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Electric field effects on fluorescence of methylene linked electron donor and acceptor compounds in solution

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[Introduction]

External electric field effects on photochemical processes such as electron transfer have been long interested. In order to elucidate the field effects on photo-induced dynamics, the measurements of the field-induced change in emission spectra are essential. Such an approach is known as electrophotoluminescence (E-PL) spectroscopy, where field-induced change in photoluminescence (PL) spectra is measured. When electron transfer process which competes with emission processes is affected by application of an electric field, for example, the quantum yield of fluorescence is affected. From the measurements of E-PL spectra, we can also obtain information of the electric dipole moment (μ) at the emitting state and the change in dipole moment ($\Delta\mu$) and in polarizability ($\Delta\bar{\alpha}$) following electronic transitions. Therefore, E-PL measurements give the information not only about the field effect on excitation dynamics but also about the electronic structure.

In the present study, we have measured polarized E-PL spectra of the series of methylene linked compounds of (carbazole)-(CH₂)_n-(terephthalic acid methyl ester) (n=2-20) in solution, where photo-induced electron transfer occurs from the excited state of carbazole to terephthalic acid methyl ester. Hereafter these compounds are denoted as C-(n)-P, where C, n and P indicating carbazole moiety, the number of methylene units, and terephthalic acid methyl ester moiety, respectively. The significant field-induced change of intensity both on fluorescence emitted from the locally excited state of donor carbazole, hereafter noted as monomer fluorescence, and on exciplex fluorescence was observed. The experimental results are explained in terms of electric field effects both on photo-induced electron transfer process and relaxation process of fluorescent exciplex. From the analysis of the polarized E-PL spectra, the electric dipole moment of exciplex has also been evaluated.

[Experimental Section]

A decalin solution of C-(n)-P with a concentration of 5×10^{-4} M was used. E-PL as well as PL spectra were measured using an electric-field modulation spectroscopy. Sinusoidal voltage having a frequency of 4 kHz was applied, and lock-in amplifier was used to detect the E-PL signal synchronized with the modulated applied voltage.

[Results]

E-PL spectra of C-(n)-P in solution as well as PL spectra are shown in Fig. 1. The E-PL spectra were obtained with $\chi = 90^\circ$ and 55° . Note that χ represents the angle between the field direction and the polarization direction of the emission light. The applied field strength was 0.2 MVcm^{-1} and the excitation wavelength was 292 nm (34246 cm^{-1}), where the field-induced change in absorbance is negligibly small. The field-induced change in fluorescence quantum yield of both monomer and exciplex emissions was observed. The E-PL spectra could be reproduced by a linear combination of the zeroth and first derivatives of monomer and exciplex fluorescence spectra, as shown in Fig.1. Based on the E-PL results, the electric dipole moment of the fluorescent exciplex is estimated to be $\sim 19 \text{ D}$ in any n, and the electric dipole moment of the fluorescent monomer is estimated to be $\sim 6 \text{ D}$ in $n=10, 20$. The D-A distance dependence of the intramolecular electron transfer process is discussed, based on the field-induced enhancement and quenching of monomer fluorescence.

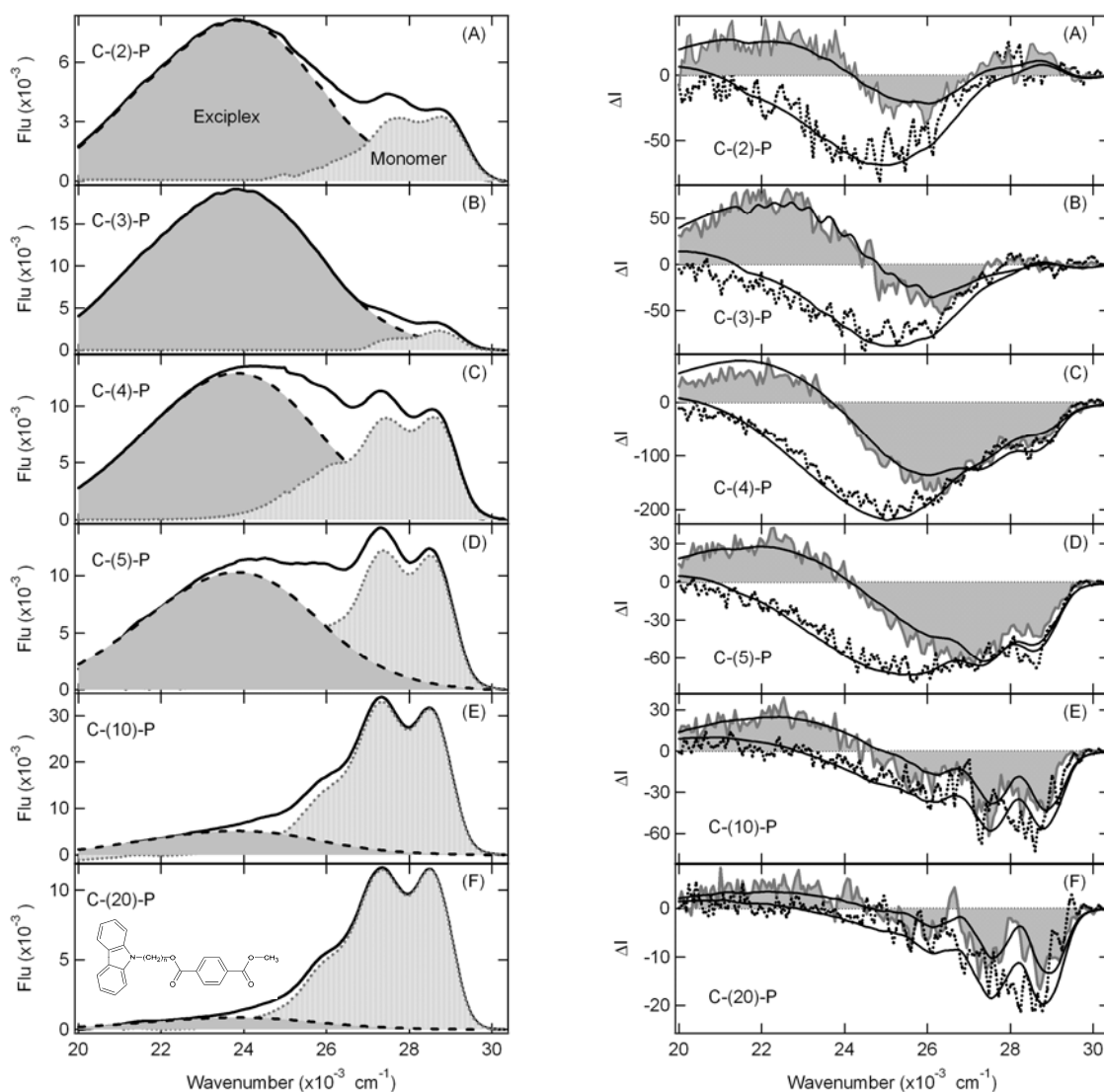


Fig. 1 PL spectra and the decomposition bands (left), and E-PL spectra (right) of C-(n)-P observed with $\chi = 90^\circ$ (dotted line) and 55° (shaded line). The simulated E-PL spectra are also shown by solid lines.