

EXTERNAL ELECTRIC FIELD EFFECTS ON PHOTOCHEMICAL PROCESSES OF PYRENE AND ITS RELATED COMPOUNDS IN THIN SOLID FILMS

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External electric field effects on photochemical processes such as an excimer formation have been examined on pyrene and its related compounds doped in a PMMA polymer film with a homogeneous distribution and deposited in an Langmuir-Blodgett (LB) film with a well-defined molecular order, based on the measurements of the electroabsorption (EA) spectra and the electrofluorescence (EF) spectra using electric field modulation spectroscopy; plots of the field-induced change in fluorescence intensity as a function of wavelength as well as plots of the field-induced change in absorption intensity were measured.

Experiments were carried out with pyrene (denoted by Py), 1,3-bis-(1-pyrenyl)propane (denoted by Py-Py) and 16-(1-pyrenyl)hexadecanoic acid (denoted by Py-(CH₂)₁₅-). A polymer film which contains Py or Py-Py was cast on the ITO-coated quartz substrate by a spin coating method. Then, a semitransparent aluminum (Al) film was deposited on the polymer film. Several mixed LB monolayer films composed of Py-(CH₂)₁₅- and stearic acid were deposited with a monolayer spacer composed of fatty acids, following the deposition of the multilayer LB films of fatty acids on the Al-coated quartz plate. More than twenty monolayer films of fatty acids were post coated to protect the mixed LB films, and then a semitransparent Al film was deposited. ITO and Al films were used electrodes. The field induced change in fluorescence intensity and in absorption intensity was measured with an electric field modulation apparatus at the first harmonic and at the second harmonic of the modulation frequency of the applied AC voltage. The procedures are the same as described elsewhere [1,2].

Figure 1 shows EF spectra of Py doped in a polymer film at different concentrations, together with the fluorescence spectra. At low concentrations, only the fluorescence emitted from the locally excited state of Py (monomer fluorescence) is observed, and the EF spectra of the monomer are given by the first derivative of the fluorescence spectrum, indicating that the field effect comes from the Stark shift induced by a change in molecular polarizability between the emitting state and the ground state [3]. At high concentrations, broad excimer fluorescence with a peak at ~470 nm, which is assigned as a sandwich-type excimer (the first excimer) appears, and the EF spectra of the monomer become closer in shape to the corresponding fluorescence spectra with a negative sign, indicating that the quantum yield of the monomer fluorescence is decreased by an electric field (F) at high concentrations [4]. In contrast with the monomer fluorescence, broad fluorescence with a peak at 415 nm, which is assigned as a partially overlapping excimer (the second excimer), is enhanced by F , indicating that the formation yield of the second excimer is enhanced by F . In contrast with the second excimer, the first excimer fluorescence is quenched by F ,