

Electrophotoluminescence spectra of pyrene solution

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[Introduction]

Electrophotoluminescence (E-PL) spectroscopy, which gives information about external electric field effects on photoluminescence (PL) spectra, is a useful method to examine the change in dipole moment and polarizability following electronic transitions and the electric field effects on excitation dynamics. In fact, E-PL measurements have been done for pyrene doped in a PMMA film, and the Stark shift and the electric field effects on excitation dynamics have been discussed [1-3].

In the present study, we have measured E-PL spectra of pyrene solution with a constructed measurement system. Field-induced enhancement of PL intensity and field-induced spectral shift of excimer fluorescence have been observed. On the basis of the E-PL measurements, the magnitude of the change in polarizability following emission process of pyrene excimer has been evaluated, and the field effect on excimer formation process is discussed.

[Experimental Section]

A benzene solution of pyrene was mixed with decaline by supersonic wave. This mixture was flowed in a home-made E-PL measurement cell. E-PL as well as PL spectra were measured using an electric-field modulation spectroscopy [4]. 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]

The observed E-PL and PL spectra of pyrene solution at a concentration of 5 mM are shown in Fig. 1. The spectra were obtained with a field strength of 0.2 MV/cm with photoexcitation at 325 nm, where the field-induced change in absorbance was negligibly small.

The PL spectrum of pyrene solution at 5 mM contains two emissions; monomer

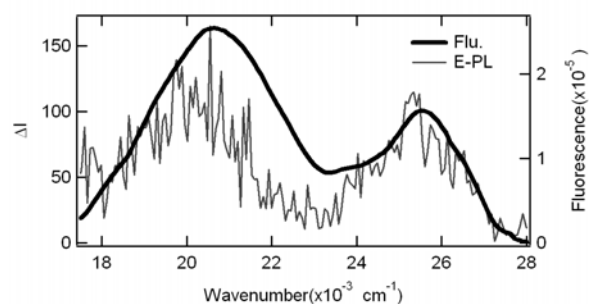


Fig. 1. Emission spectrum and E-PL spectrum of pyrene solution.

fluorescence emitted from the locally excited state of pyrene and excimer fluorescence. E-PL spectra of pyrene solution show that both monomer and excimer fluorescence are enhanced by applied electric field, but the field-induced change in quantum yield is different from each other. Besides the change in intensity, a red-shift of the excimer fluorescence spectrum was observed with application of electric fields.

E-PL spectra can be expressed as a sum of the zeroth, first and second derivatives of the emission spectra [5]. The zeroth derivative component is related to the field-induced change in excitation dynamics, and the first and second derivatives are related to the change in polarizability and dipole moment following the emission transition, respectively. As shown in Fig. 2, E-PL spectrum of pyrene solution could be simulated by a linear combination of the zeroth derivative of monomer and excimer fluorescence spectra and the first derivative of the excimer fluorescence spectrum. From the first derivative component of excimer fluorescence, the value of the difference in polarizability between the emitting state of excimer and the ground state was evaluated to be $\sim 250 \text{ \AA}^3$.

The quantum yield of monomer fluorescence relative to the excimer fluorescence can be expressed with a kinetic model under photostationary conditions. The observed E-PL spectra show that the above-mentioned relative quantum yield changes in the presence of electric field, indicating that the relaxation rate of excimer and/or excimer formation rate is affected by external electric fields. The details will be discussed in the presentation.

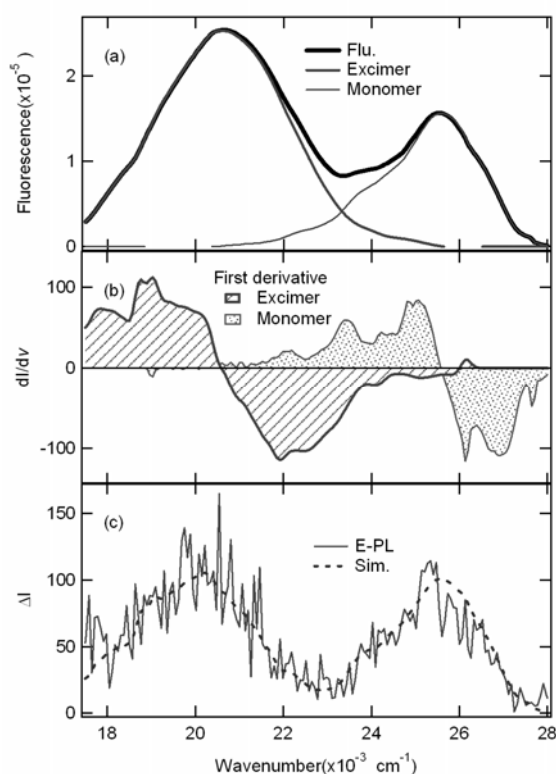


Fig. 2. (a).Fluorescence spectrum of pyrene solution 5 mM. (b) The first derivative spectra of fluorescence bands. (c) E-PL spectrum and the simulation.

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