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Extrinsic Carrier Photogeneration in Organic Pigments Based on Electric-Field Induced Fluorescence Quenching Measurements

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Extrinsic carrier photogeneration in perylene pigment was studied by means of the electric field-induced fluorescence quenching. Perylene pigment mixed with small amount of phthalocyanine exhibited the effective enhancement of carrier generation efficiency together with decreasing field-induced fluorescence quenching, contrary to the expectation that both should be enlarged owing to the competitive relation between carrier generation and carrier recombination entailing fluorescence. The model assuming the existence of another efficient channel to photogenerate geminate ion pairs through perylene/phthalocyanine molecular contacts, solved this intriguing result reasonably.

Carrier photogeneration in organic photoconductors is a key process for photoelectronic devices such as organic solar cells and electrophotographic photoreceptors. Since carrier generation and geminate recombination accompanying with fluorescence are closely linked to each other, the electric field-induced fluorescence quenching has been regarded as a powerful tool to study the carrier generation mechanism of organic photoconductors. The resultant complicated behavior of the field-induced fluorescence quenching measurements was interpreted based on original or modified Onsager model,1) which has been widely accepted for the charge photogeneration in organic materials. Yokoyama et al.2—5) measured the field-induced quenching of exciplex fluorescence of acceptor-doped poly(*N*-vinylcarbazole) and proposed the extrinsic carrier photogeneration mechanism. Popovic et al.6—9) applied this method to organic pigments like phthalocyanines and proposed the internal conversion mechanism of carrier generation.7,9)

In the researches of organic solar cell, a recent breakthrough was an all-organic p–n junction cell consisting of p-type phthalocyanine and n-type perylene pigments, which exhibited a large photocurrent of the order of milliamperes under air mass 2 solar illumination.10) Afterward, we found that three-layered cells, having an interlayer of codeposited perylene (Me-PTC) and metal-free phthalocyanine (H_2Pc) pigments sandwiched between the respective pigment layers, showed much larger photocurrent compared to two-layered cells.11,12) This photocurrent enhancement in the codeposited film was revealed to be clearly attributed to the sensitization of carrier generation by measuring microwave photoconductivity which is basically free from the carrier transport process.13) Moreover, only monolayer-like coverage of deposited H_2Pc on Me-PTC was found to increase the carrier generation efficiency of Me-PTC drastically. In a similar experiment where monolayer-like Me-PTC was inversely deposited on H_2Pc layer, the carrier generation efficiency of H_2Pc film also increased.12) These observations strongly suggest that the intermolecular contact between perylene and phthalocyanine plays an important role in charge carrier photogeneration. In this sense, it is of great interest to clarify this type of extrinsic carrier generation mechanism in mixed organic pigments by means of electric field-induced fluorescence quenching.

In this paper, we would like to report the electric field-induced fluorescence quenching of Me-PTC pigment dispersed in polymer matrix. By adding H_2Pc pigment, field-induced fluorescence quenching decreased while carrier generation increased. The model assuming an efficient channel of geminate ion pair generation through exciplex between Me-PTC and H_2Pc was proposed.

Experimental

3, 4, 9, 10-Perylenetetracarboxylic 3, 4 : 9, 10-Bis(methylimide) (Me-PTC, Dainichiseika Color & Chemicals Manufacturing Co., Ltd., Fig. 2) and metal-free phthalocyanine (H_2Pc, Tokyo Kasei Co., Ltd.) were purified two times by train sublimation method.14) Pigments were dispersed in the polycarbonate polymer matrix by the following procedure. Me-PTC or Me-PTC/H_2Pc mixture was ball-milled in tetrahydrofuran for 14 h. This slurry was added to 1,2-dichloroethane solution of polycarbonate resin and spread to 2 μm-thick uniform film on indium tin oxide (ITO) glass substrate by spin coating technique. Finally, semitransparent Au electrode was deposited by the vacuum evaporation. Ratio of Me-PTC pigment to polymer binder was kept a constant value of 5 wt%. In the following, added H_2Pc concentration is denoted as [D] defining the weight ratio of H_2Pc with respect to Me-PTC dispersed in the polymer. In some case, instead of H_2Pc, an aromatic amine, *N,N,N′,N′*-tetrakis-(*m*-methylphenyl)-1,3-benzenediamine (PDA, Nihon Jyoryu Co., Ltd.) purified by recrystallization was also mixed with Me-PTC by the same procedure.

The fluorescence of Me-PTC was observed as a probe using a spectrophotofluorometer (Hitachi Ltd., Model 850) equipped with a 150 W Xe lamp as an excitation source. The lock-in amplification technique was applied in order to detect the small modulation of fluorescence intensity. Figure 1 shows the block diagram of the field-induced fluorescence quenching measurements. Square-wave voltage of 75 Hz was applied to the sample with detecting the fluorescence intensity changing with the same frequency by using a lock-

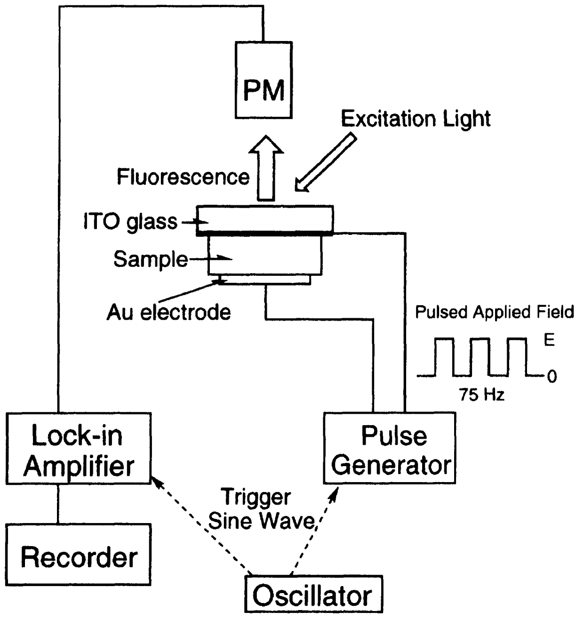

Fig. 1. Block diagram of the field-induced fluorescence quenching measurements. PM denotes the photomultiplier of spectrophotofluorometer.

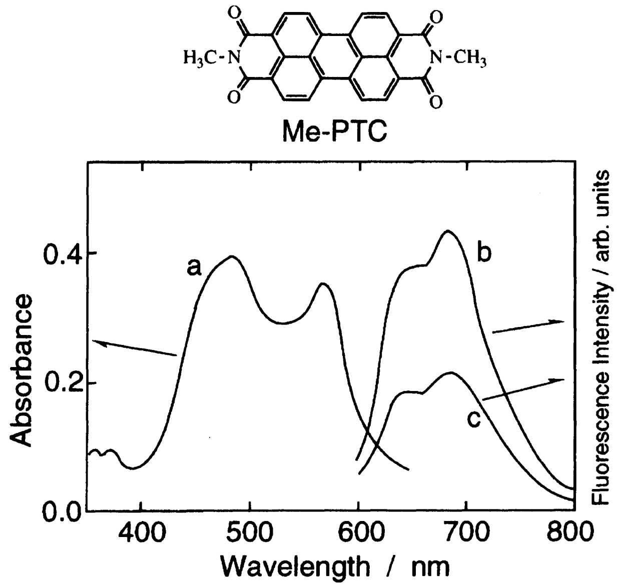

Fig. 2. Chemical formula of perylene pigment (Me-PTC) and absorption and fluorescence spectra. Absorption spectrum (curve a) is for sublimed film of the thickness of 40 nm. Fluorescence spectra are for Me-PTC dispersed in polymer matrix (5 wt%) without (curve b) and with H_2Pc of [D]=0.01 (curve c). Excitation wavelength is 490 nm.

in amplifier (NF Electronic Instruments, 5600A). Measurements were performed at room temperature in air.

Results

Absorption and fluorescence spectra of Me-PTC are shown in Fig. 2. Photoluminescence intensity of Me-PTC dispersed in polymer matrix reduced to a half only by adding H_2Pc of [D]=0.01 (Fig. 2, curves b and c). This seems to be caused by quenching due to the nonradiative exciplex formation between Me-PTC and H_2Pc or by the energy transfer from Me-PTC to H_2Pc since the spectra of absorption of H_2Pc and fluorescence of Me-PTC are considerably overlapped. The scanning electron microscopy observation indicated that larger Me-PTC particles were covered by smaller H_2Pc particles for the ball-milled powder containing both pigments. That is, when Me-PTC and H_2Pc particles are co-dispersed in polymer matrix, there certainly exists a lot of sites so that both pigments contact closely with each other.

Amount of charges photoinduced by 500 nm laser pulse at which less absorption of H_2Pc exists, was estimated from the time integration of transient photocurrent curve[5] under the bias application. Figure 3 shows the dependence of amount of photoinduced charges on applied field (E) for Me-PTC dispersed polycarbonate matrix without (curve a) and with H_2Pc (curve b). Photoinduced charge increased about twice only by adding the small amount of H_2Pc of [D]=0.05. This result clearly shows that carrier generation efficiency of Me-PTC dispersed in polymer matrix is enhanced by H_2Pc as observed in the codeposited film made by vacuum evaporation.[11—13] Namely, direct molecular contacts between H_2Pc and Me-PTC act as efficient carrier generation sites even in the dispersion system as well.

Excitation wavelength dependence of field-induced fluorescence quenching ($\Delta F/F$) for a sample contain-

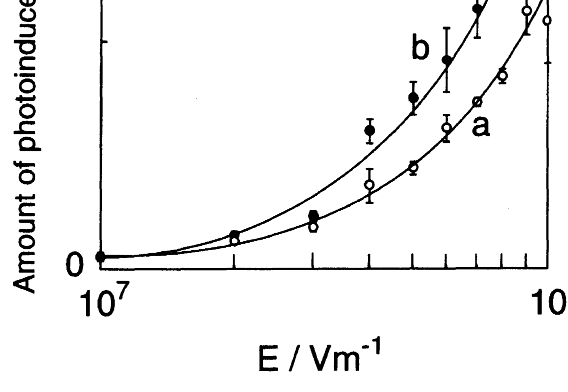

Fig. 3. Applied field (E) dependence of the amount of photoinduced charges by 500 nm laser pulse for Me-PTC dispersed polycarbonate matrix without (curve a) and with H_2Pc of [D]=0.05 (curve b).

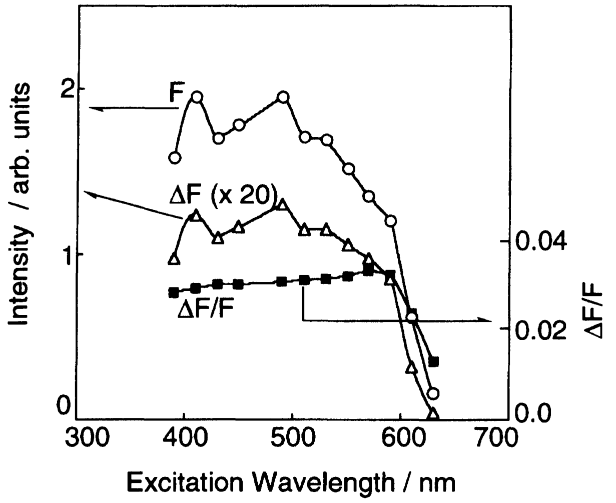

Fig. 4. Excitation wavelength dependence of fluorescence intensity (*F*), electric field-induced decrement (Δ*F*), and Δ*F*/*F* for Me-PTC dispersed in polycarbonate matrix (5 wt%). Observing wavelength is 700 nm. Applied field is 10^8 V m^{-1}.

ing only Me-PTC is shown in Fig. 4. Δ*F*/*F* is obtained from the following Eq. 1.

$$\Delta F/F = (I_f(0) - I_f(E))/I_f(0) \qquad (1)$$

Here, $I_f(0)$ and $I_f(E)$ are the fluorescence intensities without and with applying electric field, *E*, respectively. Fluorescence intensity (*F*) and its decrement (Δ*F*) showed the similar excitation wavelength dependence, hence, resulting in a constant value of Δ*F*/*F* irrespective of excitation wavelength. This means that the carrier photogeneration occurs through the same path independent of the excitation wavelengths, i.e., via vibrationally relaxed S_1 state. Δ*F*/*F* was also independent on excitation wavelengths also for the sample containing both H_2Pc and Me-PTC pigments.

Figure 5 shows the dependence of Δ*F*/*F* on the applied electric field. Δ*F*/*F* increased steeply with applied field. This reflects the strongly field-dependent dissociation probability of geminate ion pair into free carriers as predicted by Onsager model.[2)] Very interestingly, when H_2Pc was added to Me-PTC, Δ*F*/*F* decreased considerably at every applied field. In addition, Δ*F*/*F* is dependent on H_2Pc ratio added, [D], as shown in Fig. 6. Apparently, Δ*F*/*F* decreased rapidly by adding the small amount of H_2Pc below [D]=0.2.

Discussion

In the present system, surprisingly, the enhancement of carrier generation efficiency has been revealed to be accompanied with the decrease of field-induced fluorescence quenching. Because, the field-induced fluorescence quenching ought to increase with increasing the carrier photogeneration efficiency, which is in a competitive relation to carrier recombination entailing fluorescence. We concluded that above contradictory result could hardly be explained only by considering single carrier generation path.

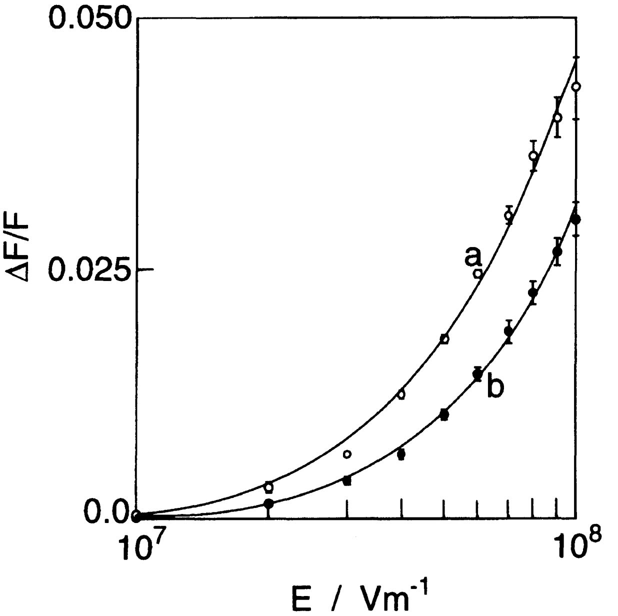

Fig. 5. Dependence of the field-induced fluorescence quenching (Δ*F*/*F*) on applied field (*E*) for Me-PTC dispersed in polycarbonate matrix without (curve a) and with H_2Pc of [D]=1.0 (curve b). Excitation and observing wavelengths are 490 and 700 nm, respectively.

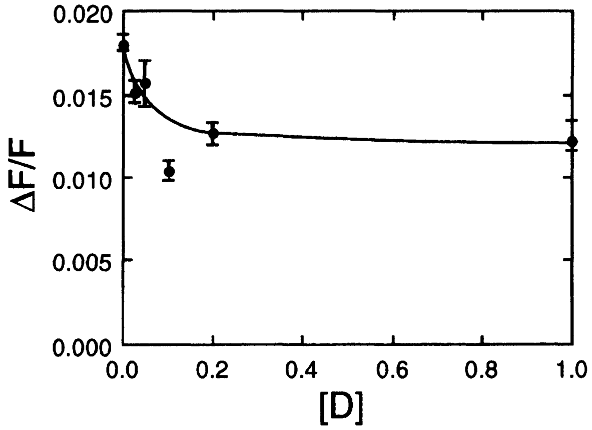

Fig. 6. Dependence of the field-induced fluorescence quenching (Δ*F*/*F*) on H_2Pc ratio added ([D]). Applied field is 5×10^7 V m^{-1}. Excitation and observing wavelengths are 490 and 700 nm, respectively.

The puzzle in the present results was solved assuming the existence of another channel of carrier generation as shown in Fig. 7. Carrier generation process of organic pigment involves a precursor, namely, a charge transfer (CT) state so-called geminate ion pair which dissociates to the free carrier by the field-dependent Onsager's dissociation probability, *P*(*E*). Without H_2Pc, a CT state formed between two adjacent molecules via vibrationally relaxed S_1 state at the field dependent rate constant, *k*(*E*), dissociates to free carrier or decays to

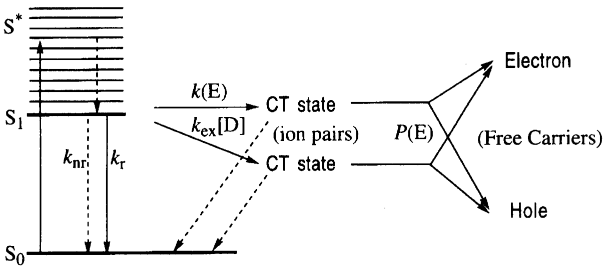

Fig. 7. Proposed carrier generation model having two channels of carrier generation. k_r and k_{nr} denote rate constants of radiative and nonradiative recombination, respectively. $P(E)$ is the Onsager dissociation probability of geminate ion pair. Other abbreviations are explained in the text.

the ground state. This type of carrier generation mechanism, which is consistent with excitation wavelengths independent behaviors of $\Delta F/F$, has been already proposed by Popovic et al.[7,9] In the presence of H_2Pc, i.e., [D], the point is to introduce another channel from relaxed S_1 state to another CT state, formed at Me-PTC/H_2Pc molecular contacts with a field independent rate constant of $k_{ex}[D]$. This new channel can be regarded as extrinsic carrier generation route.

In this model, the $I_f(E)$ is expressed by the following Eq. 2.

$$I_f(E) = I_{exc} \cdot \frac{k_r}{(k_r + k_{nr} + k(E) + k_{ex}[D])} \qquad (2)$$

Here, I_{exc} is the excitation light intensity and k_r and k_{nr} are the rate constants for radiative and nonradiative transitions, respectively. Since $\Delta F/F$ strongly depends on the applied field and nearly zero below 10^7 V m^{-1} as shown in Fig. 5, $k(0)$ is negligible compared to $k(E)$ above 10^7 V m^{-1} in the present model. So, by substituting Eq. 2 for Eq. 1, we obtain Eq. 3 by using the assumption of $k(E) \gg k(0)$.

$$\left(\frac{\Delta F}{F}\right)^{-1} = \left(1 + \frac{k_r + k_{nr}}{k(E)}\right) + \left(\frac{k_{ex}}{k(E)}\right)[D] \qquad (3)$$

As a result, the present model predicts the following points. First, the inverse of the field-induced fluorescence quenching changes linearly with the concentration of H_2Pc added. Second, both slope and intersection of Eq. 3 decreases with increasing the applied field since $k(E)$ increases with applied field.

Figure 8 shows the relation between $(\Delta F/F)^{-1}$ and [D]. Obviously, the proportional relation was obtained at every applied field. Moreover, slope and intersection decreased with increasing the applied field. Thus, the proposed carrier generation mechanism assuming two channels to CT states is applicable to explain the present results.

As mentioned above, there exist two possibilities for fluorescence quenching by adding H_2Pc, i.e., charge transfer quenching and energy transfer between Me-PTC and H_2Pc. In order to confirm that present fluorescence quenching is mainly due to the former case, H_2Pc was replaced with a donor, which has no spectral overlap between its absorption and fluorescence of Me-PTC. An aromatic amine (PDA, Fig. 9),[15] as an electron donor, also enhanced the carrier generation efficiency of Me-PTC about twice only by adding a small amount of [D] = 0.05, and under the existence of PDA molecule, field-induced fluorescence quenching ($\Delta F/F$) of Me-PTC decreased clearly as shown in Fig. 9(A). Moreover, $(\Delta F/F)^{-1}$ and [D] showed the clear linear relation and both slope and intersection decreased with increasing the applied field (Fig. 9(B)) as predicted by the present model.

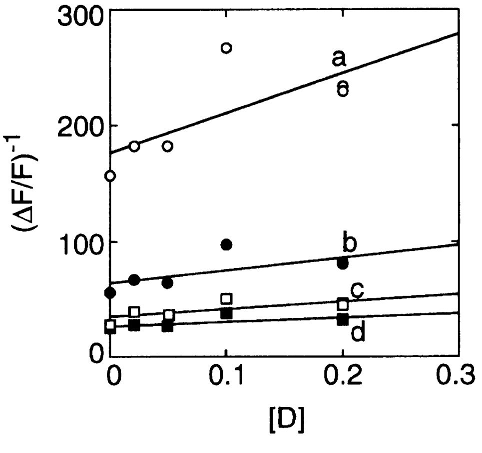

Fig. 8. Dependence of $(\Delta F/F)^{-1}$ on [D] for Me-PTC/H_2Pc system at (a) 3×10^7, (b) 5×10^7, (c) 7×10^7, (d) 9×10^7 V m^{-1}.

Figure 10 shows the applied field dependence of slope and intersection corresponding to $k_{ex}/k(E)$ and $1 + [(k_r + k_{nr})/k(E)]$, respectively, for Me-PTC/H_2Pc system (curve a) and Me-PTC/PDA system (curve b). The values of $k_{ex}/k(E)$ far larger than unity suggests that new channel of photogeneration through a CT state becomes dominant once the impurities were added. $k_{ex}/k(E)$ values for PDA is by about one order of magnitude larger than those of H_2Pc as a result of larger decrement of $\Delta F/F$ (Figs. 6 and 9(A)) which increases the $(\Delta F/F)^{-1}$ in Eq. 3. We suppose that PDA can form larger number of active sites for extrinsic carrier generation compared to H_2Pc because PDA dispersed molecularly adsorbed on Me-PTC surface more uniformly than the case of H_2Pc, which is dispersed as particle having the size of several tens nanometer. On the other hand, values of intersection obtained by extrapolating to [D] = 0 represent the carrier generation properties of Me-PTC itself. Good agreement of values obtained by using two different dopant molecules as shown in Fig. 10(B) further supports the present model.

In the present model (Fig. 7), there are two channels of carrier photogeneration under the existence of H_2Pc molecule. One is the intrinsic carrier generation route occurred at the bulk of Me-PTC particles, which is not related to the existence of H_2Pc molecules

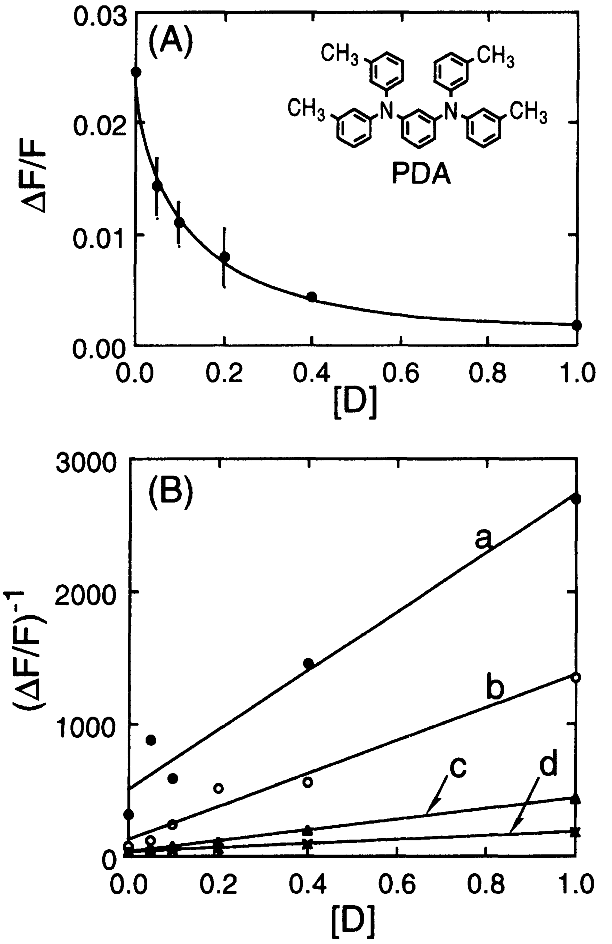

Fig. 9. (A) Dependence of $\Delta F/F$ on [D] for Me-PTC/PDA system. Here, [D] is the weight ratio of PDA with respect to Me-PTC. Applied field is 7×10^7 V m^{-1}. Excitation and observing wavelengths are 490 and 700 nm, respectively. (B) Dependence of $(\Delta F/F)^{-1}$ on [D] at (a) 2×10^7, (b) 4×10^7, (c) 7×10^7, (d) 1×10^8 V m^{-1}.

at the surface. In this case, ion pair formation seems to be initiated by the field-dependent charge transfer process between Me-PTC molecules as assumed by Popovic.[7,9] Another is the extrinsic carrier generation route occurred at the surface sites of Me-PTC particles where dopant H_2Pc and Me-PTC molecules are directly contacted, which is obviously related to the number of sites, namely, to the H_2Pc concentration, [D]. In this case, ion pair formation seems to be initiated by the charge transfer process between Me-PTC and H_2Pc molecules. However, nature of this extrinsic channel is not fully understood. At the present stage, we suppose the process involving the formation between a nonradiative exciplex, i.e., CT state, of two pigments, i.e., $(\text{Me-PTC}^{-}\cdots H_2Pc^{+})^*$, as proposed previously.[11—13] When this process is energetically favorable, ion pair seems to be formed by the field-independent rate constant (k_{ex}) as assumed in Fig. 7. There is, however, another possibility of the process involving the extrinsic exciton dissociation which has been proposed to explain the efficient carrier generation observed at the interface between 3,4,9,10-perylenetetracarboxylic bisbenzimidazole pigment and *N'*,*N'*-diphenyl-*N'*,*N'*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine.[16] On the other hand, it is also not clear that nature of CT states formed via two different channels are the same or not. It is noteworthy that the initial carrier separation distance, r_0, derived from $\Delta F/F$ vs. E curves in Fig. 5 by Onsager model[17] is not so different for two types of CT states, namely, $r_0=1.6$ and 1.5 nm for Me-PTC without and with H_2Pc of [D]=1.0, respectively. In order to clarify these problems, strict measurements of the dependence of carrier generation efficiency on the concentration of dopant molecules will be necessary.

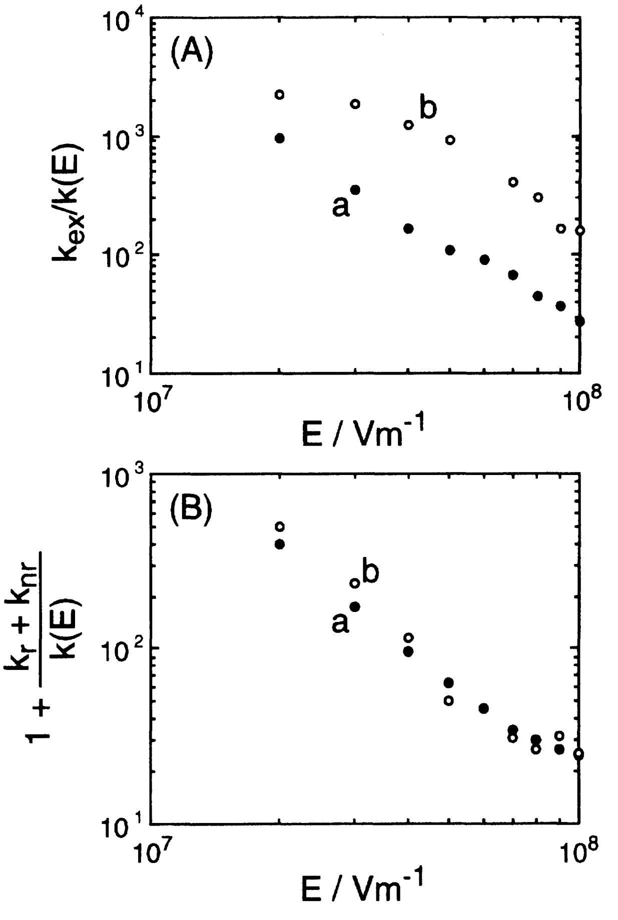

Fig. 10. (A) $k_{\text{ex}}/k(E)$ dependence on applied field (E). (B) $1+[(k_{\text{r}}+k_{\text{nr}})/k(E)]$ dependence on applied field (E). Curves a and b are for Me-PTC/H_2Pc system and Me-PTC/PDA system, respectively.

Conclusion

In conclusion, the sensitization of carrier generation of perylene pigment by adding phthalocyanine pigment was investigated by means of the electric field-induced fluorescence quenching. Enhancement of the carrier generation efficiency was accompanied with the decrease of field-induced fluorescence quenching. This observation was reasonably explained by the model assuming the existence of the additional extrinsic channel of carrier photogeneration. We think that extrinsic channel acts as the efficient CT state generation route through exciplex between perylene and phthalocyanine. The present model will be applicable to various organic systems doped with foreign molecules.

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References

1) J. Noolandi and K. M. Hong, *J. Chem. Phys.*, **70**, 3230 (1979).

2) M. Yokoyama, Y. Endo, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **49**, 1538 (1976).

3) M. Yokoyama, Y. Endo, A. Matsubara, and H. Mikawa, *J. Chem. Phys.*, **75**, 3006 (1981).

4) M. Yokoyama, S. Shimokihara, A. Matsubara, and H. Mikawa, *J. Chem. Phys.*, **76**, 724 (1982).

5) S. Shimokihara, M. Yokoyama, and H. Mikawa, *Denshishashin*, **21**, 25 (1982).

6) Z. D. Popovic and E. R. Menzel, *J. Chem. Phys.*, **71**, 5090 (1979).

7) A. -M. Hor and Z. D. Popovic, "Proceedings of IS&T 7th International Congress on Advanced Non-impact Printing Technologies," Portland, Oregon (1991), Vol. 1, p. 293.

8) Z. D. Popovic, R. O. Loutfy, and A. -M. Hor, *Can. J. Chem.*, **63**, 134 (1985).

9) Z. D. Popovic, R. O. Loutfy, and A. -M. Hor, "Proceedings of SPIE, Fluorescence Detection," ed by E. R. Menzel chair/editor, 15—16 January 1987, Los Angeles, California, Vol. 743, pp. 29—36.

10) C. W. Tang, *Appl. Phys. Lett.*, **48**, 183 (1986).

11) M. Hiramoto, H. Fujiwara, and M. Yokoyama, *Appl. Phys. Lett.*, **58**, 1062 (1991).

12) M. Hiramoto, H. Fujiwara, and M. Yokoyama, *J. Appl. Phys.*, **72**, 3781 (1992).

13) M. Hiramoto, Y. Sakaue, and M. Yokoyama, *Nihon Kagaku Kaishi*, **1992**, 1180.

14) H. J. Wagner, R. O. Loutfy, and C. Hsiao, *J. Mater. Sci.*, **17**, 2781 (1982).

15) H. Tanaka, Y. Yamaguchi, and M. Yokoyama, *Denshishashin*, **29**, 366 (1990).

16) Z. D. Popovic, A. -M. Hor, and R. Loutfy, *Chem. Phys.*, **127**, 451 (1988).

17) According to the Onsager model, geminate ion pair which does not dissociate to free carriers return to the S_0 state via S_1 state. In this case, $\Delta F/F$ is expressed as $[P(E)-P(0)]/[1-P(0)]$. Initial separation of ion pair, r_0, can be obtained by fitting the observed $\Delta F/F$ vs. E curves in Fig. 5 to the theoretical $[P(E)-P(0)]/[1-P(0)]$ vs. E curves using r_0 as a fitting parameter.