

2B02

Electric field effect on fluorescence in methylene linked compounds of pyrene and phthalimide: D-A distance dependence and temperature dependence

Kamlesh Awasthi, Tatsuo Hamada, Toshifumi Iimori, and Nobuhiro Ohta
Research Institute for Electronic Science (RIES), Hokkaido University

Introduction

Photoinduced electron transfer (PIET) rate is expected to be significantly affected by electric field because of the field induced change in free energy gap and electronic coupling between the initial and final states of the electron transfer. Intramolecular PIET reactions, where the electron transfer occurs between donor (D) and acceptor (A) through the linked methylene chain, provide unique information how the field-induced change of PIET depends on the D-A distance. The measurement of the so-called electroabsorption and electrofluorescence (E-F) spectra (electric field-induced change in absorption intensity and fluorescence intensity as a function of wavelength) is powerful for investigating PIET dynamics [1]. In the present study, we have examined both D-A distance dependence and temperature dependence of electric field effects on fluorescence of methylene linked compounds of pyrene-(CH₂)_n-phthalimide (PY-(n)-PI) having different chain lengths in a PMMA polymer film, i.e., $n = 1-3$.

Experimental

A certain amount of benzene solution of PMMA containing PY-(n)-PI was poured onto the indium tin oxide (ITO) - coated substrate by a spin coating technique. Then a semitransparent aluminum (Al) film was deposited by vacuum deposition technique. The ITO and Al films were used as electrodes. All the optical spectra were measured under vacuum conditions. Plots of field-induced change in fluorescence intensity (ΔI_F) were measured by using electric field modulation spectroscopy. A sinusoidal ac voltage was applied, and the value of ΔI_F was detected with a lock-in amplifier at the second harmonic of the modulation frequency. Measurements at different temperatures were carried out by using cryogenic refrigerating system (Diakin V202C5LR) where a cylindrical head with quartz optical window was used instead of normal cell. Measurements of the field-induced change in fluorescence decay profile were carried out by using a single-photon counting emission lifetime measurement system. The third harmonic of the output pulse from a mode-locked Ti:Sapphire laser (Spectra Physics) was used as an excitation light [2].

Results and Discussion

The fluorescence decay for PY-(n)-PI with ($n = 1-3$) shows a multiexponential decay, and the decay rate becomes slower with increasing the methylene chain length, as shown in Figure 1.

Fluorescence spectra and E-F spectra of PY-(2)-PI in a PMMA film at a concentration of 0.5 mol % were observed at $T = 295$ and 55 K (Figure 2). The applied field strength was 0.8 MVcm⁻¹. Excitation was done at the wavelength where the field-induced change in absorption intensity was negligible. The observed fluorescence spectra, which show a well-defined vibrational structure, are assigned as the spectra emitted from the locally excited (LE) state of pyrene. The shape of E-F spectra is very similar to the fluorescence spectra (Figure 2a), indicating that the LE fluorescence of PY-(2)-PI is enhanced by electric field. According to the pervious study [3, 4], the origin of the field-induced enhancement of fluorescence at room temperature is ascribed to either the field-induced change in efficiency of back electron transfer

through the methylene chain, which produced the fluorescence state of donor molecule, or the field-induced reduction in the rate of the intramolecular PIET. However, the mechanism of the electric field effect has not been clear yet.

The fluorescence spectra are essentially independent of the temperature, as far as the spectral shape is concerned, and only the fluorescence intensity increases as temperature decreases. This is probably because the nonradiative decay rate at the emitting state of LE fluorescence becomes smaller with decrease of the temperature. But the shape of the E-F spectrum at low temperature is essentially the same as the first derivative of the fluorescence spectrum (Figure 2b), suggesting that the field-induced change in fluorescence spectrum comes from the change in molecular polarizability following emission and that the fluorescence decay rate is not affected by an electric field.

With a long methylene chain ($n = 3$), on the other hand, the field-induced quenching of fluorescence was observed at room temperature. The field-induced quenching gradually increases by decreasing the temperature from 295 K to 50 K (Figure 3). The field-induced quenching of LE fluorescence is ascribed to the field-induced enhancement of the intramolecular PIET.

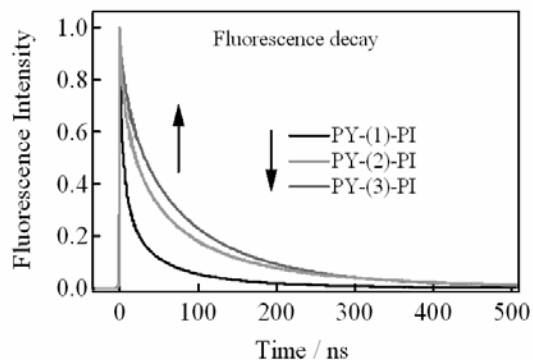


FIG. 1 Fluorescence decays of PY-(CH₂)_n-PI.

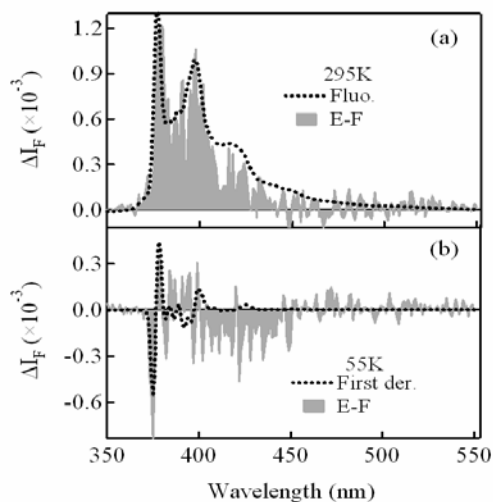


FIG.2 Temperature dependence of the electrofluorescence spectra of PY-(CH₂)₂-PI.

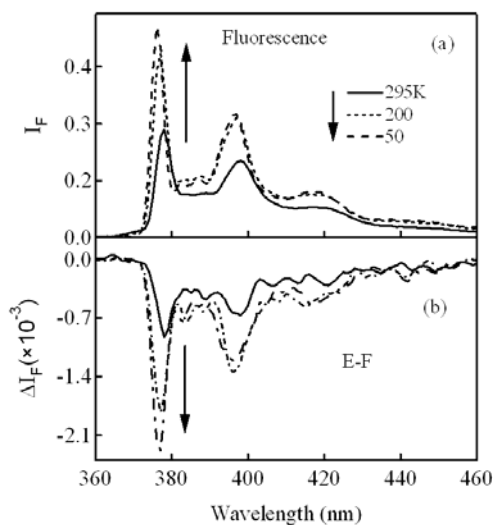


FIG.3 Temperature dependence of the fluorescence and E-F spectra of PY-(CH₂)₃-PI.

References

1. N. Ohta, Bull. Chem. Soc. Jpn. 2002, 75, 1637.
2. M. Tsushima, et.al. Rev. Sci. Instrum. 2004, 75, 479.
3. H. Kawabata, et.al. J. Chem. Phys. 2001, 114, 7723
4. M. Hilczer, M. Tachiya, J. Chem. Phys. 2002, 117, 1759.
5. K. Awasthi et. al. J. Phys. Chem. A, 2008, 112, 4432.