Study of the Photoconductivity Mechanism in Phthalocyanine Pigment Particles by Electric Field Modulated Time Resolved Fluorescence

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Abstract

Phthalocyanine pigment particles represent an important class of organic photoconductors, which are extensively used in organic xerographic photoreceptors. Despite numerous studies, a complete picture of the carrier generation process in this class of materials has yet to emerge. In this paper we will present a detailed description of the photocarrier generation mechanism in TiOPc(I), TiOPc(IV), HOGaPc and x-H_2Pc. We have studied the influence of electric field on both the integrated and time resolved fluorescence in photoconductive particles dispersed in a polymer matrix. Time resolved fluorescence decays were analyzed by fitting the data to a sum of two exponentials representing the fast and slow fluorescence components. For HOGaPc, TiOPc(I) and TiOPc (IV) the fast fluorescence component exhibits both amplitude and lifetime quenching. These results indicate that carrier generation in HOGaPc, TiOPc(I) and TiOPc (IV) originates from both relaxed and nonrelaxed intrinsic excited singlet states, while the trapped excitons do not lead to significant carrier production. In contrast, for x-H_2Pc significant amplitude quenching of the fast component is observed only at high field and the trapped excitons are an important source of photogenerated carrier. This indicates that x-H_2Pc possesses at least some bulk sensitized photocarrier generation. All of the phthalocyanines studied exhibited a quadratic dependence of integrated fluorescence quenching on electric field indicating the existence of a neutral carrier precursor state.

Introduction

In this paper we will review recent work[1,2] on the photocarrier generation mechanism in TiOPc(I),[3] TiOPc(IV),[3,4] HOGaPc[5] and x-H_2Pc.[6,7] These photogenerators are of particular interest as they are commonly utilized in xerographic copiers and printers. It is also interesting to compare the photogeneration mechanism of two polymorphs such as TiOPc (I) and TiOPc (IV). It is known from xerographic measurements that TiOPc (IV), often referred to as TiOPc-Y, is considerably more sensitive than TiOPc (I) despite possessing the same molecular structure.[3,4]

Important information on the mechanism of photoconductivity in organic materials has been obtained by electric field modulated spectroscopies. Electric field induced fluorescence quenching was studied in solution,[8] doped polymer systems,[9,10] and crystalline organic pigments.[11-14] These measurements, combined with photoconductivity measurements, enable investigation of electronic states participating in the carrier generation process. They supply additional information not available on the basis of photoconductivity measurements alone. Most electric field-induced fluorescence quenching studies have been applied to total sample fluorescence. These studies demonstrated a correlation between fluorescence quenching and photocarrier generation efficiency and thus indicated that the first excited singlet state leading to fluorescence and carrier generation are linked. However, they could not distinguish between intrinsic and impurity controlled processes or resolve if the first excited singlet state or its precursor was involved in carrier generation.

The perturbative influence of external electric fields on molecular energy levels (Stark effect) is usually quite small.[15] In this paper, we will concentrate only on processes which can produce large fluorescence changes. These processes generally involve an intermediate state in which an electron and hole are separated by a finite distance. The consequence of this charge separation is strong coupling of the intermediate state to the external electric field which leads to modulation of either (i) the initial number of excited molecules or (ii) the decay rate of the fluorescent excited state. These two different mechanisms of fluorescence quenching are a signature of underlying molecular processes. They cannot be distinguished on the basis of fluorescence intensity measurements alone. However, time resolved measurements can potentially distinguish them.

In the first case, amplitude quenching, we expect to observe a decrease in fluorescence amplitude, but unchanged fluorescence lifetime. This happens when the precursor to the fluorescent state is quenched by the electric field, i.e. photogenerated carriers and fluorescent first excited singlet state have a common precursor. In the second case, rate quenching or lifetime quenching, the initial fluorescence amplitude remains constant but the lifetime decreases. This is a signature of direct quenching of the fluorescent state by the electric field, i.e. photogenerated carriers and fluorescence both originate from the first excited singlet state. In principle both mechanisms can operate simultaneously resulting in both amplitude and rate (lifetime) quenching. Fluorescence measurements are also important in developing an understanding of the sensitized carrier generation observed in some organic systems. In these systems the presence of a small electron donor molecule on the surface of an organic dye leads to the fluorescence quenching and generation of electron-hole pairs.[16,17]

Experimental

The pigments used in this work were synthesized in house using procedures described in the literature.[3,5,7] Standard elementary analysis was used to confirm that they were of high purity with assays >98%. Most importantly, they met electrical requirements for xerographic photoreceptors, i.e. showed high sensitivity, low dark decay, and excellent cycling stability. Their polymorphic forms were determined by x-ray diffraction analysis. The pigment dispersions were prepared by roll milling 1.5 g of pigment, 1.0 g of polymer, and 47.5 g of butyl acetate with 300 g of 1/8 inch stainless steel balls in a 120 mL bottle. Total milling time was 48 hours. The pigment dispersion films were dip coated onto the NESA to about 0.2 to 0.4 microns thick, making sure the maximum optical density of absorption peak was greater than one.

All of the samples were thin film sandwich cells prepared on NESA glass substrates. The NESA was first coated with a silicon monoxide blocking layer, followed by dip coating of the phthalocyanine dispersed in a polymeric binder to a thickness of about 0.2 to 0.4 microns. The TiOPc (I), TiOPc (IV) and x-H_2Pc were all dispersed at 60 wt% in a poly(vinylbutyral) matrix. The HOGaPc was dispersed at 60 wt% in a polyvinylchloride-vinylacetate-maleic acid terpolymer matrix. These polymer matrices were chosen as they provided good pigment dispersion in the coating solvent. All pigment films were then overcoated with a 2 micron thick polycarbonate (GE Lexan) from a toluene solution in order to minimize the risk of sample breakdown at high electric fields.

For time resolved fluorescence measurements light excitation was provided by a synchronously pumped, mode locked dye laser system equipped with a cavity dumper. Excitation wavelength was 590 nm, using 5 ps pulses and a repetition frequency of 20 kHz. Fluorescence was detected by a SPEX 1681 monochromator equipped with a Hamamatsu 3809U microchannel plate photomultiplier tube. Photon counts from the PM tube were processed by an EG&G ORTEC TAC system and accumulated in a PC equipped with a multichannel analyzer board and Edinburgh Instruments software package to control the measurements. Data were taken with a resolution of 6.68 ps per channel at a wavelength corresponding to the maximum detected signal around 840 nm. The detection wavelength was close to the absorption maximum of TiOPc (I), TiOPc (IV), and HOGaPc. Therefore the pigment region close to the ITO electrode was dominating the measured fluorescence, except for x-H_2Pc, which has maximum absorbance around 780 nm. The absorption spectra were in agreement with the literature reported results.[3-7] All experiments were carried out under dry nitrogen.

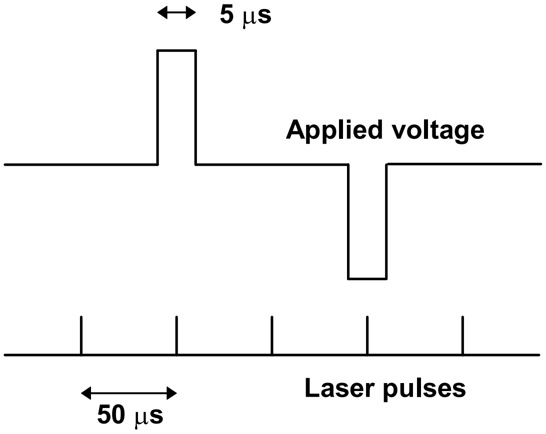

Figure 1. The waveform of the bias applied to the sample together with timing of pulsed laser illumination for time resolved fluorescence quenching measurements.

The time dependence of the sample bias and the timing of laser excitation pulses for time resolved measurements are given in Figure 1. For every applied field, three different decay curves were collected corresponding to positive, negative and zero sample bias for all samples. Positive and negative bias curves were identical for all samples, except x-H_2Pc, and therefore were averaged to a single curve before data analysis. In x-H_2Pc, small differences were observed for different bias polarities, indicating accumulation of space charge in the sample. It appears that during the charge generation process, one carrier is free, while the other becomes trapped and leads to the accumulation of space charge. This accumulation of space charge may be an indication of sensitized carrier generation. The pulse generator supplying the bipolar square wave of up to 400 V was custom built. It used two high voltage FET switches in a differential configuration.[18]

Results and Data Analysis

Integrated Fluorescence Quenching

If a neutral first excited singlet state dissociates into geminate pairs, one would expect that fluorescence quenching will exhibit a quadratic relationship at low fields.[1,19] This is a direct consequence of symmetry. At zero field, the probability of an excited state dissociating into electron-hole pairs oriented in opposite directions will be the same. When an external field is applied, the dissociation rate of a neutral excited state should not depend on the direction of the electric field. Therefore, fluorescence quenching should be an even function of the electric field, hence quadratic in the lowest order. However, if a charge transfer state dissociates into geminate pairs, a linear electric field dependence of fluorescence quenching is expected.[1]

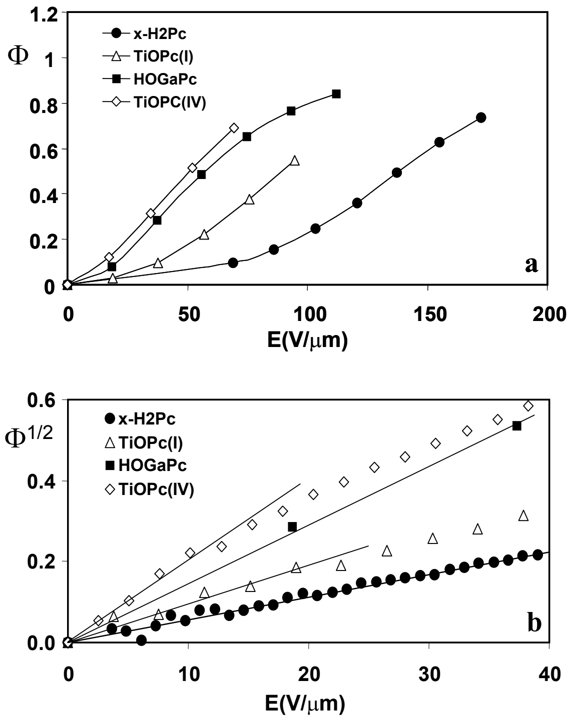

Figure 2. (a) Field dependence of integrated fluorescence quenching, Φ, in various phthalocyanines. (b) Field dependence of $\Phi^{1/2}$ *in various phthalocyanines.*

Figure 2a and 2b depicts the electric field dependence of integrated fluorescence quenching, Φ, in TiOPc(I), HOGaPc(V), x-H_2Pc and TiOPc(IV). As can be observed from figures 2a and 2b all of the phthalocyanines studied exhibit a quadratic dependence of fluorescence quenching at low fields. This similarity in field dependence for the different phthalocyanines indicates a certain amount of commonality in the carrier generation processes of these materials. As discussed previously, the quadratic dependence of fluorescence quenching on electric field indicates, the excited state, which dissociates into geminate pairs, is neutral rather than a charge transfer state.

Time Resolved Fluorescence Quenching

The time resolved fluorescence quenching experiments consistently showed both rate and amplitude quenching by the electric field. However, the degree of field dependence varied significantly between the phthalocyanines. Time resolved fluorescence decay curves were recorded for different electric fields for all the phthalocyanines. An example of time resolved fluorescence decay curves recorded at an applied field of zero field and 112 V/μm for HOGaPc is given in Figure 3. The experimental curves were fit to a sum of two exponentials,

$$I_f(t) = B_1\exp(-t/\tau_1) + B_2\exp(-t/\tau_2). \qquad (1)$$

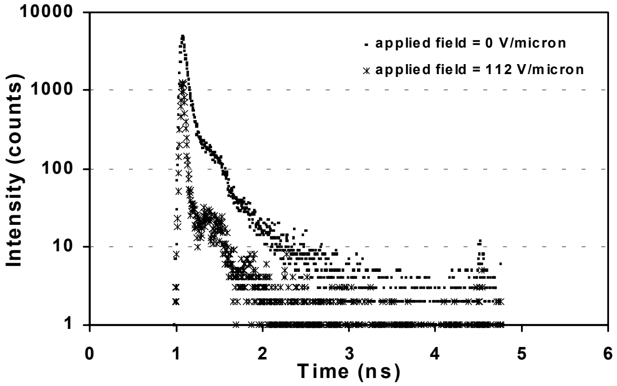

Figure 3. Time resolved fluorescence decay curves for HOGaPc recorded at an applied electric field of 0 V/μm and 112 V/μm.

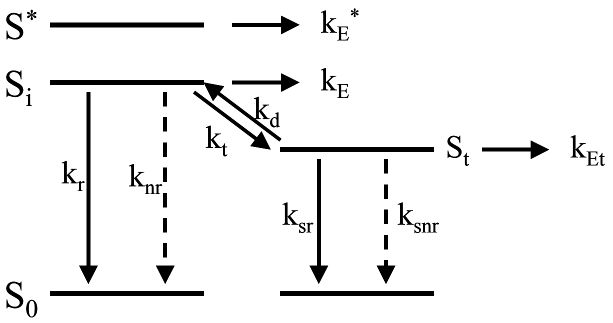

Figure 4. A schematic diagram of the carrier generation model. S_0 *represent the ground state,* S_i *represents the first excited intrinsic state,* S^* *represents a precursor to the first excited state such as a vibrationally, non-relaxed excited state, and* S_t *represents the trapped state. Broken lines represent radiationless transitions.* k_r *and* k_{sr} *are the rate constants for radiative decay for the intrinsic state and the trapped state respectively.* k_{nr} *and* k_{nsr} *are the rate constants for non-radiative decay for the intrinsic state and the trapped state respectively.* k_E , k_E*, *and* k_{Et} *are rate constants for carrier production.* k_d *and* k_t *are the rate constants for the energy transfer process between the first excited intrinsic state and the trapped state.*

Since the integrated fluorescence measurements for all the phthalocyanines studied exhibited a quadratic dependence at low fields, we will use the model of carrier generation given in Figure 4. This model was found to be consistent with all of our experimental results. In the figure, S_i represents the first excited intrinsic (host) singlet state, S^* represents a precursor to the first excited state such as vibrationally, non-relaxed excited state, and S_t represents the trapped (guest) state. The various rate constants are defined in the figure caption. As can be observed from

Figure 3, the time resolved fluorescence curve is composed of a fast component and a slow component. The fast component corresponds to fluorescence from the intrinsic (host) state, while the slow component corresponds to fluorescence from the trapped (guest) state. Since, the trapped state is vacant at time zero and must be populated by the intrinsic state, with a rate constant k_t, Equation 1 should be rearranged and expressed as,

$$I_f(t) = (B_1 + B_2)\exp(-k_1t) + B_2[\exp(-k_2t) - \exp(-k_1t)], \qquad (2)$$

where $k_1=1/\tau_1$ and $k_2=1/\tau_2$.

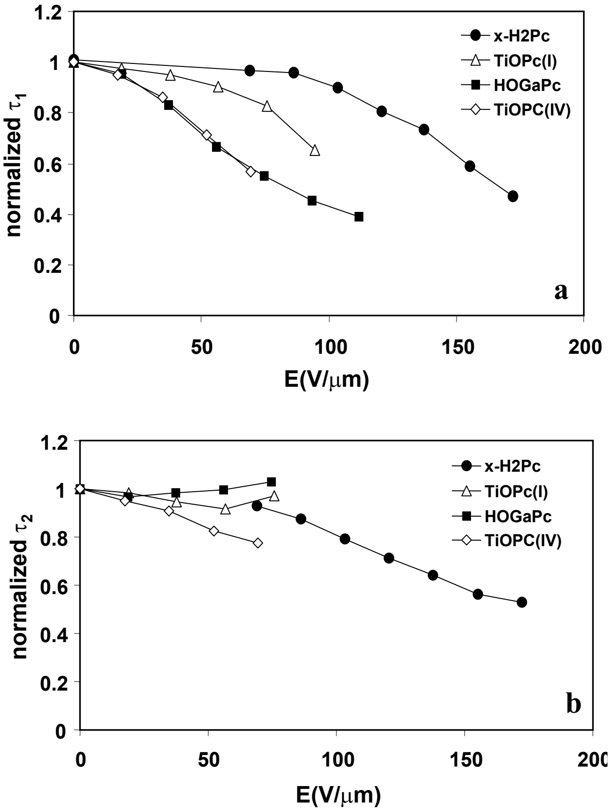

Figure 5. Electric field dependence of lifetimes for the fast component of fluorescence decay (a) and the slow component of fluorescence decay (b).

According to Equation 2, (B_1+B_2) and B_2 represent the amplitudes of the fast and slow components of the fluorescence decay, respectively and τ_1 and τ_2 represent the lifetimes of the fast and slow components of the fluorescence decay, respectively. With reference to terminology, the terms fast, intrinsic and host are equivalent, while the terms slow, trapped and guest are equivalent. Time resolved fluorescence spectra recorded at longer times are slightly red shifted with respect to spectra recorded at shorter times. This is consistent with the existence, as presented in the model, of a trapped state with lower energy that the intrinsic state.

Figure 5a and 5b depict the field dependence of the lifetime of the fast component and the slow component of the fluorescence decay respectively. The lifetime of the fast component of the fluorescence decay, Figure 5a, is clearly field dependent for all of the phthalocyanines studied, however the degree of field dependence varies between the samples. HOGaPc and TiOPc(IV) exhibit strong field dependence even at low fields, while x-H_2Pc is only significantly field dependent at higher fields. In fact, the lifetime of the fast component of the fluorescence decay for x-H_2Pc does not significantly change until ~100 V/micron. TiOPc (I) possesses intermediate field dependence. The rate or lifetime quenching of the fast component of fluorescence decay observed for HOGaPc, TiOPc (I) and TiOPc(IV) indicate the first excited state, S_i in Figure 4, is quenched by the electric field and therefore contributes to photogenerated charge carriers. While in the case of x-H_2Pc, the first excited state is only significantly quenched at high electric fields and therefore only significantly contributes to photogenerated charge carriers at higher fields. In x-H_2Pc carrier generation still occurs at lower electric fields, however at a much lower efficiency when compared to the other phthalocyanines.

Figure 5b shows the field dependence of the lifetime of the slow component of fluorescence decay. From the figure it is clear the lifetime of the slow component of fluorescence decay for HOGaPc and TiOPc (I) changes little with electric field (i.e. minimal rate quenching). This suggests the state leading to the slow fluorescence component, the trapped state S_t, is not significantly quenched and therefore does not contribute significantly to photogenerated charge carriers. However, x-H_2Pc does exhibit field dependence, thereby indicating the trapped state does contribute to photogenerated carriers. Figure 5b also indicates that the lifetime of the slow component of the fluorescence decay for TiOPc (IV) is quenched by the electric field. Therefore in the case of TiOPc (IV), the trapped state also leads to photogenerated carriers, however at a lower efficiency than the first excited intrinsic singlet state. For TiOPc (IV) the lifetime of the fast fluorescence component is quenched to ~50% its original value at 75 V/micron, while the lifetime of the slow fluorescence component is quenched to only ~80% of its original value at 75 V/micron. However, the contribution to photogenerated carriers from both trapped and intrinsic states may be a reason TiOPc (IV) is the most sensitive organic photogenerators known.

Figure 6a, 6b and 6c provide information concerning amplitude quenching of the phthalocyanines. Figure 6a depicts the field dependence of the amplitude of the slow component of fluorescence decay corresponding to the fluorescence from the trapped exciton. As can be observed TiOPc (I), TiOPc (IV) and HOGaPc all exhibit significant amplitude quenching at all applied electric fields. This suggests the precursor to the trapped state is quenched by the electric field. Referring to the model in Figure 4, the trapped state is fed by the first excited intrinsic singlet state at a rate constant of k_t. This is consistent with Figure 5a, which clearly demonstrates that the first excited singlet state, S_i, is quenched by the electric field and hence contributes significantly to photogenerated charge carriers. In contrast, x-H_2Pc does not exhibit amplitude quenching of the slow component until much higher fields than the other phthalocyanines, therefore indicating its precursor, the first excited intrinsic singlet state, is not significantly quenched at low fields. This is once again consistent with Figure 5a.

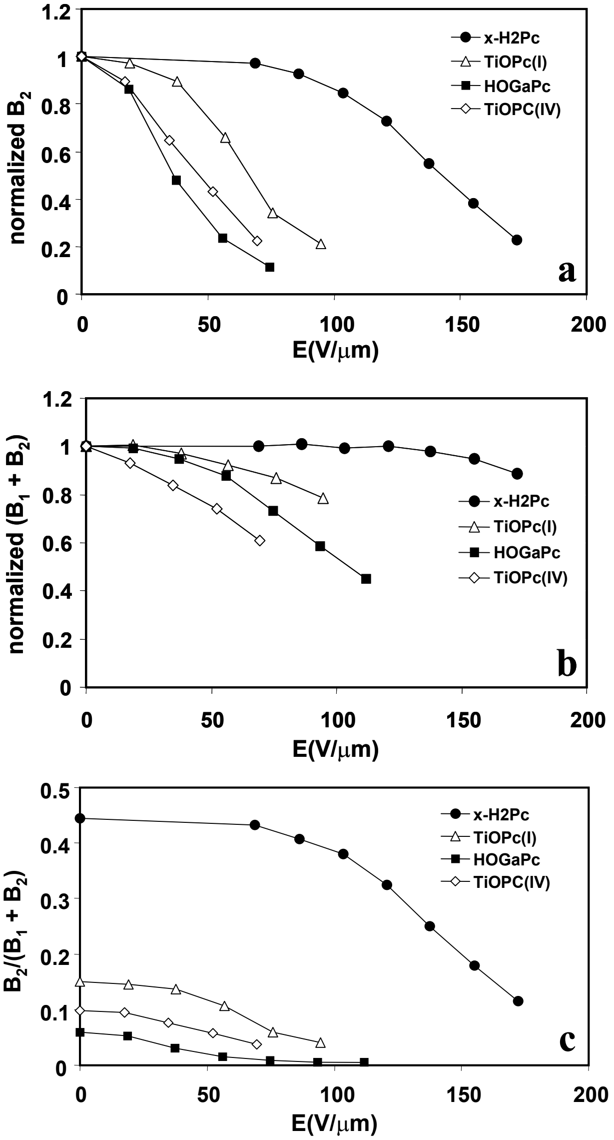

Figure 6. Electric field dependence of amplitudes for the slow component of fluorescence decay (a), the fast component of fluorescence decay (b) and the ratio of the two amplitudes (c).

Figure 6b is a plot of the normalized sum of amplitudes, which as previously mentioned is equivalent to the amplitude of the fast fluorescence component (Equation 2). Amplitude quenching is clearly visible for TiOPc (I), HOGaPc and TiOPc (IV). This indicates the presence of a precursor state, such as a vibrationally, nonrelaxed neutral excited state, S^*, which is quenched by the electric field. However, in contrast no significant amplitude quenching is observed for x-H_2Pc even at high electric fields, such as 150 V/micron. Therefore, the precursor state to the first excited state does not significantly contribute to carrier generation in x-H_2Pc.

Figure 6c illustrates the ratio between the amplitudes of the fast and slow fluorescence components as described by Equation 2. One of the interesting features of this plot is the contrast between the behavior of x-H_2Pc and the other phthalocyanines studied. For TiOPc(I), TiOPc(IV) and HOGaPc the amplitude of the fast fluorescence component is dominant, whereas for x-H_2Pc the slow or trapped component plays a major role.

Discussion

It is worthwhile at this point to summarize the time resolved fluorescence measurements for each of the phthalocyanines studied. HOGaPc, TiOPc (I) and TiOPc (IV) exhibited similar photocarrier generation properties, while x-H_2Pc clearly possesses the most unique mechanism of the four. For HOGaPc, TiOPc(I) and TiOPc (IV) the fast fluorescence component exhibits both amplitude and lifetime quenching. The amplitude quenching indicates that a precursor state, which is quenched by the applied electric field, does exist and hence contributes to carrier generation. The lifetime quenching indicates that the intrinsic excitons are also quenched by the electric field and therefore also produce photogenerated carriers. The precursor to free excitons, which is quenched by electric field, is most likely a vibrationally non-relaxed neutral excited state. The other possible candidate is a charge transfer state, which has been detected in TiOPc near the absorption edge by electroabsorption measurements.[4] However, the first possibility is supported by the quadratic dependence of integrated fluorescence on applied field. As previously mentioned this indicates both the precursor state and the fluorescing state itself are neutral. One distinguishing feature of TiOPc(IV) as compared to TiOPc(I) and HOGaPc, is the contribution to photocarrier generation from the trapped state. This additional contribution may explain the improved sensitivity of TiOPc(IV) as compared to the other pigments.

Of all the pigments studied in this paper, x-H_2Pc possesses the most unique photocarrier generation mechanism. In x-H_2Pc the fast fluorescence component exhibits minimal amplitude quenching and significant lifetime quenching only at high fields. Therefore, the intrinsic excitons only significantly contribute to photogenerated carriers at higher fields. However, the lifetime of the slow fluorescent component exhibits quenching at all applied electric fields, thereby indicating trapped excitons are contributing to photocarrier generation. In x-H_2Pc, the trapped state significantly contributes to the number of photogenerated carriers, particularly when compared to the other phthalocyanines studied. As mentioned above this is an indication that x-H_2Pc possesses at least some bulk sensitized photocarrier generation.

An important fundamental question is what excited state properties govern high carrier generation efficiency in some phthalocyanines. The hypothesis of Yamasaki et al.[20] that it is the proximity in energy and the coupling of the lowest lying charge transfer and neutral excited states is very appealing. The quadratic dependence of fluorescence quenching in many phthalocyanines would indicate that the lowest excited singlet state is neutral and that the charge transfer state is higher in energy. In that case, the field dissociation of the first excited singlet state leads to carrier production possibly through an intermediate charge transfer state.[13]

Conclusions

Analysis of time resolved electric field induced fluorescence quenching measurements clearly show that for HOGaPc, TiOPc(I) and TiOPc (IV) the fast fluorescence component exhibits both amplitude and lifetime quenching. The amplitude quenching indicates a precursor state exists and is quenched by the electric field. The lifetime quenching indicates that the intrinsic excitons are also quenched by the electric field and therefore also contribute to photogenerated carriers. One distinguishing characteristic of TiOPc (IV), when compared to HOGaPc and TiOPc (I), is the contribution to photocarrier generation from the trapped state. Of all the phthalocyanines studied x-H_2Pc possesses the most unique generation mechanism in that the trapped state is an important source of photogenerated carriers. The recorded data indicate that x-H_2Pc possesses some bulk sensitized carrier generation. The quadratic dependence of fluorescence quenching on electric field for all of the phthalocyanines indicates both the precursor state to the first excited singlet state S_1 and S_1 itself are neutral.

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Biography

Zoran D. Popovic received his Ph.D. degree in Materials Science from McMaster University, Hamilton, Ontario, Canada. In the same year he joined Xerox Research Centre of Canada where he presently holds a position of Research Fellow. Dr. Popovic's main research interests are in photoelectronic properties of organic materials, particularly as they relate to xerographic technology and organic electroluminescent devices. He is a member of the IS&T and the American Physical Society.