Electric Field Effects on Excitation Dynamics in Electron Donor and Acceptor Pairs of Porphyrin and Fullerene

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Electroabsorption and electrofluorescence spectra have been measured using electric field modulation spectroscopy for a mixture of tetraphenylporphyrin (TPP) and fullerene (C\textsubscript{60}) in a PMMA film. Fluorescence of TPP is enhanced and de-enhanced by an electric field in zinc and free-base compounds, respectively, indicating that the electron transfer from the excited state of TPP to C\textsubscript{60} is decelerated in zinc compound and accelerated in free-base compound by an electric field. TPP was also found to form complex upon mixing with C\textsubscript{60} which exhibits a broad emission in the wavelength region longer than that of TPP emission. The electroabsorption spectra show that a charge separation occurs upon photoexcitation to the absorption band located near the Soret band. The complex emission is significantly quenched by an external electric field in both zinc and free base compounds, suggesting that the nonradiative decay of the excited complex is accelerated by an electric field.

Introduction

Fullerene and porphyrin have strong electron accepting and electron donating ability, respectively, and their large \(\pi\) surfaces allow the release and uptake of an electron with minimal structural perturbation (1-5). Thus, the reorganization energy toward the photoinduced electron transfer is very small, which expedites the productive forward electron transfer and diminishes the unfavorable back electron transfer. These compounds also have distinguishable spectroscopic features in the UV and visible region, harvesting the UV and visible light intensity. Fullerene and porphyrin therefore have emerged as an attractive donor-acceptor pair for building models of the photosynthetic reaction center as well as for developing supramolecular functional devices.

The large \(\pi\) surfaces of porphyrin and fullerene are favorable to interact with each other, which results in the formation of ground state complex or cocrystalate (6-9). This property allows us to prepare various types of multi-dimensional supramolecular fullerene and porphyrin systems exhibiting photoinduced electron transfer and/or energy transfer. However, detailed knowledge on electronic properties of the supramolecular system is essential for optimizing its physical properties for specific applications. External electric field effects on optical spectra have been extensively applied in molecular spectroscopy for examining electronic properties and photoexcitation dynamics of molecules (10-12). The so-called electroabsorption and electrofluorescence spectra (plots of the electric-field-induced change in absorption intensity and fluorescence intensity as a function of wavelength, respectively) provide unique information on the differences in electric dipole moment and molecular polarizability between the ground state and the excited state. Measurements of these spectra are also
useful to clarify the mechanism of molecular dynamics following photoexcitation. These spectra are especially powerful for studying electron transfer dynamics because of its high sensitivity to an electric field (13,14).

In the present study, electroabsorption and electrofluorescence spectra have been measured for tetraphenylporphyrin (both free-base and its zinc analog), fullerene, and their mixtures doped in a poly(methyl methacrylate) (PMMA) film (15-17). Based on the results, the field-induced change in photoexcitation dynamics as well as the change in electronic properties following photoexcitation has been discussed.

**Experimental**

Commercially available free-base tetraphenylporphyrin, zinc-tetraphenylporphyrin and fullerene, detonated by H2TPP, ZnTPP and C60 respectively, were used without further purification. Commercially available PMMA was purified by precipitation with a mixture of methanol and benzene and by extraction with hot methanol. The concentration of ZnTPP or H2TPP doped in a PMMA film was fixed to be 0.5 mol% in a monomer unit of PMMA, while the concentration of C60 was in the range of 0 - 2.0 mol% in a monomer unit of PMMA. Hereafter, the sample of a mixture of C60 having a concentration of X and porphyrin (0.5 mol%) is denoted by ZnC60(X) or H2C60(X) for ZnTPP and H2TPP, respectively. Hereafter the monomer of free-base teraphenylporphyrin and its zinc compound is designated as H2M and ZnM, respectively.

A certain amount of toluene solution of PMMA containing each mixture was poured onto an ITO-coated substrate by a spin coating technique. Then, the polymer film was dried in vacuo to eliminate toluene completely, and a semitransparent aluminium (Al) film was deposited on the dried polymer film by a vacuum vapor deposition technique. Al and ITO films were used as electrodes. The thickness of the polymer films was determined by using a thickness measurement system.

All the optical spectra were measured at room temperature under vacuum condition. For electroabsorption (E-A) and electrofluorescence (E-F) measurements, a field-induced change in transmitted light intensity (ΔI) or fluorescence intensity (ΔIf) as a function of wavelength was measured using the same apparatus as reported elsewhere (16,17). A sinusoidal ac voltage was applied, and the value of ΔI ΔIf was detected with a lock-in amplifier at the second harmonic of the modulation frequency. Applied field strength was estimated from the applied ac voltage divided by the thickness of the polymer film.

**Results and Discussion**

Absorption and emission spectra of H2TPP, ZnTPP and their mixtures with C60 at different concentration of C60 in a PMMA film are shown in Figure 1. As the C60 concentration increases, the Soret absorption band both of H2TPP and of ZnTPP becomes broader, and the peak intensity becomes weaker. This consequence was attributed to a formation of the ground state complex between TPP (H2TPP/ZnTPP) and C60. The absorption and electroabsorption spectra of the complex between TPP and C60 will be described later in detail. A quenching of TPP fluorescence is also discernible in the presence of C60, and the magnitude of quenching becomes larger with an increase of the C60 concentration. As a result of the complex formation, TPP monomer fluorescence is reduced in the presence of C60. It is also considered that TPP fluorescence is quenched by the following mechanisms: 1) Intermolecular electron transfer from the excited state of TPP to C60; 2) excitation energy transfer from the excited state of TPP to the complex.
Figure 1. Fluorescence spectra of H₂TPP (upper) and ZnTPP (lower) doped in a PMMA film with C₆₀ at different concentrations from 0 to 2.0 mol%. Absorption spectra are also shown in an inset. Fluorescence spectra were obtained with excitation at the peak of the Soret absorption band of H₂TPP (417 nm) and ZnTPP (423 nm). The concentration of TPP was 0.5 mol% in every case.

Both in H₂TPP and in ZnTPP, a comparison between the normalized fluorescence spectra of the mixtures and the monomer fluorescence spectra of TPP shows a tiny existence of a broad emission in the longer wavelength region for the mixture. The quantum yield of the broad emission increases with an increase of the C₆₀ concentration, when the photoexcitation is done at the peak of the Soret band of TPP. To examine the origin of the broad emission, emission spectra of a mixture of TPP and C₆₀ were measured at different excitation wavelengths. The results are shown in Figure 2 for the mixture of H₂TPP (0.5 mol%) and C₆₀ (2.0 mol%). As shown in the figure, fluorescence spectrum similar in shape to that of TPP monomer was observed following excitation at around the peak and at the blue edge of the Soret absorption band. On the other hand, an intense broad emission with a peak at 772 nm in H₂TPP and 815 nm in ZnTPP was observed following excitation at the red edge of the absorption spectrum of the mixture, besides the structured monomer fluorescence of TPP. The broad emission was attributed to the fluorescence of the complex formed between TPP and C₆₀. The excitation spectrum of a mixture indicates that the complex fluorescence appears not only following direct excitation of the complex but also following excitation of TPP. It is considered that excitation energy transfer to a neighboring complex occurs from the fluorescent state of
TPP in competition with the electron transfer to C_{60}. However, it is worth mentioning that the weak broad emission following excitation at the peak of the Soret band both of H_{2}TPP and of ZnTPP implies a limited efficiency of the energy transfer.

**Figure 2.** Fluorescence spectra of a mixture of H_{2}TPP (0.5 mol%) and C_{60} (2 mol%) observed, respectively, with excitation wavelengths of 418, 440 and 445 nm.

**Figure 3.** Fluorescence spectra (solid line) and E-F spectra (shaded line) for the mixtures of H_{2}TPP and C_{60} (left) and for the mixture of ZnTPP and C_{60} (right). The concentration of C_{60} was 0 and 2.0 mol% at upper and lower spectra, respectively, while the concentration of H_{2}TPP and ZnTPP was 0.5 mol% in every case. Maximum fluorescence intensity is normalized to unity in every case. The applied field strength was 1.0 MVcm^{-1}.

E-F spectra as well as fluorescence spectra of the mixtures of TPP and C_{60} were measured with a field strength of 1.0 MVcm^{-1}. The results are shown in Figure 3, together with the E-F spectra of TPP observed in the absence of C_{60}. These E-F spectra were
obtained with the excitation wavelength where the field-induced change in absorption intensity was negligible. In the mixture of TPP and C$_{60}$, the field-induced change in fluorescence intensity (both enhancement and de-enhancement) is predominant, indicating that excitation dynamics in a mixture is strongly influenced by an electric field. It is noted that the magnitude of the field-induced change is proportional to the square of the applied electric field.

E-F spectra as well as fluorescence spectra observed for the mixture of H$_2$TPP (0.5 mol%) and C$_{60}$ (2.0 mol%) and for the mixture of ZnTPP (0.5 mol%) and C$_{60}$ (2.0 mol%) are shown in Figure 4. Fluorescence spectrum of the mixture can be decomposed into two spectra; one is a sharp structured fluorescence (monomer fluorescence) emitted from the S$_1$ state of TPP (F$_1$ for H$_2$TPP and F$_1'$ for ZnTPP), and the other is the broad emission emitted from the complex between TPP and C$_{60}$ (F$_2$ for H$_2$TPP and F$_2'$ for ZnTPP). The electric field effect on the monomer fluorescence for the mixture of H$_2$TPP and C$_{60}$ is entirely different from that for the mixture of ZnTPP and C$_{60}$; the former fluorescence shows the field-induced de-enhancement, while the latter shows the field-induced enhancement, implying that the field effects on excitation dynamics of H$_2$TPP and ZnTPP are completely opposite from each other in the mixture.

Figure 4. (a) Fluorescence spectra for the mixture of H$_2$TPP (0.5 mol%) and C$_{60}$ (2.0 mol%) (left) and for the mixture of ZnTPP and C$_{60}$ (right), and their decomposition into two constituents (F$_1$, F$_2$ for H$_2$TPP, and F$_1'$, F$_2'$ for ZnTPP). (b) E-F spectra observed with a field strength of 1.0 MVcm$^{-1}$ for the mixture of H$_2$TPP and C$_{60}$ (left) and for the mixture of ZnTPP and C$_{60}$ (right), and their simulated spectra (dotted line). The TPP fluorescence spectrum as well as the broad fluorescence is also given in (b) by a chain line. The concentration of TPP and C$_{60}$ was 0.5 and 2.0 mol%, respectively.

Similar electric field effects were observed for porphyrin and fullerene dyads where intramolecular photoinduced electron transfer occurs from the excited state of porphyrin to fullerene (18,19). The opposite behavior of the electric field effects on fluorescence
between zinc and free-base compounds is attributed to the difference of the potential barrier for electron transfer between the excited state of porphyrin and C\textsubscript{60}. It is suggested that photoinduced electron transfer in zincporphyrin-fullerene dyads occurs in the "barrierless regime", where the magnitude of the free-energy gap for reaction is very close to the reorganization energy, while the barrier height is considerably large in linked compounds of free-base porphyrin and C\textsubscript{60}. The same interpretation seems to be applicable; intermolecular electron transfer from the excited state of TPP to C\textsubscript{60} occurs in the "barrierless regime" for ZnTPP, while the barrier height of the reaction is considerably large for H\textsubscript{2}TPP, and the electron transfer to C\textsubscript{60} is decelerated and accelerated by an electric field for ZnTPP and H\textsubscript{2}TPP, respectively. Then, the opposite behavior of the electric field effects on the monomer fluorescence is expected for H\textsubscript{2}TPP and ZnTPP, as observed in the present experiments.

In contrast with the monomer fluorescence of TPP, the broad emission from the complex is reduced by an electric field in both cases of H\textsubscript{2}TPP and ZnTPP. The large magnitude of the field-induced quenching of the complex fluorescence shows that the fluorescent state of the complex is highly susceptible to the external electric field.

As a mechanism of the fluorescence quenching of the complex, two possibilities may be pointed out. The emitting state of the broad fluorescence may have a charge-separated character of the complex, just like the exciplex produced following photoinduced electron transfer. Then, the field-induced quenching of the complex emission may occur, if the field-assisted dissociation occurs from the fluorescent state of such a complex. Another mechanism can be also pointed out. If the fluorescent state of the complex is regarded as a kind of charge-separated state, the nonradiative process from the excited state of complex to the ground state complex, which competes with the radiative process providing the broad emission, is regarded as a back-electron transfer process. As the initial step of electron transfer is significantly influenced by an electric field, this back electron transfer process may be also significantly influenced by an electric field. In the present, it is not easy to distinguish these two mechanisms.

Absorption as well as E-A spectra of the complex were extracted from the observed spectra. Absorption and E-A spectra of H\textsubscript{2}C\textsubscript{60}(X) or ZnC\textsubscript{60}(X) are considered to be a superposition of the spectra of TPP, C\textsubscript{60} and complex formed between TPP and C\textsubscript{60}. Since the absorption intensity of H\textsubscript{2}TPP is very small at 331 nm, the absorption spectrum of C\textsubscript{60} was subtracted from the observed absorption spectra by assuming that the intensity at 331 nm in H\textsubscript{2}C\textsubscript{60}(X) is only due to C\textsubscript{60} and that the shape of the absorption spectrum of C\textsubscript{60} is not affected by a mixing of H\textsubscript{2}TPP or ZnTPP. The E-A spectrum of C\textsubscript{60} (15) was subtracted from the E-A spectrum of each mixture with the method similar to the one used for the normal absorption spectra; the subtraction factor was determined by using the E-A signal of C\textsubscript{60} at 331 nm. The subtracted spectra of H\textsubscript{2}C\textsubscript{60}(X) are regarded as a superposition of the spectra of the H\textsubscript{2}M and complex formed between H\textsubscript{2}TPP and C\textsubscript{60}. Note that the E-A spectra of H\textsubscript{2}M and ZnM are given by the first derivative of the absorption spectrum in shape (see Figure 5), indicating that the change in molecular polarizability is significant upon optical transition in TPP monomer. By comparing the spectral features of H\textsubscript{2}C\textsubscript{60}(X) and ZnC\textsubscript{60}(X) at different concentrations of C\textsubscript{60} with those of H\textsubscript{2}M and ZnM, it can be easily envisioned that the absorption band of the complex is located contiguous to the Soret band of the porphyrin monomer. The absorption spectrum as well as the E-A spectrum of the complex was extracted and simulated with the following assumptions: (1) absorption and E-A spectra of the monomer species which exist in H\textsubscript{2}C\textsubscript{60}(X) and ZnC\textsubscript{60}(X) are the same in shape as the ones of H\textsubscript{2}M and ZnM irrespective of the difference of X, and the subtraction of the monomer spectrum from the...
mixture yields the spectrum of the complex; (2) absorption and E-A spectra of the complex which exists in H$_2$C$_{60}$(X) and ZnC$_{60}$(X) are independent of the C$_{60}$ concentration; (3) the mixture spectrum can be reproduced by a linear combination of the monomer spectrum and some Gaussian curves. Two Gaussian curves, each of which gives the same shape at different concentrations of C$_{60}$ were obtained. A sum of these two Gaussian curves was supposed to give the absorption spectrum of the complex. The simulated absorption spectrum of the complex as well as its second derivatives are shown in Figure 5. The extracted E-A spectrum of the complex is very similar in shape to the second derivative, indicating that the change in electric dipole moment ($\Delta\mu$) is dominant following excitation to the complex. The magnitude of $\Delta\mu$ for the absorption band of the complex located around the Soret band of TPP was evaluated to be 3.3 and 3.0 D for H$_2$TPP and ZnTPP, respectively.

Figure 5. E-A spectra of H$_2$M (upper left), ZnM (upper right), complex between C$_{60}$ and H$_2$TPP (lower left) and complex between C$_{60}$ and ZnTPP (upper left). The applied field strength was 0.75 MVcm$^{-1}$. Absorption spectrum is shown by a solid line in every case, and the first derivative of the absorption spectrum is shown by a dotted line for H$_2$M and ZnM, and the second derivative of the absorption spectrum is shown by a dotted line for the complex.

**Conclusion**

Intermolecular electron transfer from the excited state of TPP to C$_{60}$ is decelerated in zinc compound and accelerated in free-base compound by an electric field. TPP forms complex upon mixing with C$_{60}$ which exhibits a broad emission in the wavelength region longer than that of TPP emission. The E-A spectra show that a charge separation occurs upon photoexcitation to the absorption band of the complex located near the Soret band. The complex emission is significantly quenched by an external electric field in both zinc and free base compounds, suggesting that the nonradiative decay of the excited complex is accelerated by an electric field in both cases.
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References