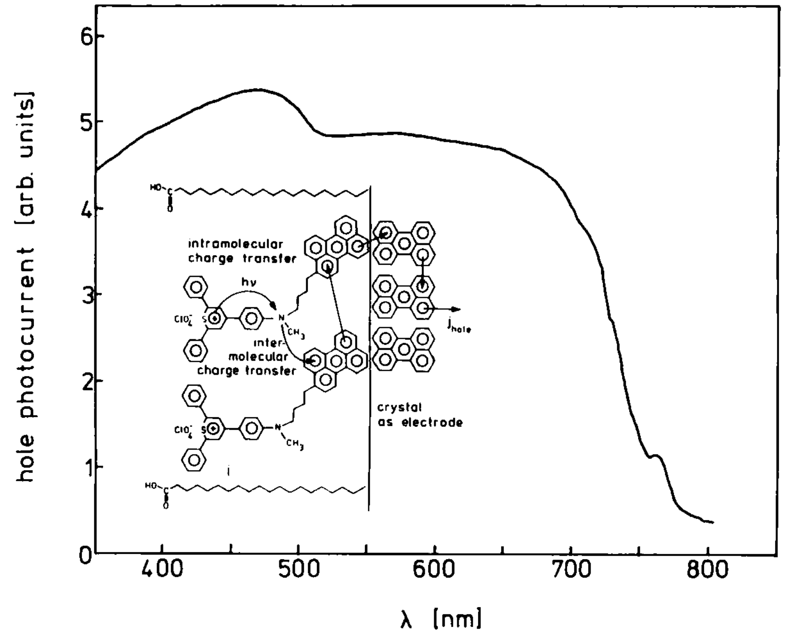

FIGURE 9 Excitation spectrum for hole injection current from LB film of arachidic acid with TA(4)P clusters (x = 0.3) incorporated, into an α-perylene single crystal as electrode. The insert shows a schematic model for the structure and the interface and for the sequence of reactions leading to hole injection.

latter photocurrent is at least by a factor of 20 smaller than the photocurrent injected from an adsorbed dye monolayer.[34] It is further reduced by at least a factor of 10 when an LB film of arachidic acid is deposited on the perylene crystal due to the hindered access of O_2 to the crystal surface. Thus the hole photocurrent shown in Figure 9 does not contain any significant contribution from the latter mechanism but is due to hole injection from the deposited monolayer.

At 600 nm the photocurrent yield, i.e. collected holes per incident photons, varied between 1×10^{-3} and 8×10^{-3}. Since the absorption of the functionalized film is one percent here, these values correspond to yields between 0.1 and 0.8 holes per absorbed photon. This is a reasonable range of values considering the complex molecular structures and the simple preparation procedures for assembling these samples. The dip in the absorption spectrum at around 490 nm that occurred also in the excitation spectrum of the electron injection current at the n-SnO_2 electrode in Figure 8 is missing in Figure 9. This is a special energy transfer effect arising from the extremely good overlap of the E-excimer emission spectrum of the α-perylene crystal[26] with the absorption spectrum of the TA(4)P clusters in the LB film. A few per cent absorption at the absorption edge of the α-perylene crystal leads to the same number of excited TA(4)P clusters as direct illumination at 600 nm when one per cent is absorbed. This effect will not be discussed further in this context.

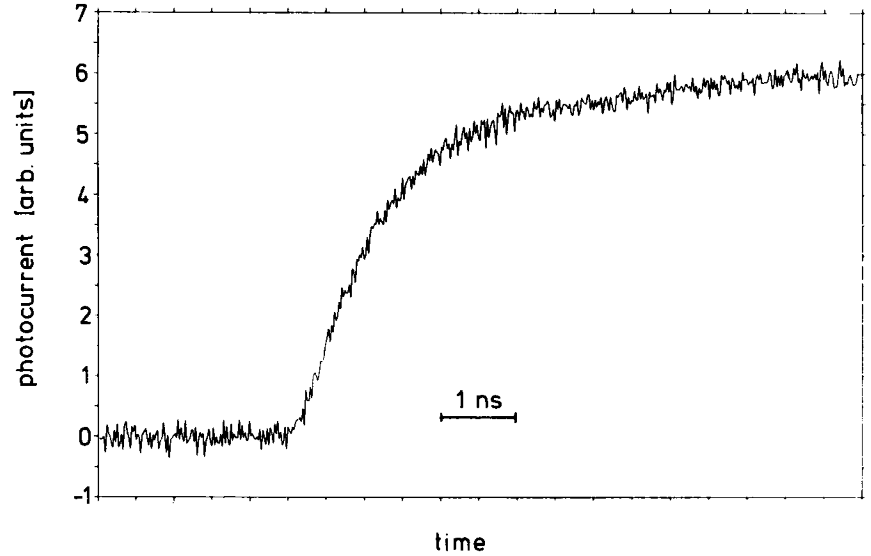

FIGURE 10 Time-resolved (70 ps resolution) hole injection current in the system shown in Figure 9, for excitation with a train of laser pulses at 600 nm as applied for the fluorescence decay measurements. The applied external field was 2 × 10^5 V cm^{-1}.

We carried out also 70 ps time-resolved measurements of the hole injection current in the α-perylene crystals[17] to obtain information on the residence time of the holes in the perylene part of the TA(4)P clusters. Details of the measuring technique have been described already elsewhere.[17,35] The rise time of the hole injection transient is shown in Figure 10. It was measured with 2 × 10^5 V cm^{-1} external electric field applied. This is in the saturation range of the current voltage curve obtained for this system. Extrapolating results obtained at anthracene crystals[36] we can assume that hole escape from the crystal surface into the bulk of the perylene crystal is much faster than 1 ns at an applied electric field of 2 × 10^5 V cm^{-1}. The rise time of the injection current is then controlled by the time dependent hole generation, i.e. here arrival of holes at the surface of the perylene crystal electrode. The experimental rise time in Figure 10 is nonexponential with a leading time constant of about 1 ns. We will discuss this point in more detail below.

DISCUSSION

The most important sets of information that we can deduce from the experimental section are the following. The fluorescence from TA(4)P clusters (x = 0.3) aligned in an LB film decayed extremely fast (sub ps) and there was no slow-down in this decay between room temperature and 80 K. Holes were injected from the perylene side of the TA(4)P clusters into a perylene crystal when the excited singlet state of the TA units was populated in the TA(4)P clusters. The yield of this injection current approached 1 in the best experimental cases and its excitation spectrum followed the absorption of the TA(4)P clusters.

We interpret these findings as due to extremely fast hole transfer from the excited singlet state of a TA unit to a perylene moeity of a TA(4)P molecule that is occupying a nearest neighbor position in the cluster. From there the hole can move about in the perylene part of the TA(4)P cluster and thus reach the surface of the perylene crystal. From there it can move onwards into the bulk of the crystal when an external electric field of sufficient strength is applied.

The fast initial hole transfer step with subpicosecond speed independent of temperature can be ascribed to two different mechanisms. The first has been quantified and involves a non-adiabatic hole transfer reaction where the high speed combined with the absence of a temperature influence would require the so called activationless case to be realized (compare e.g. references 2 and 3). In the free energy versus configuration coordinate space the product state crosses the reactant state near the latter's equilibrium coordinates. This happens only when the standard free energy difference for the downhill charge transfer reaction has the same value as the reorganisation energy in the system. Corresponding postulates have been made for the two consecutive electron transfer reactions in the bacterial photosynthetic apparatus.[2] There is also the suggestion that the second step in that system involves an adiabatic reaction with stronger electronic interaction.[3] For hole transfer in the TA(4)P clusters this mechanism would require a by chance matching for the values of the standard free energy difference and of the reorganisation energy.

The second mechanism involves transport of a polaron-type particle following an adiabatic reaction path along the supermolecule, which is in our case an aligned TA(4)P cluster in the LB film. There are no quantitative treatments of this case for supermolecules at present but we can assume the change carrier transport to be very similar to that occurring in van der Waals type organic crystals of the anthracene type. The mobility increases in these crystals from values around 1 cm^2/Vs at room temperature to values of several 100 cm^2/Vs when approaching liquid He temperature.[8] When an external electric field is applied the drift velocity of the holes reaches a saturation value in the range of 10^6 cm s^{-1} near liquid He temperature in naphthalene crystals[8] and of 5.7×10^5 cm s^{-1} in anthracene crystals at room temperature.[9] In the latter case the potential gradient set up by the external electric field has to reach a value of 0.1 V over 10 Å, which corresponds to the center to center nearest neighbor distance in the c' direction in anthracene crystals.

It appears very likely that the three main experimental requirements for the adiabatic transport, similar to polaron hopping, are indeed fulfilled in the TA(4)P clusters, i.e. an uphill step in the ionisation energy, i.e. downhill in the hole energy, of the order of 0.1 V or more between the excited singlet state of the TA unit and perylene, and a sufficient electronic interaction of the order of magnitude > 100 cm^{-1} between the TA unit and the perylene unit of a nearest neighbor TAP molecule in the TA(4)P cluster. Delocalisation over several neighbor TA and perylene moeities in the TA(4)P cluster is not required for an adiabatic hopping reaction but is required for a band-type polaron motion. The relaxation seen in the Stokes' shift of 794 cm^{-1} between the absorption and fluorescence band of the TA(4)P clusters might occur in combination with or after hole transfer to the nearest neighbor perylene moeity. Approach of nearest neighbor molecules to within van der Waals distances as in organic crystals of the anthracene type is suggested by the observation of Davydov splitting for anthracene moeities with alkane chains in an LB film that is of comparable magnitude as in the pure anthracene crystal,[37] and by a very similar packing in pure anthracene single crystals and those composed of anthracene moeities with alkane chains attached that form a single crystal consisting of bilayers analogous to LB multilayers of this compound.[38] Clusters of perylene moeities with alkane chains attached showed only E-excimer emission,[25] again in agreement with a nearest neighbor packing with intermolecular distances similar to those in the pure α-perylene single crystal.

Though certainly not appropriate for a description of dynamic details in the TA(4)P clusters we can derive some of the gross kinetic features already from a simple rate constants model shown in Figure 11. Light absorption leads to excited singlet states of the TA units (TA*) with rate σI where σ = absorption cross section and $I(t)$ = number of incident photons per area and per second multiplied by the apparent laser pulse shape. Hole transfer from the TA* units to the nearest neighbor perylene moeities is described by the rate constant k_v. The remaining occupation of the TA* units by holes is described as back transfer by the rate constant k_b. Fluorescence is assumed to occur in the observed spectral range $630 < \lambda < 800$ nm only with the holes residing on the TA* units. The fluorescence to yield the ground state TA is represented in Figure 11 by the rate constant k_f and the nonradiative decay parallel to k_f by k_{nr}. k_g describes slow direct recombination of the hole from the nearest neighbor perylene molecule directly with the electron residing on T.

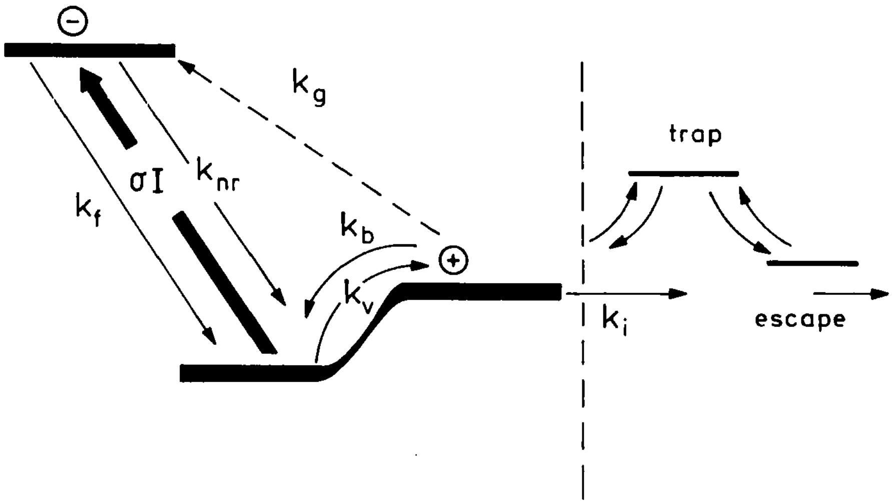

FIGURE 11 Rate constants scheme for description of the gross features of time dependent fluorescence and hole generation in the TA(4)P clusters in the LB film. The definitions for the rate constants are given in the text.

The effect of hole motion in the perylene part of the TA(4)P cluster is considered only as trapping and detrapping events illustrated on the right hand side of the scheme in Figure 11. The slow rise of the photocurrent (Figure 10) indicates that the hole was trapped in the perylene part of the TA(4)P cluster before it reached the crystal surface. Transfer of holes to relatively deep traps with detrapping times that are longer than the time window for the observation of the fast initial fluorescence decay (Figure 6) can be treated in this early time window as pseudo-irreversible escape with rate constant k_i from the nearest neighbor perylene chromophore. The rate constants model with trapping and detrapping events predicts fluorescence decay with three exponentials. However, the gross features of the initial fast fluorescence decay (Figure 6) can be simulated already with a biexponential decay curve. In this case only the pseudo-irreversible escape via k_i to deep traps is considered in the scheme and trapping and detrapping events in shallow traps are neglected. In this case the effective value for the rate constant k_b takes over some of the effect of the shallow traps in keeping the concentration of the holes small on TA$^-$ where they can recombine via a radiative and a non-radiative channel. A fit of this model to the experimental curve in Figure 6 is shown in Figure 12, where a simple Gaussian was introduced as shape of the apparent laser

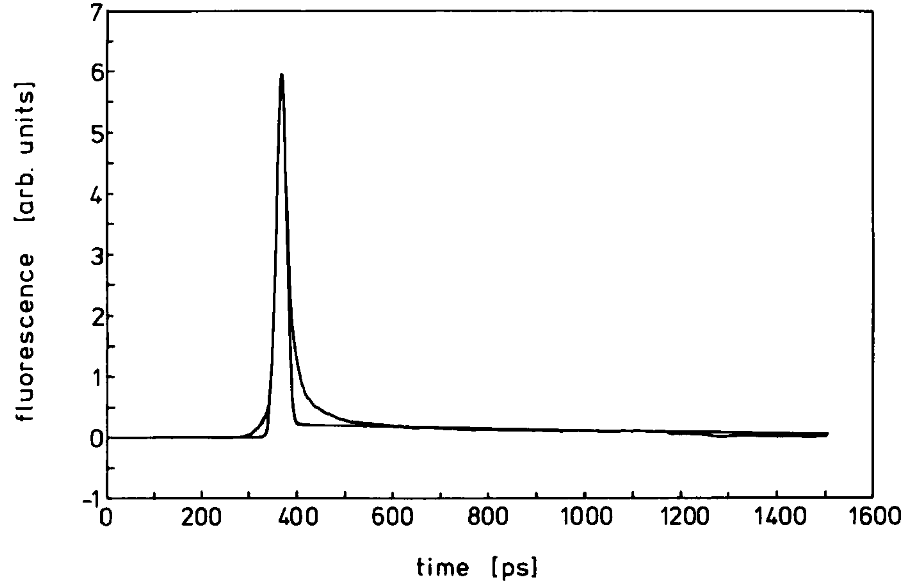

FIGURE 12 Comparison of the biexponential decay predicted by the simple rate constants scheme shown in Figure 11 (with trapping and detrapping, see text) with the experimental fluorescence decay curve shown in Figure 6. The fit parameters when taking into account the reduction in peak height by a factor of 50 are the following: $k_v = 2 \times 10^{12}\ s^{-1}$, $k_b = 1.3 \times 10^9\ s^{-1}$, $k_f = 1 \times 10^9\ s^{-1}$, $k_{nr} = 1 \times 10^8\ s^{-1}$, $k_g = 1 \times 10^8\ s^{-1}$ and $k_i = 1 \times 10^9\ s^{-1}$. The fast decay and reduction in peak height is controlled by k_v. The apparent laser pulse, i.e. pulse shape for the generation rate σI, was introduced as simple Gaussian of 25 ps halfwidth which gives a reasonable approximation to 80 per cent of the apparent laser pulse measured over a long integration time with the synchroscan streak camera. Deviations of the experimental curve from the simple model are real on the falling side of the fluorescence signal (compare text).

pulse. The fast decay of the fluorescence requires that the dominating rate constant k_v is much greater than the reciprocal apparent width of the laser pulse. A further experimental observation, i.e. the reduction by a factor of 50 in the initial height of the fluorescence signal in the presence of the perylene units in the cluster (see above), fixed the value of the forward rate constant for hole transfer at $k_v = 2 \times 10^{12}\ s^{-1}$ to obtain the fit. This initial fast decay is the most interesting feature of the fluorescence decay curve. The long tail of the fluorescence decay curve (Figures 6 and 7) indicates the range of lifetimes for the separated electron-hole pairs in the TA(4)P clusters.

The height of this slow component of the fluorescence decay is controlled by the probability of the hole to reside on the TA^- unit. This probability is small when k_b is small compared to k_v. It is further reduced when the holes can escape to traps in the perylene part of the TA(4)P clusters. Not only the height but also the decay constant of this slow component is greatly reduced by hole transfer away from TA^- and residence in traps. These two effects show up in the solution of the corresponding rate constant scheme but are obvious already in the graphic representation of the scheme in Figure 11. One can also see from the scheme and in the solution of the rate constants model that the slow rise time of the injection current (Figure 10) can be attributed to intermittent trapping and detrapping of the holes before they can reach the crystal surface. The decay of the fluorescence tail in Figure 7 indicates separation times for the electron-hole pairs in the range of ns. In view of the complexity of the system we have not made the attempt of introducing further parameters for distribution curves instead of simple rate constants. Distribution curves would take into account the disorder in the TA(4)P clusters.

We consider it already encouraging that we have achieved light-induced electron-hole pair separation in a molecular system with time constants shorter than one ps and electron-hole pair separation that lasts for one ns and longer. The present experimental system is complicated since it consists of clusters of supermolecules. A semiquantitative insight has been obtained with a rate constants model. Alignment of the clusters in a supporting Langmuir-Blodgett film allowed for directional electron-hole pair separation and the injection of the photo-generated holes into a suitable organic crystal as electrode. The missing influence of temperature and the extremely high speed of hole transfer indicate medium strong electronic coupling of the reactant chromophores of the order of $100\ cm^{-1}$ or larger as is known to occur in molecular crystals of the anthracene type. A more refined description of charge transfer in such a system is expected to be found somewhere in the direction of the model suggested by Friesner *et al.*[39]

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