

Electric Field Assisted Non-adiabatic Tunneling in Methylene Linked Phenanthrene-(CH₂)_n-Phthalimide as Revealed by Electrophotoluminescence

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[Introduction] Photoinduced electron transfer (PIET) rate is significantly affected by an electric field because of the field-induced change in free energy gap and in electronic coupling between the initial and final states of the electron transfer [1-3]. Intramolecular PIET reaction where the electron transfer occurs between donor (D) and acceptor (A) through the methylene chain provide unique information how the field-induced change in PIET rate depends on the D-A distance and the surrounding temperature. The so-called electro-photoluminescence spectroscopy (electric field-induced change in photoluminescence intensity measured as a function of wavelength) is powerful for investigating PIET dynamics. In the present study, we have examined the D-A distance and temperature dependence of the electric field effects on photoluminescence of methylene linked compounds of phenanthrene-(CH₂)_n-phthalimide (PH-(*n*)-PI) having different chain lengths (*n* = 1-5) in a PMMA film.

[Experimental] The sample films of PH-(*n*)-PI embedded in PMMA were deposited on indium tin oxide (ITO)-coated quartz substrates by a spin coating technique from benzene solution in which a mixture of PH-(*n*)-PI and PMMA with a weight ratio of about 1 to 50 was dissolved. The thickness of the sample was ~0.5 μm, measured with an interferometric microscope (Nano Spec/AFT-010-0180, Nanometric). Then a semitransparent aluminum (Al) film was deposited by vacuum deposition technique. The ITO and Al films were used as electrodes. Electric-field-induced changes in photoluminescence spectra were measured using the electric field modulation spectroscopy. Electromodulation of the photoluminescence intensity was induced by a sinusoidal ac voltage with a frequency of 40Hz. The field-induced photoluminescence changes were detected with a lock-in amplifier (SR830, SRS) at the second harmonic of the modulation frequency. Measurements at different temperatures were carried out by using cryogenic refrigerating system (Diakin V202C5LR).

[Results and Discussion] Photoluminescence (PL) and electrophotoluminescence (E-PL) spectra of PH-(1)-PI in a PMMA film were observed at T= 295 and 50 K, respectively (Fig. 1). The field strength was 1MV cm⁻¹. Excitation was done at the wavelength where the field-induced change

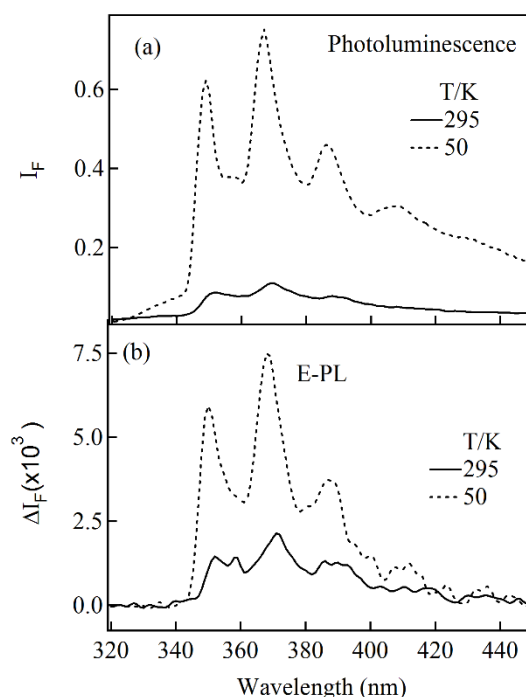


Fig. 1 Temperature dependence of PL and E-PL spectra of PH-(CH₂)₁-PI

in absorption intensity was negligible. The observed PL spectra, which show a well-defined vibrational structure, are assigned as the spectra emitted from the locally excited state of phenanthrene. The shape of E-PL spectra is very similar to the shape of PL spectra, indicating that the locally excited photoluminescence of PH-(1)-PI is enhanced by an electric field. The field-induced enhancement of PL at room temperature is ascribed to the field-induced reduction in the rate of intramolecular PIET.

The PL and E-PL spectra are essentially independent of the temperature, as far as the spectral shape is concerned [Fig. 1], and only the intensity increases as the temperature decreases. But, the field-induced-reduction rate of PIET, which was estimated from the ratio between E-PL and PL intensity at the peak of PL spectra (~370 nm), at first increases till the temperature 200K and then start decreasing with further decreasing the temperature; at 50K the field-induced reduction rate remains ~50% of at room temperature [Fig. 2], suggesting that the field-induced reduction rate of the intramolecular PIET become less efficient at low temperatures.

With a longer methylene chain ($n = 3$), at room temperature field-induced enhancement of the PL spectra was observed, but surprisingly the field-induced quenching of the PL was observed at 50K [Fig. 3]. The field-induced quenching of PL at low temperature is ascribed to the field-induced enhancement of the intramolecular PIET rate. With further increasing the methylene chain ($n = 5$), even at room temperature the electric field-induced quenching of PL was observed, and that quenching rate decreases as the temperature decreases.

A theoretical consideration has been done to understand the recent experimental results concerning the electric field-induced enhancement and quenching of PL spectra with respect to the donor-acceptor distance and temperature (a part of the result is shown in figure 2). The theoretical model predicts that the field assisted tunneling plays important role in the mentioned changes under the electric field.

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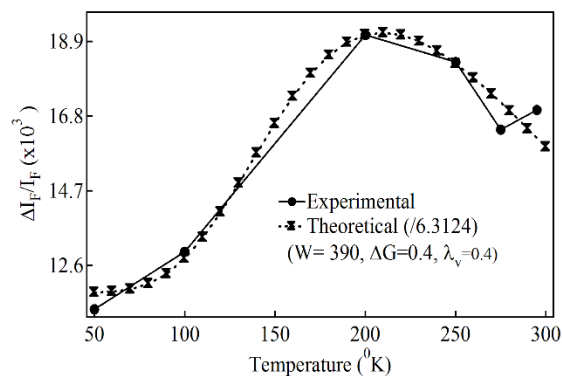


Fig. 2. Plots of $\Delta I_F / I_F$ as a function of temperature

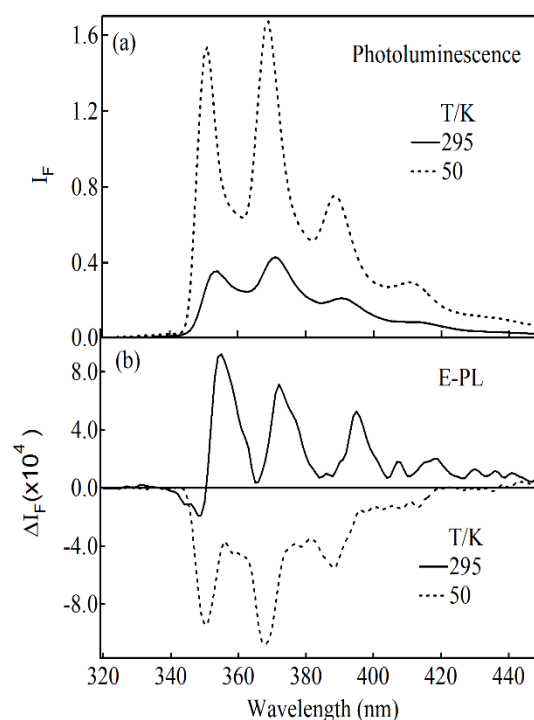


Fig. 3 Temperature dependence of PL and E-PL spectra of PH-(CH₂)₃-PI.