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学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Study on electroabsorption and electrophotoluminescence
of optoelectronic functional materials in solution

(光電変換機能物質の溶液中における電場吸収と電場発光に関する研究)

Electroabsorption (E-A) and electrophotoluminescence (E-PL) spectroscopies i.e., field-induced changes in absorption and photoluminescence spectra, respectively, give information not only about the electronic structure but also about the field effect on excitation dynamics. Both E-A and E-PL measurements are useful for probing the change in electronic and structure following optical transition because the results can be directly related to the difference in the sample's dipole moment ($\Delta\mu$) and polarizability ($\Delta\alpha$) between the excited state and ground state. Both parameters contribute significantly to our understanding of charge transfer and related processes in the excited state.

In the present work, the author utilizes electric field modulation E-A and E-PL spectroscopies to study the electronic structure and electric field effects on excitation dynamics of optoelectronic functional materials in solutions:

1. Electroabsorption spectra of DAST microcrystal

Polarized E-A spectra of 4-*N*,*N*-dimethylamino-4'-*N*'-methyl-stilbazolium tosylate (DAST) microcrystals suspended in decalin have been measured. On the basis of the results, the magnitude of the electric dipole moment in the ground state of DAST microcrystals whose size is about 0.35 μm is determined to be $\sim 3 \times 10^4$ D, and $\Delta\mu$ is estimated to be $\sim 3 \times 10^3$ D. The transition moment of the DAST crystal is also found

to be a little affected by application of electric fields.

2. Electric field effect on fluorescence and excitation dynamic of pyrene in solution

E-PL spectra have been measured for pyrene solution. At high concentrations of pyrene where excimer fluorescence is observed along with the monomer fluorescence emitted from the locally excited state, both excimer fluorescence and monomer fluorescence are enhanced by application of electric fields. The results show that the nonradiative decay process at the excimer emitting state is decelerated by application of electric fields. It is also found that the polarizability of pyrene excimer is larger than that of pyrene monomer by $\sim 270 \pm 90 \text{ \AA}^3$, based on the analysis of the Stark shift of the excimer fluorescence spectra.

3. Electric field effects on exciplex formation of methylene linked compounds of electron donor (D) and acceptor (A) in solution

Polarized E-PL spectra of homologous series of carbazole-(CH₂)_n-terephthalic acid methyl ester (C-(n)-P) (n=2-5, 10, 20) have been measured in decalin. The D-A system composed of carbazole and terephthalic acid acquires extensive charge transfer character following excitation of carbazole. Field-induced quenching in monomer fluorescence and Stark shift of the exciplex fluorescence spectrum were observed. Based on the analysis of the polarized E-PL spectra, the magnitudes of the dipole moment in the emitting state of both exciplex fluorescence and monomer fluorescence were estimated to be $\sim 19 \text{ D}$ and 6 D , respectively. The D-A distance dependence of the field-induced quenching of monomer fluorescence suggests that the intramolecular charge transfer process is affected by electric fields.

The present thesis reports the experimental determination of dipole moment and molecular polarizability of DAST microcrystals, pyrene excimer and fluorescent exciplex of C-(n)-P, based on the E-A and E-PL measurements. Electric field effects on dynamics of pyrene excimer and C-(n)-P exciplex are also discussed.