Sensitized and Intrinsic Carrier Generation in Phenethylperylene/Tritolylamine Thin Film Structures

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Abstract

The photoconductivity mechanism was investigated for vacuum evaporated phenethylperylene (PPEI) films deposited on a thin polycarbonate film doped with varying concentrations of tritolylamine (TTA) and subsequently exposed to methylene chloride vapors. Compared to structures without TTA in the polycarbonate layer, the presence of TTA leads to an increase of carrier generation efficiency and strong quenching of perylene fluorescence indicating a surface sensitized carrier generation process. Fluorescence quenching measurements on samples with and without TTA show a linear correlation between fluorescence quenching and carrier generation at high fields. In the presence of TTA, significant photoconductivity is observed much before the appearance of fluorescence quenching. A marked change of curvature (inflection point) in carrier generation accompanies the appearance of fluorescence quenching at fields in excess of 100 MV/m. These results demonstrate that in the samples containing TTA, two different carrier generation mechanisms are operating simultaneously. At low fields, carrier generation is dominated by the sensitized component. At high fields, although the sensitized component saturates, the intrinsic component causes a further increase in overall carrier generation. The change of slope in carrier generation at high fields is coincident with appearance of fluorescence quenching. The experimental results are consistent with the notion that the intrinsic photoconductivity component originates from direct dissociation of the fluorescent first excited singlet state into free carriers.

Introduction

The mechanisms of charge carrier generation in photoconductive solids have been the subject of extensive experimental and theoretical studies. Both intrinsically and extrinsically controlled processes in solid state systems have been described. In intrinsic photoconductors, carrier generation is an intrinsic property of the bulk material and the presence of uncontrolled impurities can adversely affect photoconductive properties. In extrinsic photoconductors, pure materials usually show no or very small photoconductive response. Only the addition of suitable sensitizers makes the photoconductive response significant. Photoconductors can be further divided into surface sensitized or bulk sensitized types, depending on the sentisizer location.

Both surface and bulk sensitized carrier generation have been well documented in the scientific literature. In a number of inorganic[1] and organic systems,[2] increased photoconductive response has been obtained by adding suitable dopants to the material bulk. Surface sensitization of photoconductivity has been observed in anthracene, perylene and dibenzanthracene crystals.[3] Phthalocyanines also exhibit increased photoconductivity in the presence of sensitizers.[4] In addition, surface sensitization is responsible for efficient carrier generation in aggregate type photoconductors[5] where carrier generation was shown to originate at the interface of the filamentary crystallized dye and the amorphous hole transport layer phases. It was also observed in thin films of benzimidazole perylene 3,4,9,10 tetracarboxylic acid (BZ perylene) overcoated with tetraphenyldiamine (TPD)/ polycarbonate hole transport layer[6] and in azo pigments in contact with a number of hole transport molecules.[7]

In the present work the carrier generation mechanism is investigated for vapor deposited thin films of perylene bis(phenethylimide) (PPEI or phenethylperylene) on a polycarbonate polymer layer doped with varying concentrations of tritolylamine (TTA) hole transport molecules and then exposed to methylene chloride vapors. The structures of these materials are given in Fig. 1. Recently it has been shown that excitons in PPEI are strongly quenched by electron donor molecules,[8] leading to the conclusion that exciton diffusion lengths are very long, possibly exceeding 1 µm. In this work it is shown that TTA strongly quenches phenethyl perylene fluorescence. In addition, by measuring the electric field induced fluorescence quenching and carrier generation using a delayed field collection technique it is shown that carrier generation has two components: (i) extrinsic, involving exciton dissociation by the TTA at the pigment surface and (ii) intrinsic, originating from direct dissociation of excitons into free carriers.

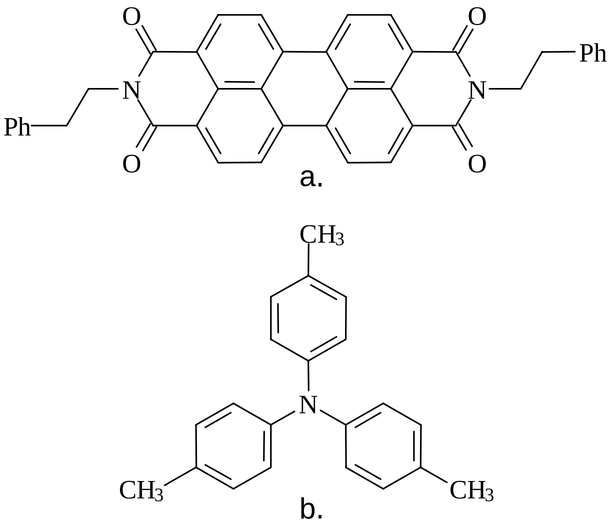

Figure 1. Structures of the molecules used in this work: (a) phenethylperylene, (b) tritolylamine.

Experimental

The phenethyl-perylene pigment (Fig. 1a) was synthesized by cyclizing perylene tetracarboxylic dianhydride with an excess of phenethylamine, as described in Reference 9. Tritolyl-amine (Fig. 1b) was synthesized as described in Reference 10. Makrolon 5705 polycarbonate polymer was purchased from Mobay Chemicals and used as received. The sample preparation procedure was as follows. A thin layer of hexamethyldisilazane (HMDS, Olin Microelectronics Materials) was first spin coated on a NESA glass substrate, rotating at 5000 rpm to form a barrier layer of HMDS. A doped polycarbonate layer solution , containing tritolyl-amine (1% to 20% by weight) and Makrolon binder to form a 3% weight solids solution in a dichloromethane/1,1,2-trichloroethane solvent system, was then spin coated on the HMDS barrier layer by pipetting 2ml of the 3% solids solution onto the substrate (in the static mode), then ramping to 500 rpm for 10 seconds, followed by 2000 rpm for 1 minute to form a 1 micron charge transport layer. The perylene was then vapor deposited onto the charge transport layer to a thickness of 0.1 micron and solvent treated with dichloromethane vapors to undergo a polymorphic conversion to the photoactive form. At the end a thin Al electrode was vacuum evaporated to form a sandwich cell. This lead to highly reproducible samples as demonstrated in Fig. 2. The difference in absorbance around 400 nm is due to different concentrations of TTA which has an absorption edge in that wavelength region.

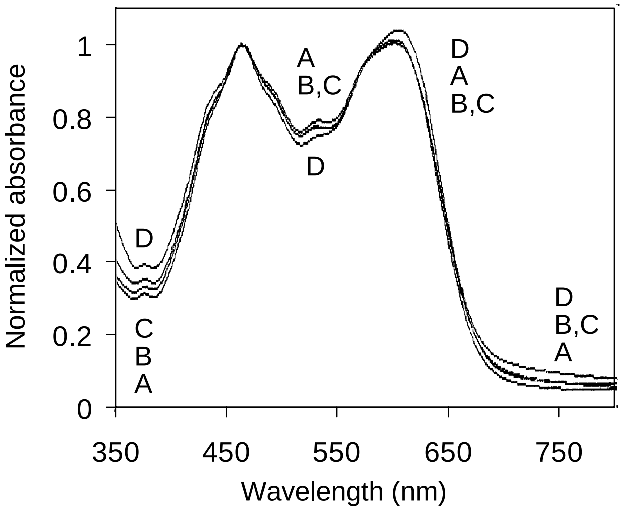

Figure 2. Absorption spectra of phenethyl perylene films obtained by vacuum evaporation and subsequent exposure to methylene chloride vapors. Spectra A, B, C, and D were obtained at concentrations of TTA in the polycarbonate matrix of 0%, 1%, 5%, and 20% by weight, respectively. At 465 nm absorbance of all samples was about 1 ± 0.1. For comparison the spectra are normalized to the same value at 465 nm for all samples.

The electric filed in the pigment layer was calculated from the applied voltage, V_{appl}, as

$$E_{appl} = (CV_{appl})/(A\varepsilon_0\varepsilon_r), \qquad (1)$$

where A= 0.4 cm^2 is the cell area, ε_r = 5.3 is the relative dielectric constant of phenethylperylene,[11] and the other symbols have their usual meanings. It is interesting to note that Eq. (1) is generally valid for a plane capacitor with any number of layers with different dielectric constants. In order to calculate the electric field in any specific layer, it is only necessary to know the total sample capacitance, sample area and the dielectric constant of that particular layer. The dielectric constants of other layers are not important. This is a direct consequence of the continuity of the dielectric displacement vector across interfaces dividing materials of different dielectric constants.

Carrier generation was measured using a delayed field collection technique and the electric field induced quenching of total fluorescence as described in detail in Reference 12. Samples were illuminated with 532 nm, 5 ns pulses from a frequency doubled Nd-YAG laser. In order to prevent carrier injection, the samples were biased in a unipolar fashion and measured at low repetition rates of about 0.1 Hz. Reproducible measurements were only obtained when erase light pulses were applied to shorted samples prior to each biased measurement. Time resolved fluorescence with no applied sample bias was measured using single photon counting with picosecond 590 nm light pulses for sample excitation, 670 nm light detection, and the experimental setup described in Reference 13. Time resolved electric field induced fluorescence quenching measurements were also attempted,[13] but these were not possible due to unipolar sample bias which lead to charge accumulation and quick electric breakdown in the sample.

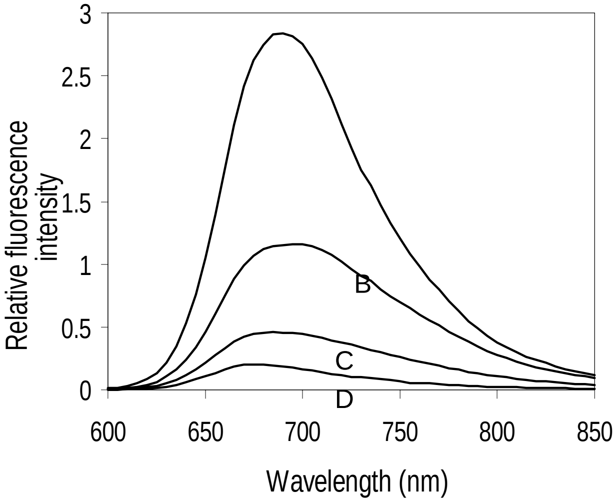

Figure 3. Fluorescence spectra of samples A, B, C, and D. The presence of TTA in the polycarbonate matrix leads to a significant fluorescence decrease.

Results and Discussion

Figure 3 shows the fluorescence spectra of four samples with 0%, 1%, 5%, and 20% TTA by weight in the polycarbonate layer, which will be referred to as samples A, B, C, and D, respectively. For these measurements the samples were excited with 550 nm light illuminating the evaporated pigment film from the glass substrate side. As the concentration of TTA increases the fluorescence dramatically decreases but the shape of the fluorescence spectra does not appear to change significantly. Only a small shift to shorter wavelengths is observed when the concentration of TTA increases. The ratio of peak fluorescence for 0% TTA to 20% TTA is about 14. This significant decrease of fluorescence can only be explained in terms of a charge transfer reaction induced by the presence of TTA at the pigment surface. This conclusion is also supported by photoconductivity measurements (presented later).

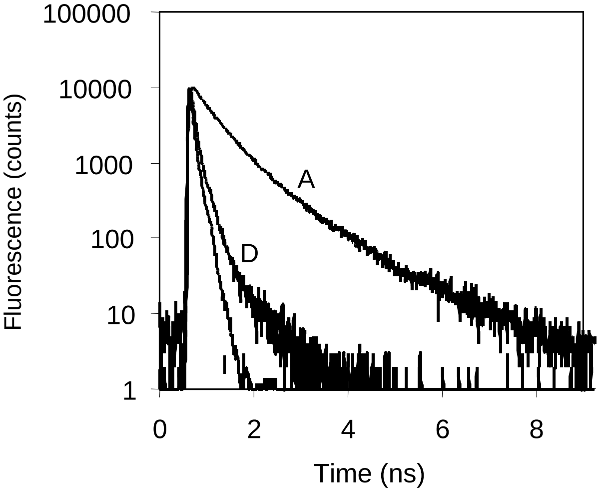

Figure 4. Time resolved fluorescence decays for samples A *(0% TTA) and* D *(20% TTA) with illumination from the glass side. Curve* I *shows the instrument response function.*

Figure 4 shows the time resolved fluorescence decay for samples A and D containing 0% and 20% TTA in polycarbonate with illumination from the glass side. As the concentration of TTA in the Makrolon layer increases the decay becomes significantly faster. In the sample with 20% TTA the lifetime of the dominant component is only about 30 ps which is close to the detection limit of our instrumentation. In contrast, the dominant decay component for 0% TTA sample is about 600 ps. Surface quenching by TTA is very efficient and leads to a decrease in fluorescence lifetime by about factor of 20 with almost complete disappearance of the longer lived tail of fluorescence observed in samples with 0% TTA. This is consistent with the assumption that long lived fluorescence observed in samples with no TTA corresponds to trapped excitons, most probably located on the surface of grains comprising the polycrystalline pigment film. 20% TTA in Makrolon completely suppresses the long-lived fluorescence component. This is an indication that the remaining fluorescence predominantly originates from mobile excitons which decay radiatively before reaching the TTA quenching sites. This conclusion will be important later for the interpretation of electric field induced fluorescence quenching in samples containing 20% TTA. It is also consistent with the blue shift of the fluorescence peak as TTA concentration increases (Fig. 3).

The quantitative measure of electric field induced fluorescence quenching is fluorescence quenching efficiency, $\Phi(E)$, defined by

$$\Phi(E) = [I_f(0) - I_f(E)]/I_f(0), \tag{2}$$

where $I_f(E)$ is integrated fluorescence at field E applied to the sample. Figure 5a shows fluorescence quenching as a function of the electric field for samples A and D. In the case of sample A, which does not contain TTA in the polymer film, fluorescence quenching can be detected at about 60 MV/m and gradually increases with increasing applied field. For sample D, with 20% of TTA in the polymer film, no fluorescence quenching is observed until the electric field reaches 100 MV/m. Figure 5b shows the plot of fluorescence quenching as a function of relative photoresponse measured by the delayed collection field method. Assuming that fluorescence quenching is caused by exciton dissociation into carriers by the electric field, a linear relationship is expected between the carrier generation efficiency, $\eta(E)$, and fluorescence quenching:[12]

$$\Phi\,(E) = [\eta(E) - \eta(0)]/[1 - \eta(0)], \tag{3}$$

where $\eta(0)$ corresponds to a part of carrier generation, which is not connected to electric field, induced fluorescence quenching. In the case of samples with 20% TTA, $\eta(0)$ is assumed to represent saturation value of the sensitized carrier generation.

Let us introduce the relative photoresponse, R, which is defined as

$$R(E) = \Delta V / I_{\mathrm{light}}, \tag{4}$$

where ΔV is a voltage drop induced on a sample by a light pulse of energy I_{light}. The carrier generation efficiency is proportional to relative photoresponse,

$$\eta(E) = C\,R(E), \tag{5}$$

and by combining Eqs. (3), and (5) at high fields we obtain,

$$\Phi(E) = C\,R(E)\,/[1 - \eta(0)] - \eta(0)/[1 - \eta(0)]. \tag{6}$$

It therefore follows that at high fields a linear correlation is expected between relative photoresponse and fluorescence quenching (Figure 3b). The slope and intercept of this linear plot determine constant C, which enables rescaling of relative photoresponse, R, to quantum efficiency, η (Eq. 5).[12]

Rescaled data are shown in Fig 5c. At low fields, the sample without TTA shows much smaller carrier generation efficiency than the sample with 20% TTA, although the latter samples do not show detectable electric field induced fluorescence quenching. These results can only be interpreted as a surface sensitized carrier generation by TTA. The shape of carrier generation efficiency curve at high fields is very interesting. It shows a tendency to saturate, but around 100 MV/m an inflection point appears and change of curvature occurs. This coincides with the appearance of fluorescence quenching around the same field and indicates a change in the dominant carrier generation mechanism. In the discussion of time resolved fluorescence decays (Figs 4a,b) we concluded that in the presence of TTA, fluorescence must originate from mobile intrinsic excitons which decay radiatively before reaching TTA quenching sites. It therefore follows that the continuing increase in carrier generation in samples with TTA originates from carriers generated by the direct dissociation of the intrinsic mobile singlet excitons.

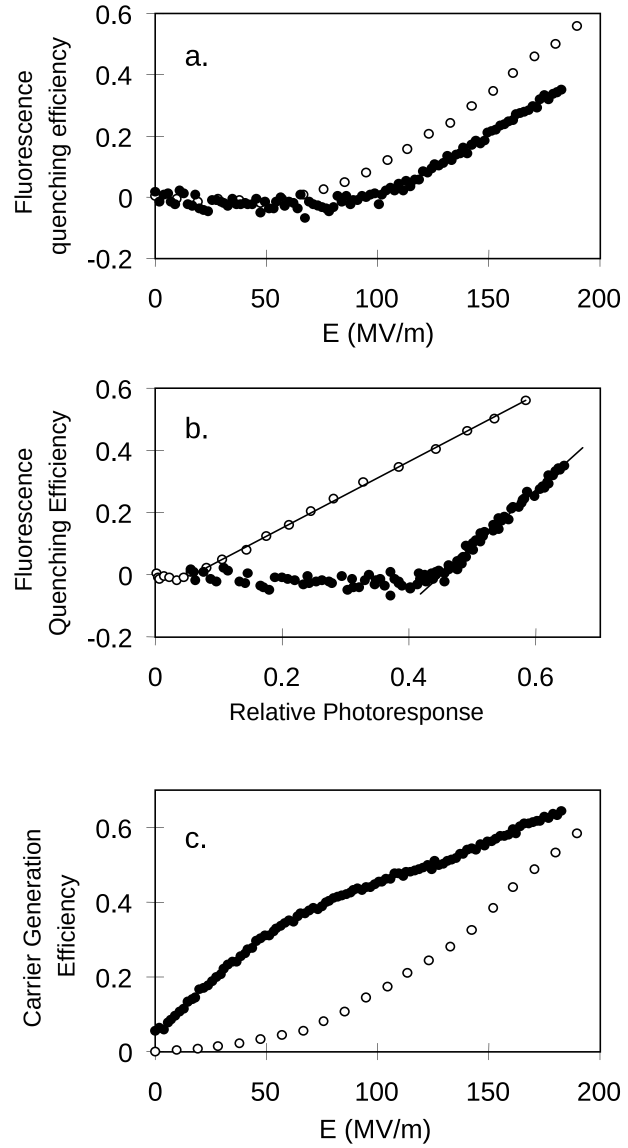

Figure 5. (a) Fluorescence quenching, Φ, as a function of electric field for samples A (open circles) and D (filled circles). (b) Fluorescence quenching plotted as a function of relative photoresponse, R. Straight lines are best least square fits to high field data. (c) Rescaled carrier generation efficiency, η, for the samples A and D.

Direct dissociation of the first excited singlet state at high applied fields is not surprising. Electric fields lead to gradients in the valence and conduction energy levels. If they are strong enough it is energetically possible that the bound singlet energy levels match the energy of electron-hole pairs at some distance accessible by tunneling. For example, a field of 100 MV/m will produce an energy change of 0.2 eV at 2 nm, which may be enough to lead to excited state quenching by tunneling to separated electron and hole pair states.

It is interesting to compare values for carrier generation efficiency determined in this work for samples without TTA to xerographic measurements by Magin and Borsenberger[11] on thin evaporated films of phenethylperylene. For polycrystalline samples, which should be similar to ours, they measured a quantum efficiency of 10% at a field of 50 MV/m. At this same field we obtained a quantum efficiency of 4% which is in reasonable agreement considering the differences in the sample preparation procedures.

Conclusions

The relative photoresponse and fluorescence quenching were measured in thin films of phenethylperylene pigment induced by the presence of hole transport molecule TTA and by the electric field. The results clearly demonstrate that TTA is a surface sensitizer greatly enhancing photoconductivity when compared to samples, which do not contain TTA. Electric field induced fluorescence quenching measurements, combined with relative photoresponse measurements, indicate that in samples with TTA a change of carrier generation mechanism occurs at high fields. Although the sensitized carrier generation saturates, further increase of carrier generation is observed originating from direct dissociation of the intrinsic mobile excitons into free carriers. Carrier generation from the first excited singlet state at high fields should be a universal property of many materials. High enough fields will lead to sufficient gradients in conduction and valence energy levels to enable electron tunneling from the bound excited states into separated carriers.

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Biography

Zoran Popovic received his Dipl. Eng. and M.Sc. degrees in electrical engineering from University of Belgrade, Yugoslavia, in 1965 and 1968, respectively. From 1965 until 1971 he was a Teaching Assistant at the Department of Electrical Engineering at the University of Belgrade, and he also worked on semiconductor research at the Institute for Physics, Belgrade. In 1974 he received his Ph.D. degree in Materials Science from McMaster University, Hamilton, Ontario, Canada and joined Xerox Research Centre of Canada where he presently holds a position of Research Fellow. His main research interests are in photoelectronic properties of organic materials.