  Bull. Chem. Soc. Jpn., 62, 1458—1462 (1989) [Vol. 62, No. 5

Light-Induced Generation of Charge Carriers in Porphyrin Solids Doped with Electron-Accepting and Donating Molecules

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(Received November 24, 1988)

Fluorescence and photocurrent generation efficiencies of thin films of 5,10,15,20-tetraphenylporphyrin (TPP) and its zinc complex (ZnTPP) doped with electron-accepting and -donating molecules were investigated to get an insight into a charge-carrier generation in organic solid films upon irradiation. Photogeneration of charge carriers in I_2-doped ZnTPP solids was found to consist mainly of a direct ionization process via an excited singlet state of ZnTPP while that in TPP solids was consistent with an exciplex formation model. From a practical view point, the doping of acceptor molecules into p-type porphyrin solids was effective to improve photovoltaic efficiencies of Al/porphyrin/Au sandwich-type cells.

The effect of electron acceptors or donors upon the conductivity and photoconductivity of molecular solids is well-known. As early as in 1960, Calvin et al. examined electrical properties of phthalocyanine (Pc) films on addition of *o*-chloranil and found the increase in the dark conductivity and photoconductivity by orders of magnitude.[1,2] Based on the ESR measurement, they ascribed the striking enhancement of the currents to an electron transfer from Pc to the acceptor molecule in the dark, which produces holes in the Pc layer and *o*-chloranil anion radicals. More recently, Loutfy and Menzel have investigated a correlation between fluorescence and charge-carrier photogeneration efficiencies of an X-type Pc film doped with 2,4,7-trinitrofluorenone (TNF).[3] In consequence, they have found that with an increase in TNF concentration the carrier generation efficiency increases while the fluorescence is quenched. Their finding is explained by the singlet exciton diffusion to the surface of the X-Pc at the dopant site, followed by the exciplex formation and its subsequent dissociation into charge carriers. In other words, the former authors have postulated a dominant role of the ground-state complex for the doping effect, which is equivalent to the band model of doped semiconductors,[4] as opposed to the exciplex formation proposed by the latter.

The electronic processes in molecular solids are complicated and their interpretation occasionally requires molecular level considerations.[5-8] However, a close examination of the doping effect on the organic semiconductors could be a clue to understand the electronic processes such as a charge-carrier generation upon irradiation, the process being essential in photosynthesis and in solar energy conversion.

In this report, we describe the effects of doping with electron acceptors and donors on the fluorescence intensity of porphyrin films as well as on the performance of photovoltaic cells based on these porphyrins. The reasons of using porphyrins as host molecules are four-fold: 1) Electronic processes in nondoped porphyrin films have been the subject of recent investigations.[9,10] Especially, the choice of the two porphyrins, i.e. 5,10,15,20-tetraphenylporphyrin (TPP) and its zinc derivative (ZnTPP), is due to the large differences in exciton diffusion length[9,10] and in oxidation potential[11] between these porphyrins. 2) Different from phthalocyanines most investigated, porphyrins are soluble in some organic solvents to allow a preparation of organic thin films by use of a spinner coating method. This enables us to distribute guest molecules into the porphyrin layers uniformly. In most of previous studies[2,3,12] a surface doping in place of our bulk doping is employed. 3) Fluorescence from porphyrin solids is intense and gives us the information on the fate of excited states. 4) Aggregates of porphyrin molecules, organic oxidizing agents (quinones, coenzyme Q, etc.) and reducing agents (carotenoids) occur together in photosynthetic materials, and their interaction may be of importance in the primary quantum conversion process.

Experimental

TPP and its metal complex (ZnTPP) were purchased from Strem Chemicals Inc. ZnTPP was purified according to the literature method to remove a trace of chlorin.[13] Thin films of TPP and ZnTPP are known to exhibit a p-type semiconducting behavior. Iodine (I_2) was of reagent grade from Katayama Chemicals and used without further purification. Tetracyanoquinodimethane (TCNQ) from Tokyo Kasei Co. was recrystallized twice from ethyl acetate. *o*-Chloranil (Chl) and phenothiazine (Pz) from Tokyo Kasei Co. were purified by recrystallization from acetone and toluene, respectively. I_2, TCNQ, and Chl are well-known to be electron acceptors while Pz is an electron donor. Dichloromethane was redistilled after desiccation with calcium hydride. Sandwich-type photovoltaic cells of Al/(porphyrin+dopant)/Au were fabricated by first evaporating aluminum directly onto a precleaned glass substrate at 10^{-4} Pa by use of a Tokuda CFS-8EP vacuum deposition apparatus. The transmittance of the aluminum film was 20—50%. Porphyrin films doped with acceptors and donors were prepared using a Kyowa-Riken K359SW spinner as follows: a given amount of dopant molecules was dissolved into a 8 mM (1 M=1 mol dm^{-3}) TPP or ZnTPP solution of dichloromethane, and then one drop of the solution of

porphyrin plus dopant was put onto the aluminum-coated glass slide spinning at the rate of 4600 rpm. Absorbance of the films prepared in this manner was 0.8—1.0 at the Soret band of the porphyrin films irrespective of the amount of dopant molecules involved. Only uniformly prepared samples were used for further vacuum-deposition of gold on the porphyrin films to make an ohmic contact. Measurements of spectral responses of the short-circuit (s.c.) photocurrents were performed with the aid of a microcomputer, where photocurrents were normalized in such a way that the intensity of monochromatic light incident on the interface between the dye film and Al was at 10 μW cm^{-2}. The light source consisted of a 300 W tungsten halogen lamp and a JASCO CT-10S monochromator. Open-circuit photovoltages (V_{oc}) of photovoltaic cells were measured by a Takeda Riken TR8651 electrometer. Samples for fluorescence measurements were prepared by the spinner coating onto Pyrex glass substrates. Measurements of fluorescence from spun films of porphyrins were made by use of a Hitachi MPF-4 fluorescence spectrophotometer. In most experiments, the angle of the exciting light to the normal of the sample side of the glass slides was adjusted within 65±5° to give a maximum fluorescence intensity, and the luminescence was detected at the right angle to the exciting beam. All measurements were carried out at room temperature.

Results

Figure 1 depicts spectral responses of s.c. photocurrents for a) Al/TPP/Au and b) Al/ZnTPP/Au photovoltaic cells with and without doping of electron accepting I_2 and TCNQ molecules. In all cases, illumination is carried out from the Al/p-type porphyrin interface which provides an effective site for the light-induced generation of charge carriers. Photocurrents (i_p) flow from Au to Al through the external circuit. It is seen that the addition of I_2 or TCNQ enhances the photocurrents greatly over the entire spectral range investigated. In addition, the spectral responses of photocurrents for the doped samples coincide well in shape with the absorption and action spectra of the corresponding pure porphyrin films, suggesting that no spectral sensitization by the dopants takes place. The photocurrent quantum yield (η), defined as the number of electrons produced per photon incident on the dye film, at the Soret band changes from 1.4% for pure TPP to 6.3% for I_2-doped TPP and from 2.9% for pure ZnTPP to 11% for I_2-doped ZnTPP. In addition to this, no appreciable decay of i_p with a lapse of time indicates that the doping is an important technique to improve efficiencies of solar cells based on organic materials.

Figure 2a shows changes of s.c. photocurrents at the Soret band for the Al/TPP/Au photovoltaic cells when I_2, Chl, TCNQ, or Pz are doped into the TPP solids at various mole fractions, where η_0 in ordinate denotes the η value in the absence of dopant. Figure 2b depicts similar plots for the Al/ZnTPP/Au photovoltaic cells with I_2 or TCNQ as a dopant. With I_2 being doped, the photocurrents for the both cells start to increase at the I_2 mole fraction as high as 0.1, whereas the TCNQ doping is effective at its mole fraction as low as 0.01. In the TCNQ case, the photocurrents for TPP as well as ZnTPP level off at a 0.2 mole fraction and decrease with TCNQ mole fractions beyond this value. The photocurrent reduction when TCNQ is doped heavily might be ascribed to a steric effect which prevents an intermolecular interaction between porphyrin molecules. As is seen in Fig. 2a, the doping of Chl into the TPP film was the most effective and enhanced the photocurrent by almost one order of magnitude. On the other hand, the photocurrent is slightly reduced by the addition of electron-donating Pz molecules into the TPP film.

Figure 3 summarizes the results of fluorescence measurements, where F and F_0 correspond to intensities of fluorescence from porphyrin solids with and

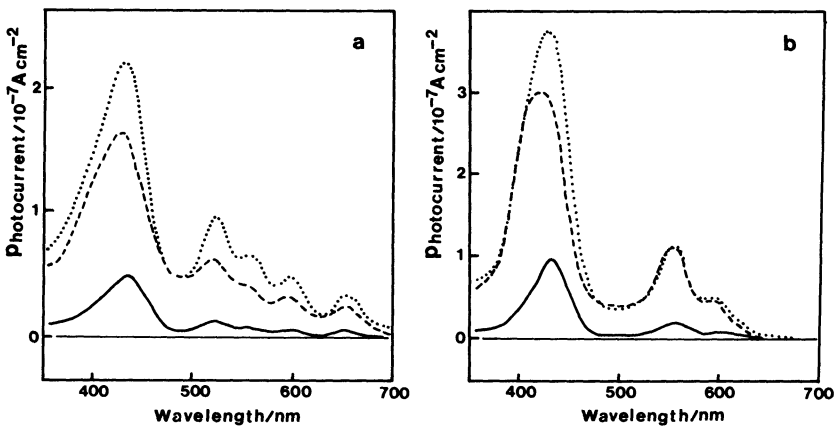

Fig. 1. Spectral responses of s.c. photocurrents for a) Al/TPP/Au and b) Al/ZnTPP/Au photovoltaic cells, where porphyrin solids are nondoped (solid line) and doped with I_2 (dotted line) and TCNQ (broken line).

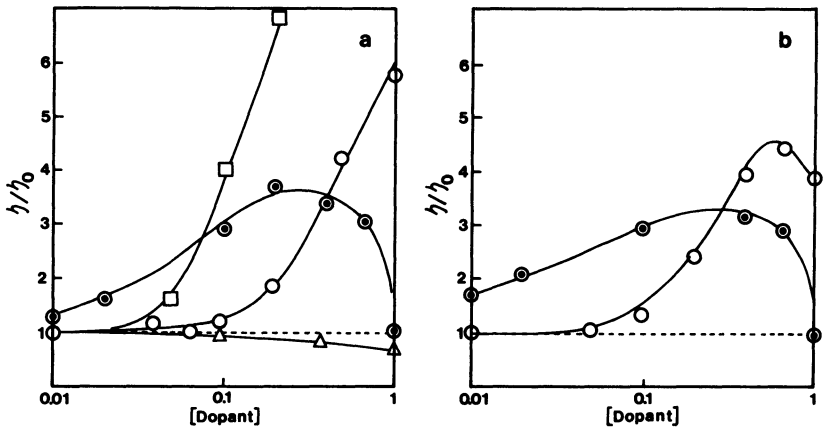

Fig. 2. Effect of doping on photocurrent quantum yield (η) for a) Al/TPP/Au and b) Al/ZnTPP/Au photovoltaic cells, where photocurrents are measured at the respective Soret bands of TPP and ZnTPP solids. Abscissas in Figs. 2 and 3 denote a mole fraction of the respective dopants: (○) I_2; (◉) TCNQ; (□) Chl and (△) Pz.

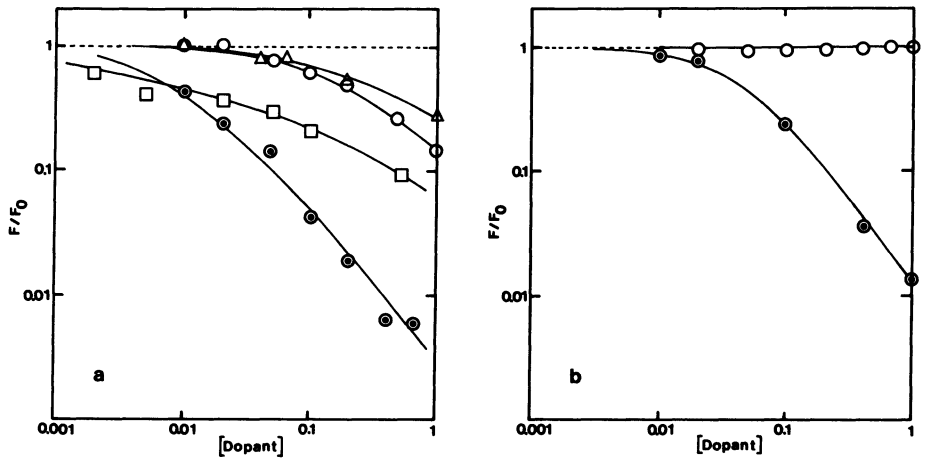

Fig. 3. Effect of doping on fluorescence intensity (F) of TPP and ZnTPP films, where excitation is made at 430 nm in both cases and emission is detected at 655 nm for TPP and 605 nm for ZnTPP. Each symbol has the same meaning as that of Fig. 2.

without doping, respectively. The excitation is made at the respective Soret bands of TPP and ZnTPP films, and the emission is detected at 655 nm for TPP and 605 nm for ZnTPP. It is seen from this figure first that TCNQ is the most effective in quenching ability among dopants used in the present study and second that fluorescence of TPP is quenched by TCNQ or I_2 more strongly than that of ZnTPP is. The second feature of the fluorescence quenching may be associated with the exciton diffusion length being greater for TPP than ZnTPP,[9] if the quenching ability of either of the dopants is similar between the two porphyrins. It should be noticed in Fig. 3 that fluorescence from the ZnTPP films is not quenched at all by I_2 ranging in mole fraction up to unity although the photocurrents are enhanced by the factor of 4 at the highest I_2 mole fraction. In contrast to this, fluorescence of the TPP films is quenched by Pz with an electron donating character although the photocurrents for the Pz-doped porphyrin films are almost constant irrespective of the amount of Pz doped. When the data in Fig. 3 were replotted as a reciprocal of a fluorescence intensity against a dopant mole fraction, all the plots yielded straight lines in the ranges of mole fractions up to 0.2—0.5 depending on the sort of the dopant. This finding indicates that the present bulk-doping technique using the spinner is successful to attain a uniform distribution of dopants in the solid films at low doping levels, at least.

Figure 4 displays the effect of I_2-doping on relative

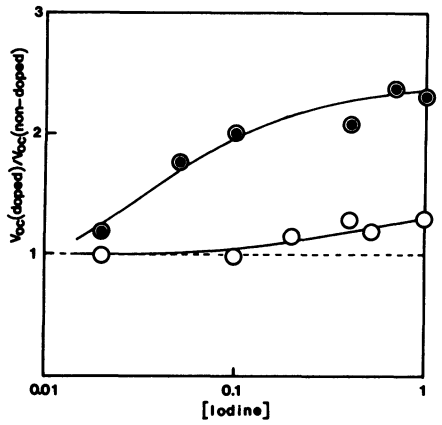

Fig. 4. Effect of I_2-doping on relative photovoltages of (○) Al/TPP/Au and (◉) Al/ZnTPP/Au photovoltaic cells.

open-circuit photovoltages of a) Al/TPP/Au and b) Al/ZnTPP/Au cells, where V_{oc}'s for the doped samples are divided by V_{oc} for the nondoped sample. V_{oc} for TPP stays almost constant irrespective of concentrations of I_2 doped, while that for ZnTPP increases with increasing I_2 concentration.

Discussion

According to the exciplex formation model,[3] deactivation routes for singlet excitons (S_1) consist of the following two competitive reactions:

$$S_1 \longrightarrow S_0 + h\nu(\text{fluorescence}) \quad (1)$$

$$S_1 + Q \longrightarrow (S.Q)^* \quad (2)$$

where Q is the quencher or the electron acceptor in the present case, S_0 the ground state of an organic dye molecule and (S.Q)* denotes the exciplex. The exciplex is assumed to dissociate into free charge carriers with a probability of $\phi(E)$ or into S_0 and Q as follows:

$$(S.Q)^* \xrightarrow{\phi(E)} e^- + h^+ \quad (3)$$

$$(S.Q)^* \xrightarrow{1-\phi(E)} S_0 + Q \quad (4)$$

Obviouly, this mechanism predicts the increase in charge carrier photogeneration efficiency on addition of Q concomitant with a decrease in fluorescence, in accord with the observations for the I_2-, TCNQ-, and Chl-doped TPP films. The same effects of doping can be expected also by assuming a dissociation of the exciton due to a local electric field caused by the charge-transfer complex between S_0 and Q in the dark. However, neither of these mechanisms explains the increase in photocurrents of the Al/ZnTPP/Au cell on addition of I_2, accompanied by no quenching of fluorescence. Concurrent changes in efficiencies of fluorescence and charge-carrier generation are essential in both models because a charge-carrier generation and a fluorescence quenching follow the reaction of S_1 with Q or with the CT complex comprising S_0 and Q.

One possible way to account for the results with ZnTPP is to assume, in place of the above impurity-dependent route, a direct charge-carrier generation from the S_1 state and/or the excited state of ZnTPP together with the band model description of the ZnTPP solid. In a preceding paper,[10] we have estimated diffusion lengths of excitons as 3±2 nm for ZnTPP and 15±10 nm for TPP on the basis of the analysis of the optical filtering effect observed for the Al/porphyrin/Au photovoltaic cells. In view of the fact that our estimate of the exciton diffusion length involves a contribution from the direct ionization process as well, the short exciton diffusion length found for the ZnTPP solid suggests that the direct charge-carrier generation may prevail in the ZnTPP solid in support of the above assumption. On the other hand, the ZnTPP molecule is known to be more easily oxidized than the TPP molecule.[11] This suggests that the valence band edge of the ZnTPP solid locates above that of TPP. Therefore, the postulated relative positions of energy levels denote that the acceptor doping should be more effective in ZnTPP than in TPP or that the acceptor molecule is likely to produce a ground-state complex, as suggested by Calvin et al.,[2] with the ZnTPP molecule more easily than with TPP. The ground-state complex formation leading to a production of the majority carrier (hole) in the ZnTPP solid in the dark induces a shift of the Fermi level of the molecular solid toward the valence band. The lowering of the Fermi level of the p-type solid leads to the increase of a built-in potential in the ZnTPP bulk close to Al, consistent with the increase in V_{oc} with increasing I_2 concentrations as shown in Fig. 4. Furthermore, the increase in the built-in potential can be responsible for the improvement in the photocurrent quantum yield since the enhanced electrostatic field in the depletion layer reduces a recombination probability of electron-hole pairs produced by the direct ionization process. It is quite evident that this model, in place of the exciplex formation model, does not necessarily require a parallelism between the fluorescence quenching and the improvement in the photocurrent quantum yield.

A spectroscopic attempt to detect the ground-state complex between ZnTPP and I_2 was performed by measuring absorption and fluorescence spectra of pure ZnTPP films and ZnTPP films doped with I_2 at various concentrations. However, no change at all was found in both spectra, suggesting that the equilibrium concentration of the ground-state complex is very low in comparison with that of the dopant added unless it has an absorption and a fluorescence spectra essentially indistinguishable from those of ZnTPP itself. The low concentration is not in conflict with the

observed changes in V_{oc} and i_p on addition of I_2 because even a small amount of the ground-state complex, if its concentration being higher than the hole concentration of the pure ZnTPP film, can be sufficient to alter electrical properties of the ZnTPP solids greatly.

For the TCNQ-doped ZnTPP solids, one can expect a similar carrier generation mechanism with the above one. In this case, however, fluorescence was quenched highly on addition of TCNQ. The result shows clearly an involvement of deactivation routes of S_1 such as expressed by Eqs. 1 and 2 besides, probably, the direct carrier generation path, which is predominant in the illuminated I_2-doped ZnTPP film.

Finally, the fluorescence quenching and no change of i_p observed with the Pz-doped TPP film are understandable by assuming the exciplex model with a small $\phi(E)$ value.

In conclusion, the present study shows that the mechanism of photogeneration of charge carriers depends on the combination of a dopant and an organic solid. Measurements of fluorescence and charge-carrier generation efficiency for the TPP solids doped with Chl, I_2, TCNQ, or Pz were consistent with those expected from the exciplex formation model. On the other hand, the mechanism of charge-carrier generation upon irradiation for the I_2-doped ZnTPP was explained based on the band model for the doped semiconductors together with the assumption of the direct photoionization process, in which the photocurrent increase was ascribed to a reduction in recombination rate of electron–hole pairs in the depletion layer. In the case of TCNQ-doped ZnTPP, both direct and indirect processes appeared to prevail.

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