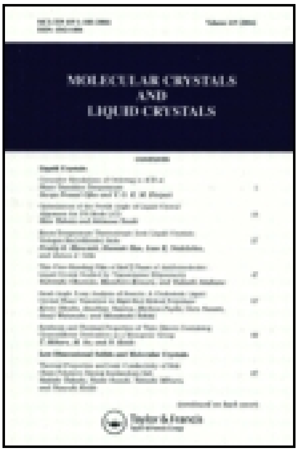

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PHOTOCONDUCTIVITY STUDIES OF TITANYL PHTHALOCYANINE

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Abstract

Recently, a new polymorph of TiOPc with characteristic XRD peaks at $2\theta = 9.5$ and 27.3° has been identified as having a quantum efficiency of carrier generation in the infrared approaching unity. In this paper, we will discuss the use of electric field induced fluorescence quenching technique in investigating the photoconductivity of this highly sensitive form of TiOPc. Linear correlation found between electric field induced fluorescence quenching and carrier generation in this material indicates that the photogeneration involves the field assisted dissociation of the first excited singlet state which is typical of other phthalocyanines. However, the highly sensitive TiOPc exhibits a smaller overall field dependence of carrier generation and an efficient carrier generation is "switched on" at much lower applied fields. Furthermore photoconductive and fluorescence responses are humidity dependent indicating that water plays an important role in the photogeneration processes.

INTRODUCTION

Infrared sensitive phthalocyanines (Pc's) have been extensively studied for their applications in electrophotography[1]. Pc's can usually exist as several polymorphs with different crystalline packing structures which have greatly different photoelectrical properties.[2] The objective of this work is to study the carrier generation mechanism in a recently discovered[3a] highly sensitive TiOPc by using electric field induced fluorescence quenching and delayed collection field photoconductivity techniques.[4-7] The present paper expands our previous work on this material[8] to include the influence of water. We will also compare the results obtained with those previously established for other Pc's.

EXPERIMENTAL

The highly sensitive TiOPc polymorph was synthesized as described in Reference 8. Conventional dual-layer photoreceptor devices consisting of a thin generator layer and a thick transport layer were used in this work. The devices had the following configuration: aluminized Mylar / 1 µm Nylon / 0.5 µm 50 wt% TiOPc : polyvinyl butyral / 20 µm 35 wt% TPD hole transport molecule[9] : polycarbonate. Measurements were performed in a sandwich cell configuration with NESA glass as a top electrode, pressed on the sample surface. Good pressure contact was assured by measuring cell capacitance which was equal to the value deduced from the cell thickness measurements. Photoexcitation was accomplished by 580 nm, 5 ns dye laser pulses.

Simultaneous detection of the photoinduced electrical response by a delayed collection field technique and electric field induced fluorescence quenching was performed as described in detail previously[4,5]. The magnitude of the collection field (20 V/μm) was determined from the onset of saturation of zero field photoconductive response as the collection field is increased. The environment of the photoconductivity cell was controlled by exposing it to ambient atmosphere, purging it with dry nitrogen or air, or with nitrogen containing water vapor at the desired relative humidity (RH). All experiments were conducted at room temperature.

RESULTS AND DISCUSSION

Relative photoresponse was determined as

$$R = \frac{\Delta V}{I_{excit}}, \tag{1}$$

where ΔV is the light pulse induced voltage drop on the sample and I_{excit} is the pulsed excitation light intensity. The fluorescence quenching efficiency is defined as:

$$\Phi(E) = \frac{I_f(0) - I_f(E)}{I_f(0)}, \tag{2}$$

where $I_f(E)$ is the fluorescence signal normalized to the incident laser pulse intensity at the electric field E applied to the sample. According to the kinetic scheme presented in Figure 1, $\Phi(E)$ is connected to the efficiency of the charge-transfer (CT) state (geminate electron-hole pair) formation, $\eta_{CT}(E)$, through the relation

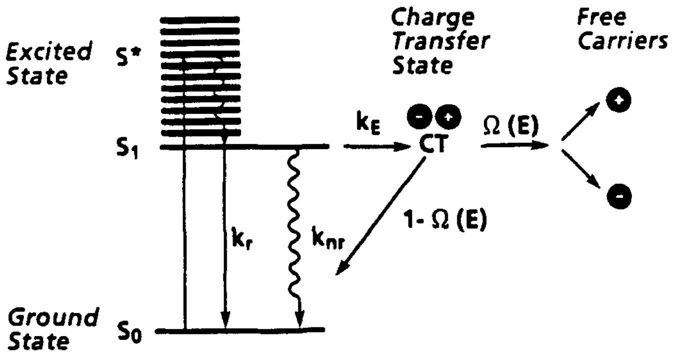


FIGURE 1 Model for carrier generation from the first excited singlet state. k_r, k_{nr}, and k_E are the rate constants for radiative decay, radiationless relaxation, and formation of charge-transfer (CT) state respectively. $\Omega(E)$ is the field dependent probability for dissociation of the CT state into free carriers.

$$\Phi(E) = \frac{\eta_{CT}(E) - \eta_{CT}(0)}{1 - \eta_{CT}(0)} . \tag{3}$$

The carrier generation efficiency is given by

$$\eta(E) = \eta_{CT}(E)\cdot\Omega(E), \tag{4}$$

where $\Omega(E)$ is the probability that the CT dissociates into free carriers. At high fields $\Omega(E) = 1$ and a linear correlation is expected between fluorescence quenching and carrier generation. Carrier generation is proportional to the relative photoresponse

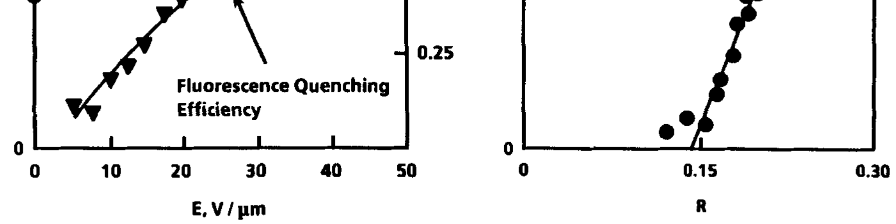
$$\eta(E) = C\cdot R(E), \tag{5}$$

and at high field we can write

$$\Phi(E) = \frac{C}{1 - \eta_{CT}(0)} R(E) - \frac{\eta_{CT}(0)}{1 - \eta_{CT}(0)} . \tag{6}$$

If we now fit a straight line to a plot of Φ as a function of R, from the intercept and the slope one can obtain both the proportionality constant C and $\eta_{CT}(0)$. Using equation (5), the true quantum efficiency $\eta(E)$ is then calculated.

The field dependence of photoresponse, R, and the electric field induced fluorescence quenching, Φ, on the applied field at 50% RH is shown in Figure 2a. Using Equation (6) the scaling factor C is determined from the linear fit of Φ vs R, as shown in Figure 2b. C is used to scale R to the true



(a) (b)

FIGURE 2 (a) The field dependence of carrier generation efficiency (●) and fluorescence quenching (▼) at 50% RH. (b) Plot of fluorescence quenching vs. photoresponse at 50% RH.

quantum efficiency, η, which is marked on the right-hand vertical axis in Figure 2a. The carrier generation efficiency is very high and weakly field dependent. Even at zero applied field, an estimated generation efficiency of 0.40 was observed which is 3 to 4 times larger than the values previously measured for H_2Pc [4,5], and ClInPc [6].

The fluorescence quenching efficiency, Φ, in Figure 2a monotonically increases as the electric field is increased. A 60% of quenching was observed at 40V/μm which again differentiates TiOPc from other phthalocyanines[4,5,6] where the same magnitude of quenching occurred at much higher applied fields in the range of 100 to 150 V/μm.

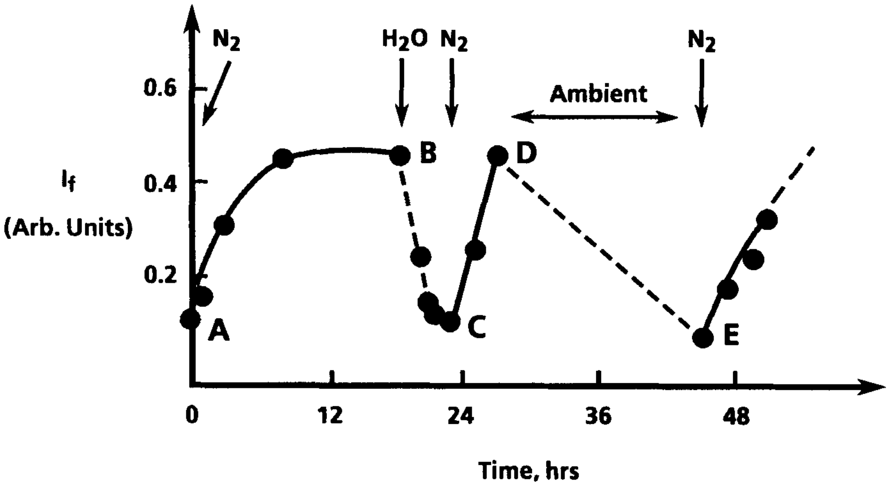
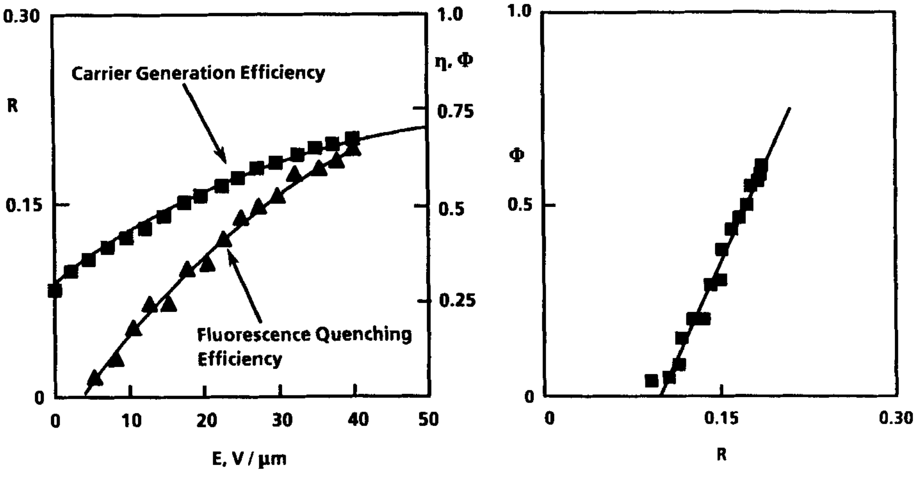


FIGURE 3 Effect of relative humidity on fluorescence intensity, I_f.

The fluorescence intensity of TiOPc photoreceptor devices was found to vary with the relative humidity of its surrounding atmosphere as shown in Figure 3. By replacing dry nitrogen gas with dry air, identical results were observed indicating that oxygen in the ambient atmosphere does not participate in the fluorescence quenching. A 70% reduction in fluorescence intensity is observed as the relative humidity changes from zero to 50%. Films containing only a TiOPc generator layer without the TPD transport layer also exhibited a similar trend like a full photoreceptor device. Hence TPD molecules do not participate in the fluorescence quenching of TiOPc.

The pulsed photoconductivity and electric field-induced fluorescence quenching measurements at 0% RH are shown in Figure 4a. The carrier generation had generally dropped as compared to the curve in Figure 2a obtained at RH of 50%. The overall field dependence behavior remained unaffected. The field dependence of fluorescence quenching curve at zero RH in Figure 4a is identical, within experimental error, to fluorescence quenching at 50% RH shown in Figure 2a. As before, the linear fit of the fluorescence quenching vs. generation plot in Figure 4b, gives the scaling factor C for quantum efficiency. The zero field generation efficiency at zero RH had a value of 0.27 which is about 30% less than the value observed at higher RH. The field dependencies of both carrier generation efficiency and fluorescence quenching were not affected by changing RH, which suggests that the photogeneration mechanism remains basically unaffected by RH. The role of extra adsorbed water molecules appears simply to increase somewhat the zero field carrier generation. A large 70% reduction in fluorescence intensity induced by RH change from 0% to 50% is accompanied only by a relatively small absolute change of 0.13 of the carrier generation efficiency.



(a) (b)

FIGURE 4 (a) The field dependence of carrier generation efficiency (■) and fluorescence quenching (▲) at 0% RH. (b) Plot of fluorescence quenching vs. photoresponse at 0% RH.

It has been reported[3b] that a dramatic reduction in photoconductivity of TiOPc is accomplished by removing water molecules under a vacuum of 10^{-6} torr at 140°C. A carefully annealed TiOPc surface cell showed a very large, 98%, drop in photoconductivity after being heated to 140°C in vacuum. The photoconductivity could be partially recovered by exposure to water vapour. It was also determined that, as prepared, TiOPc contains as much as 0.7 moles of water per mole of TiOPc. It is not clear at present if this water is incorporated into the crystal lattice or only adsorbed on the surface of small TiOPc particles. Since our sample had not been subjected to such severe conditions, in the subsequent discussion we will assume that change of RH affects only water adsorbed on the pigment surface. The large observed fluorescence quenching by water of 70% then implies that most observed fluorescence originates from excitons which have migrated to and were trapped at the pigment surface. This appears reasonable as the size of TiOPc pigment particles is about 500 A to 1000 A. The fact that the zero field carrier generation efficiency increases somewhat suggests that water induced fluorescence quenching can also lead to carrier production. One possible model explaining the weak dependence of photogeneration and electric field induced fluorescence quenching on RH involves the assumption that carriers are generated by dissociation of excitons in the pigment bulk as they diffuse to the surface, but that the observed fluorescence originates from excitons trapped at the surface which are not influenced by the electric field. The consequence of this model is that field induced portion of carrier generation should be RH independent. This is indeed observed as increment in carrier generation efficiency as electric field changes from zero to 40 V/μm is about 0.36 for both 0% and 50% RH (Figs. 2a and 4a).

The model described above is consistent with Fig. 1 if one interprets k_r as an effective rate constant for exciton diffusion and trapping on the particle surface. To measure fluorescence quenching it is only important that surface trapped excitons have a detectable fluorescence.

CONCLUSION

The highly photosensitive TiOPc polymorph shows an excellent correlation between electric field induced fluorescence quenching and carrier generation. The photogeneration involves the field assisted dissociation of singlet excitons which is similar to other phthalocyanines. Reversibly adsorbed water molecules increase the photogeneration efficiency and at the same time reduce fluorescence intensity. The large magnitude of water induced fluorescence quenching accompanied by a relatively small change in photogeneration efficiency and no observable change in field induced fluorescence quenching can be explained by assuming bulk carrier generation and fluorescence originating from excitons which have diffused to the particle surface. This model, however, is highly speculative at this time and we are planning further experiments to explore its validity.

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