

ARTICLES

Study of Carrier Generation in Titanyl Phthalocyanine (TiOPc) by Electric-Field-Induced Quenching of Integrated and Time-Resolved Fluorescence

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We have studied the influence of electric field and humidity on photoconductivity and fluorescence in particles of highly photoconductive Y-form TiOPc dispersed in a poly(vinylbutyral) polymer matrix. Both integrated and time-resolved fluorescence quenching by electric field were measured. Integrated fluorescence quenching showed a linear dependence at low applied fields and a linear correlation with carrier generation efficiency. Time-resolved fluorescence decays were analyzed by fitting the data to a sum of two exponentials representing fast and slow fluorescence components. Qualitative features of fluorescence decay were the same for low and high humidity levels. The amplitude and lifetime changes of the two fluorescence components upon the application of the electric field are in agreement with theory which describes energy transfer between free and trapped exciton states. These results indicate that carrier generation in Y-TiOPc originates from both relaxed and nonrelaxed intrinsic excited singlet states, while the trapped excitons do not lead to significant carrier production. The field dependence of integrated fluorescence quenching supports the existence of a carrier precursor state with charge-transfer character.

1. Introduction

There are important fundamental differences in the carrier generation mechanism in crystalline inorganic and organic photoconductors. The process of carrier generation in inorganic crystalline semiconductors involves direct optical excitation of a free electron–hole pair. In these materials, carrier generation efficiency may approach unity and is largely independent of the applied electric field. In amorphous and organic materials carrier generation usually proceeds via an intermediate state. This state generates a geminate electron–hole pair, which, when assisted by an electric field, can subsequently thermally dissociate into free carriers. As a result carrier generation efficiency is strongly field-dependent.

Phthalocyanines represent an important class of organic photoconductors, both as model systems and materials extensively used in organic xerographic photoreceptors. Despite numerous studies, a complete picture of the carrier generation process in this class of materials has still to emerge. Many phthalocyanines appear in several crystalline forms (polymorphs) with distinctly different X-ray diffraction patterns. Different polymorphs of the same molecular materials usually have quite different photoconductive properties. Titanyl phthalocyanine, with a TiO group in the middle of the phthalocyanine ring, also shows polymorphism. Of particular interest is a polymorph with a characteristic X-ray powder diffraction peak at 27.2° which shows quantum efficiencies of carrier generation approaching

unity at high fields. This polymorph is usually referred to as Y-TiOPc.¹ It is significantly more sensitive than other polymorphs containing the same molecule as a building block and will be the object of this study.

Important information on the mechanism of photoconductivity in organic materials has been obtained by electric-field-modulated spectroscopies. The influence of electric field on both optical absorption and fluorescence has been studied in these materials. Electroabsorption measurements have revealed the importance of charge-transfer states in the mechanism of free carrier generation of phthalocyanines.^{2,3} Electric-field-induced fluorescence quenching was studied in solution,⁴ in doped polymer systems,^{5,6} and also in crystalline organic pigments.^{7–10} These measurements, combined with photoconductivity measurements, enable investigation of electronic states participating in the carrier generation process. They thus 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 the photocarrier generation. It was also found that in some phthalocyanines photoconductivity depends strongly on the presence of impurities, for example oxygen^{11,12} and also electron donors and acceptors.¹³

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The perturbative influence of external electric fields on molecular energy levels (Stark effect) is usually quite small.¹⁴ In the subsequent discussion, we will concentrate only on processes that can produce large fluorescence changes. These processes generally involve an intermediate state in which an electron and a 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 potentially can 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; that is, photogenerated carriers and fluorescent first excited singlet states 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; that is, photogenerated carriers and fluorescence both originate from the first excited singlet state. The schematic diagrams of these two mechanisms are shown in Figure 1a,b. 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.^{15,16}

Time-resolved electric-field-induced fluorescence quenching studies have been previously reported for two materials belonging to perylene and phthalocyanine classes. Time-resolved fluorescence experiments on the organic photoconductor *N,N'*-bis(methyl)perylene-3,4,9,10-tetracarboxyl diimide showed multiphasic character, but deconvolution of the data demonstrated that the host (intrinsic) fluorescence was strongly quenched by the electric field by the rate-quenching mechanism and that the mechanism was of the rate-quenching type.¹⁷ It therefore follows that the intrinsic carrier generation process originating from the first excited singlet state did exist in this material. It is reasonable to expect that organic systems other than those containing perylene might also exhibit photoconductivity originating from the first excited singlet state.

A second study on the Y-form of titanyl phthalocyanine confirmed the dissociation by an electric field of the first excited singlet state.¹⁸ In this paper, we will broaden this study and present the results of our investigation on the time-resolved and integrated electric-field-induced fluorescence quenching of Y-TiOPc exposed to different humidities. We have also studied this material previously by electric-field-induced quenching of integrated fluorescence.¹⁹ Both types of measurements will be discussed here to present a consistent picture of the carrier generation process.

2. Experimental Section

Samples were thin film sandwich cells prepared on NESA glass substrates. On top of NESA, a silicon monoxide blocking layer was first sublimed, followed by dip coating of 0.3 μm of Y-TiOPc pigment dispersed at 60 wt % in a poly(vinylbutyral)

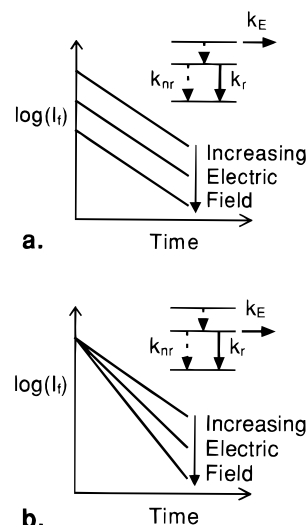


Figure 1. In the amplitude-quenching mechanism (a), the precursor state is affected by the electric field while the fluorescent state itself is not, leading to a decrease of fluorescence amplitude, but not the lifetime. In the rate-quenching mechanism (b), the fluorescent state itself is affected by the electric field while the precursor state is not, leading to a decrease in fluorescence lifetime, but not the amplitude. I_f is the time dependent fluorescence intensity. k_r , k_{nr} , and k_E are the rate constant for radiative decay, radiationless decay, and charge generation, respectively.

matrix. The dipped pigment layer was then overcoated by a second layer of either a 2.5 μm polycarbonate (Lexan) blocking layer or a $\sim 8\text{-}\mu\text{m}$ -thick charge transport layer containing tetraphenylamine (TPD) hole transport molecule.²⁰

For time-resolved measurements, samples with the blocking layer were used. 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 at 868 nm 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. Integrated fluorescence and carrier generation measurements were performed on samples containing a charge transport layer using delayed collection field technique⁸ at 532-nm illumination from a frequency-doubled Nd:YAG laser.

Measurements were performed under 0% and about 42% relative humidity (RH) at room temperature (20 $^{\circ}\text{C}$) under nitrogen atmosphere. The presence of oxygen was found not to influence fluorescence and carrier generation. The time dependence of the sample bias and the timing of laser excitation pulses for time-resolved measurements are given in Figure 2. For every applied field, three different decay curves were collected corresponding to positive, negative, and zero sample bias. Positive and negative bias curves were identical, and were therefore averaged to a single curve before data analysis. 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.¹⁷

3. Experimental Results and Data Analysis

3.1. Integrated Fluorescence and Photoconductivity. Before presenting experimental results, we will first briefly

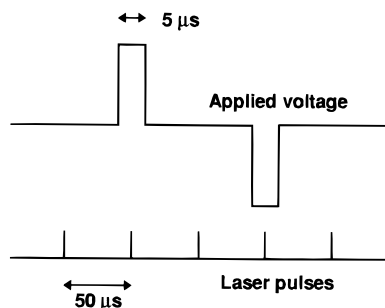


Figure 2. Waveform of the bias applied to the sample together with timing of pulsed laser illumination for time-resolved fluorescence-quenching measurements.

discuss two different frameworks used for interpretation of integrated fluorescence quenching results. These frameworks are simplified and assume the existence of only a single electronic state that leads to fluorescence. We will also define the main experimental quantities measured.

Fluorescence quenching efficiency, Φ , is a measure of the influence of electric field on fluorescence. It is defined as

$$\Phi(E) = [I_f(0) - I_f(E)]/I_f(0) \quad (1)$$

where $I_f(E)$ is integrated fluorescence at field E applied to the sample.

As discussed in the Introduction, fluorescence quenching can occur by two different mechanisms. The fluorescent excited singlet state or its precursor can be quenched by the electric field, resulting in either rate quenching or amplitude quenching, respectively.

The model associated with rate quenching is usually referred to as the internal conversion model.^{9,21} It assumes that the first step in the energy relaxation of the optically generated excited state is relaxation to the first excited singlet state. This state can then either fluoresce or, aided by the electric field, dissociate to form geminate electron-hole pairs with the efficiency $\eta_G(E)$. The relationship between fluorescence quenching and geminate pair yield is⁹

$$\Phi(E) = [\eta_G(E) - \eta_G(0)]/[1 - \eta_G(0)] \quad (2)$$

If the dissociation probability of the geminate electron-hole pairs to form free carriers is $\Omega(E)$, the efficiency of generation of free carriers is given by

$$\eta(E) = \Omega(E) \eta_G(E) \quad (3)$$

At sufficiently high fields we can assume that all geminate pairs will dissociate to form free carriers which means that $\Omega(E) = 1$. Let us introduce the relative photoresponse, R , which is defined as

$$R(E) = \Delta V/I_{\text{light}} \quad (4)$$

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,

$$\eta(E) = CR(E) \quad (5)$$

and by combining eqs 2, 3, and 5 at high fields, we obtain

$$\Phi(E) = CR(E)/[1 - \eta(0)] + 1/[1 - \eta(0)] \quad (6)$$

It therefore follows that at high fields a linear correlation is expected between relative photoresponse and fluorescence

quenching. The slope and intercept of this linear plot determine constant C , which enables rescaling of relative photoresponse, R , to quantum efficiency, η (eq 5).

If a neutral first excited singlet state dissociates into geminate pairs, we would expect that fluorescence quenching will show a quadratic relationship at low fields. This is a straightforward consequence of symmetry. When the electric field is applied, the increase in dissociation probability in the direction of the field is balanced by the decrease of the dissociation probability against the field, leading to cancellation of a linear term in the electric field and consequently quadratic dependence in the lowest order.

If the optical excitation yields a precursor to the first excited singlet state which is quenched by the electric field, we should observe amplitude quenching. The Onsager model of carrier generation²¹⁻²³ is an example of this case. It assumes that optical excitation leads to the creation of geminate electron-hole pairs, which are separated to a finite initial distance r_0 . Aided by the electric field, the geminate pair can either dissociate to form free carriers or recombine. If recombination leads to generation of the fluorescent first excited singlet state, the linear relationship between fluorescence quenching and carrier generation,

$$\Phi(E) = [\eta(E) - \eta(0)]/[1 - \eta(0)] \quad (7)$$

now holds for all fields. In the Onsager model, carrier generation is a linear function of the applied field at low fields.^{21,22} Consequently the field dependence of fluorescence quenching is also expected to be linear. This should be generally the case when the precursor to the first excited singlet state represents a separated electron-hole pair, that is has charge-transfer character.

Linear electric field dependence of fluorescence quenching of charge transfer states and quadratic dependence of neutral states can be shown using a one-dimensional model. Let us assume that a molecule in an excited state is perturbed by an electric field in the $+x$ direction. The total rate constant for dissociation, $k(E)$, will be equal to the sum of the rate constants for dissociation in the $+x$ direction, $k_+(E)$, and $-x$ direction, $k_-(E)$,

$$k(E) = k_+(E) + k_-(E) \quad (8)$$

If the excited state is neutral,

$$k_-(E) = k_+(-E) \quad (9)$$

as charge transfer in the positive and negative directions are equivalent (only the electric field has a different direction with respect to the direction of charge transfer). Expansion of eq 8 in a power series in E then leads to

$$k(E) = 2k_+(0) + [d^2k_+/dE^2]_{E=0}E^2 + \dots \quad (10)$$

where eq 9 leads to a cancellation of terms linear in E . Therefore, a fluorescent neutral excited state will show quadratic dependence of fluorescence quenching on the applied electric field.

Let us now consider a charge-transfer excited state with positive charge displaced in the $+x$ direction. In that case symmetry for charge separation for the positive and negative x direction is broken. Equation 9 will not hold, and the lowest nonzero term in the expansion of eq 8 will be linear in electric field,

$$k(E) = k_+(0) + k_-(0) + [dk_+/dE + dk_-/dE]_{E=0}E + \dots \quad (11)$$

Consequently for a fluorescent charge-transfer state, electric-field-induced fluorescence quenching will be a linear function at low electric fields. In the case where a precursor state to the fluorescent state is quenched by an electric field, the charge transfer or neutral character of the precursor state will determine if the quenching of the amplitude of the fluorescent state is linear or quadratic at low electric fields.

We will now discuss the results of integrated fluorescence quenching measurements. In Figure 3a, the electric field dependence of fluorescence quenching, Φ , in Y-TiOPc is given for two different humidities. Fluorescence quenching is consistently higher for high humidity, and at high fields quenching reaches about 80%. At low electric fields, Φ shows linear dependence for both low and high humidity. This is in contrast with measurement results on a highly photoconductive polymorph of metal-free phthalocyanine (x-H₂Pc) presented in Figure 3b, where the field dependence is clearly quadratic.⁸ Many other phthalocyanines studied also show quadratic dependence of fluorescence quenching at low electric fields. This indicates that Y-TiOPc is different in some way from other phthalocyanines. As discussed previously, the linear dependence of Φ on electric field is consistent with a picture where the precursor charge-transfer state is quenched by the electric field or the fluorescent state itself has charge-transfer character.

In Figure 4a, the correlation between fluorescence quenching and relative photoresponse is shown. The plot is linear with some small deviations at low fields. This linear relationship can be used to rescale the relative photoresponse data to true carrier generation efficiency (eq 5), Figure 4b. As shown, humidity has a significant influence on carrier generation, which increases as humidity increases.

It is also of interest to investigate the changes in the fluorescence spectra due to humidity. Within experimental error, the spectral shape of the fluorescence spectra is humidity-independent, Figure 5.

We also measured the change in fluorescence intensity as a function of humidity, Figure 6. The fluorescence intensity is constant in about 30 min after humidity conditions have changed (Figure 6a), and the process is completely reversible. The reciprocal of relative fluorescence intensity appears to be a linear function of relative humidity (Figure 6b).

3.2. Time-Resolved Fluorescence Quenching. Time-resolved measurements show that electric field influence on fluorescence is more complicated than described previously by the simple models to discuss the results of integrated fluorescence quenching experiments. We found that both lifetimes and amplitudes are affected by the electric field. Time-resolved fluorescence decay curves were recorded for different electric fields at two different humidity levels. The experimental curves were fit to a sum of two exponentials,

$$I_f(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) \quad (12)$$

and gave the goodness-of-fit parameter values, χ^2 , between 1.1 and 1.7. At every applied field, zero-bias data were also taken as explained in the Experimental Section. They were all virtually identical, indicating that the application of an external bias did not perturb the sample significantly. The fitting parameters at different fields and humidities are given in Table 1. They represent averages over nine measurements at 0% RH and seven measurements at 42% RH. Amplitudes for high-humidity decays were scaled to reflect the 45% decrease in the integrated fluorescence.

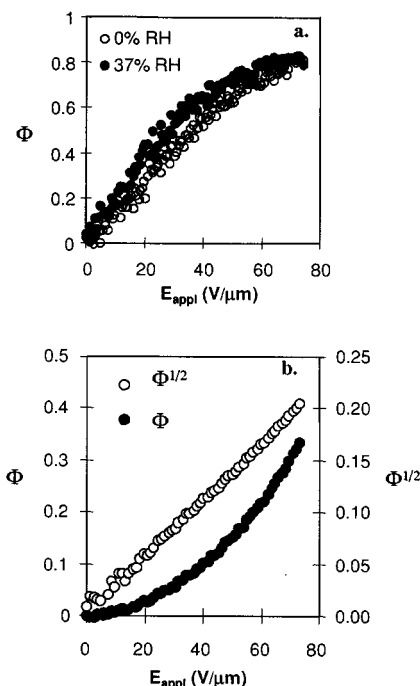


Figure 3. (a) Field dependence of Φ in Y-TiOPc at two different humidities. (b) Field dependence of Φ in x-metal-free phthalocyanine.

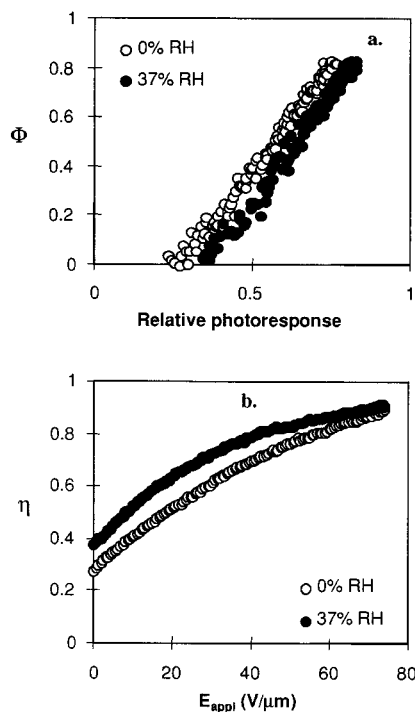


Figure 4. (a) Correlation between fluorescence quenching, Φ , and relative photoresponse, R . (b) Rescaled photoresponse to quantum efficiency, η , as a function of applied electric field.

The relative changes in fluorescence decay parameters with increasing electric field are shown in Table 1 by ratios X_{\max}/X_{\min} and also in Figure 7.

The slow component of fluorescence decay described by parameters τ_2 and B_2 shows significant amplitude quenching, while the lifetime changes little with the applied electric fields. This suggests that the precursor to the excited state leading to the slow fluorescence component must be quenched by the electric field, while this state itself is not significantly quenched and therefore does not contribute significantly to photogenerated charge carriers. It is reasonable to assume that the slow

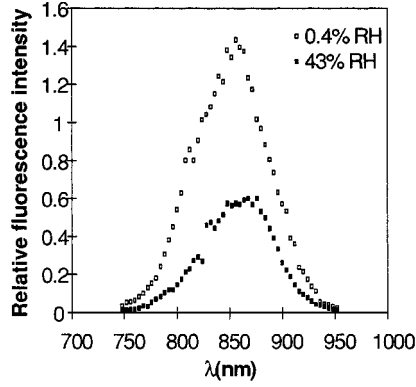


Figure 5. Fluorescence spectra at two different humidity levels. The spectra have not been corrected for the response characteristics of the light detection system.

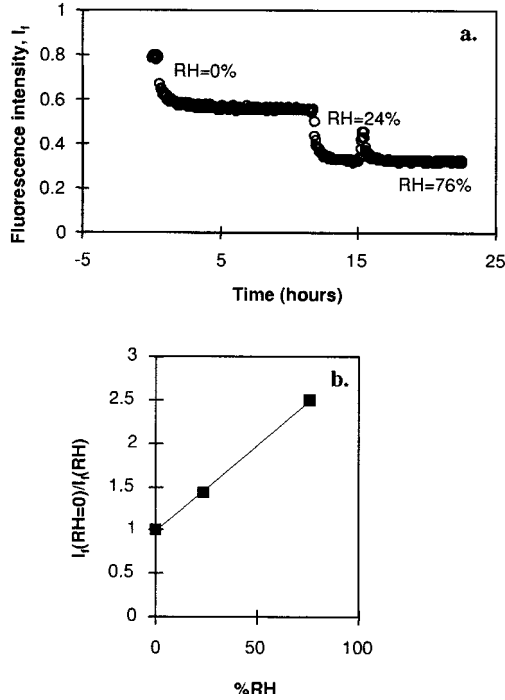


Figure 6. (a) Effect of humidity on fluorescence dynamics. (b) Relative humidity dependence of integrated fluorescence.

fluorescence corresponds to trapped (guest) excitons which are produced by energy transfer from intrinsic (host) excitons. The intrinsic excitons are mobile, and their decay leads to the fast fluorescence component. If this assumption is correct, then the ratio of the trapped, I_t , and intrinsic, I_i , fluorescence intensities should be proportional to the intrinsic exciton lifetime, τ_1 ,²⁴

$$I_t/I_i = \text{const} \times \tau_1 \quad (13)$$

The physical interpretation of eq 13 is straightforward. If intrinsic excitons have very short lifetimes, the trapped fluorescence will approach zero, as there is not enough time for excitons to diffuse and find traps. If intrinsic excitons have very long lifetimes, almost all the excitons will transfer energy to traps, and therefore the trapped exciton fluorescence will be dominant, while intrinsic fluorescence will be close to zero.

The relative intensities of intrinsic and trapped fluorescence can be determined by rewriting eq 12 in the form

$$I_f(t) = (B_1 + B_2) \exp(-t/\tau_1) + B_2[\exp(-t/\tau_2) - \exp(-t/\tau_1)] \quad (14)$$

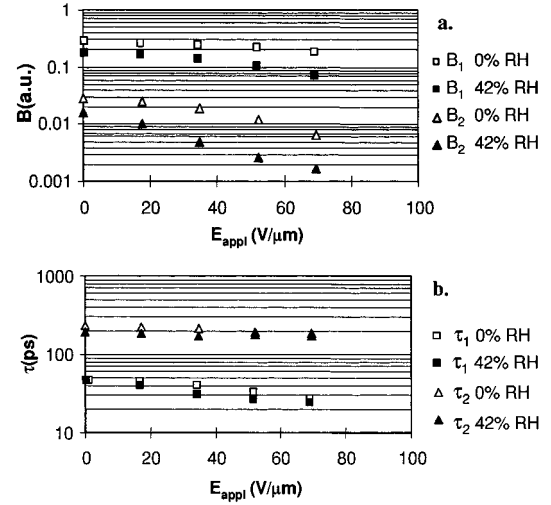


Figure 7. Electric field dependence of amplitudes (a) and lifetimes (b) of the two-exponential fit for different humidities.

TABLE 1: Fitting Parameters for Different Applied Fields

	E_{appl}	τ_1 (ps)	τ_2 (ps)	B_1	B_2
0% RH	0.0	44.79	234	0.262	0.0286
	17.4	42.59	222	0.245	0.0256
	34.8	38.64	213	0.225	0.0185
	52.2	32.00	194	0.203	0.0124
	69.6	25.62	182	0.171	0.0065
$X_{\text{max}}/X_{\text{min}}$		1.75	1.29	1.53	4.42
42% RH	0.0	43.87	196	0.158	0.0163
	17.4	38.07	183	0.150	0.0105
	34.8	29.14	173	0.128	0.0049
	52.2	24.76	175	0.097	0.0025
	69.6	23.63	168	0.065	0.0016
$X_{\text{max}}/X_{\text{min}}$		1.86	1.16	2.43	9.98

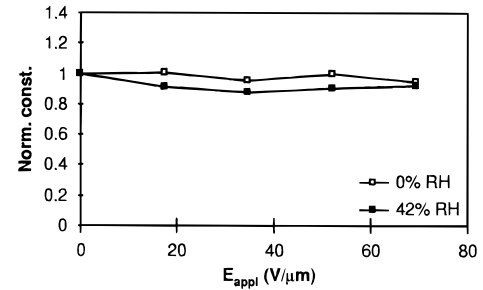


Figure 8. Ratio given by eq 17 as a function of the electric field.

Under the assumption of energy transfer from the short-lived to long-lived state, the second (slow) fluorescence component must show a rise time corresponding to the decay of the first (fast) component. Integration over time gives the relative fluorescence intensities of the intrinsic and trapped fluorescence,

$$I_i = (B_1 + B_2)\tau_1 \quad (15)$$

$$I_t = B_2(\tau_2 - \tau_1) \quad (16)$$

Combining eqs 13, 15, and 16 yields the ratio

$$I_t/(I_i\tau_1) = B_2(\tau_2 - \tau_1)/[(B_1 + B_2)\tau_1\tau_2] = \text{const} \quad (17)$$

which should be independent of the field applied to the sample. In Figure 8, the calculated ratio is plotted against the applied field. The ratio remains constant within 10%, while the amplitudes and lifetimes change significantly. For example, B_2 changes by a factor of 5–10 depending on humidity (see also Table 1). This result is therefore consistent with the

assumption that the fast fluorescence component corresponds to fluorescence decay of free mobile excitons and the slow component corresponds to the decay of trapped excitons.

4. Discussion

The fast fluorescence component exhibits both amplitude and lifetime quenching. The amplitude quenching indicates that 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 produce photogenerated carriers. The precursor to free excitons that is quenched by the electric field could be a vibrationally nonrelaxed neutral excited state. The other possible candidate is a charge-transfer state that has been detected in TiOPc near the absorption edge by electroabsorption measurements.^{2,3} The second possibility is also supported by the integrated fluorescence quenching dependence on applied field, which is linear at low fields and therefore indicates that either the precursor state or the fluorescing state itself or even perhaps both of these states have charge-transfer character.

It is interesting to compare our results with recent pulsed picosecond laser measurements on Y-TiOPc by Gulbinas et al.²⁵ Using samples similar to ours, they measured the dynamics of electrical response and fluorescence as a function of the time delay between two picosecond pulses with sufficient intensity to produce singlet-singlet exciton annihilation events. From their measurements, they concluded that the state that is a precursor to photogenerated carriers has a very short lifetime, on the order of a 1 ps or less, while the fluorescence lifetime was much longer (about 100 ps). The results presented in this paper also indicate the existence of a carrier precursor state with a short lifetime, which leads to the appearance of amplitude quenching in our experiments. However, our results also indicate that a second state with a lifetime of about 40 ps also participates in the carrier generation process. While Gulbinas et al. did observe a fluorescence component with a longer lifetime, they concluded that this state did not contribute to carrier production. We believe that their experiments, which operate in a highly nonlinear regime, at light levels that produce space-charge-limited conditions in their samples, may be suppressing the observation of the slower component in the photocarrier generation process.

Our results are also in good qualitative agreement with the interpretation of Yamasaki et al.³ on electroabsorption and carrier generation efficiency data for a related highly photosensitive series of compounds based on gallium phthalocyanine. They propose that a CT state, to which a higher excited state decays, is both fluorescent and a charge carrier precursor. Our results show clearly that in TiOPc a carrier precursor has charge-transfer character, which is reflected in a linear dependence of fluorescence quenching on the applied field. Our measurements, however, indicate the existence of two precursor states: one with a very short lifetime that does not give measurable fluorescence and the other that gives rise to the dominant fluorescence component. In our previous publications, we have assumed that fluorescence originates from singlet excitons that do not have charge-transfer character.^{19,26} In view of the work of Yamasaki et al.³ and Gulbinas et al.,²⁵ combined with the results presented in this paper, it appears possible that charge-transfer and fluorescent states are one and the same. It should be possible to elucidate the exact nature of the fluorescent states by measuring the wavelength dependence of fluorescence spectral shape changes as a function of the applied electric field (analogous to electroabsorption experiments). We have at-

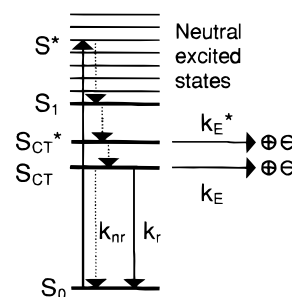


Figure 9. Schematic diagram of the carrier generation model in Y-TiOPc. Excited charge transfer states are denoted with subscript CT. Nonrelaxed states are denoted by an asterisk (*). Broken lines represent radiationless transitions. k_r is the rate constant for radiative decay, and k_E and k_{E^*} are rate constants for carrier production. The process of energy transfer from S_{CT} to the trapped exciton has been omitted for clarity.

tempted these experiments, but the accuracy of our measurements was not sufficient to detect spectral shape changes induced by the electric field. One of the problems is that the signal is dominated by uniform fluorescence quenching across the whole emission band.

Another signature of a fluorescent CT state would be a linear dependence of lifetime on the electric field. Although our results show some scatter, it appears that both the amplitude and the lifetime of the fast fluorescence component have linear dependences at low fields (Table 1). This indicates that both the short-lived precursor and the longer lived fluorescent state have charge-transfer character. This model of carrier generation, Figure 9, is also similar to, but not identical with, the model proposed by Yamasaki et al.³

The role of water is very interesting. High-humidity conditions lead primarily to a reduction in the amplitude of the fast and slow fluorescence components, whereas the lifetimes, particularly τ_1 , are much less affected (Table 1). This indicates that water molecules interact primarily with the short-lived precursor state, leading partially to carrier production. This is reflected in increased carrier generation efficiency at high humidities, as is observed experimentally (Figure 4b) and is also consistent with humidity-independent shape of fluorescence spectra (Figure 5). Why water interacts primarily with the precursor state is not clear. One possibility may be that the precursor state has a larger dipole moment than the fluorescent state and therefore interacts more strongly with water. Clarification of the role of water in Y-TiOPc and the exact mechanism of water sensitization of carrier generation will require additional studies. Any explanation will also have to take into account that Y-TiOPc has tightly bound water as a part of its structure and also contains a weakly bound water, which is affected by relative humidity.¹

An important fundamental question is what excited-state properties govern high carrier generation efficiency in some phthalocyanines. The hypothesis of Yamasaki et al.³ 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 then indicate that the lowest excited singlet state is neutral and that the CT 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 CT state.⁹ In Y-TiOPc, on the other hand, it may be that the CT state has lower energy than the neutral states. In that case, the precursor to both fluorescence and photogenerated carriers is a CT state itself.³ This would naturally explain both linear

dependence of fluorescence quenching on the applied electric field and higher efficiency of carrier generation in Y-TiOPc compared to other phthalocyanines.

5. Conclusions

Analysis of time-resolved electric-field-induced fluorescence quenching measurements shows clearly that in Y-type TiOPc pigment the intrinsic (host) fluorescence is strongly quenched by the electric field and that the mechanism involves both amplitude quenching and rate quenching. It therefore follows that the intrinsic carrier generation process originating from the first excited singlet state does occur in this material and also that the intrinsic exciton has a precursor, most likely a charge-transfer state, which is quenched by the electric field and therefore produces carriers. The lowest excited singlet state that leads to fluorescence may itself also have charge-transfer character. Water appears to be a sensitizer for carrier generation through a predominant interaction with the precursor state. The present work strongly supports the idea that relative position of neutral and CT excited states is a primary determinant of high carrier generation efficiency. When the CT state is close to or below the lowest lying neutral excited singlet state, high carrier generation efficiencies are observed. The present work also proposes a general methodology, based on time-resolved fluorescence quenching measurements, to determine neutral or charge-transfer character of different states involved in carrier generation. Linear dependence, at low fields, of a lifetime or amplitude indicates that the state itself or its precursor, respectively, have charge-transfer character. Quadratic dependence, on the other hand, is an indication of a neutral state. In our future work we hope to measure time-resolved fluorescence quenching at low applied fields in different materials and determine the character of different states involved in carrier generation.

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