

Exciton diffusion and excimer formation dynamics of perylene in polymer films

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Pyrene or perylene-dispersed films have been paid attention recently as color-tunable emissive materials[1]. In this work, the photo-relaxation processes in perylene-dispersed PMMA films were studied by fluorescence up-conversion(UPC) and time-correlated single photon counting (TCSPC) spectroscopy. Film samples were prepared by spin-casting of CHCl_3 solutions containing different weight ratios (<0.01 wt% to 10 wt%) of perylene and PMMA.

While a 5 wt% dispersed film exhibited only broad excimer emission at around 550nm (Fig. 1), intense emission from S_1 of perylene monomer was observed at around 450 nm in time-resolved emission spectra. The monomer emission was then decayed within 200ps, followed by the rise of excimer emission. The decay rate of the monomer emission increased with increasing dispersion density. Time-resolved fluorescence anisotropy at 450nm for a 3 wt% film (Fig. 2) showed biexponential decay with 46 ps and ~ 3 ns time constants. The former time constant, decreasing with the dispersion density, corresponds to energy migration of free monomer exciton while the latter, almost independent of the concentration, would be due to self-trapped exciton.

Assuming that free excitons are quenched by small amount of perylene dimer sites, the temporal profiles of the monomer emission decay were analyzed using the Smoluchowski's diffusion-controlled reaction model [2]. With consideration of the presence of small amount of self-trapped excitons, the observed temporal profiles were well reproduced by the diffusion-controlled reaction model using the diffusion constants determined from the anisotropy (red line in Fig. 3).

[1] Pujari, S. R. *et al.*, *Mater. Res. Bull.*, **2002**, 37, 1641; Ito, F. *et al.*, *J. Phys. Chem. B*, **2013**, 117, 3675. [2] Naqvi, K. R. *et al.*, *J. Phys. Chem. B*, **2000**, 104, 12035.

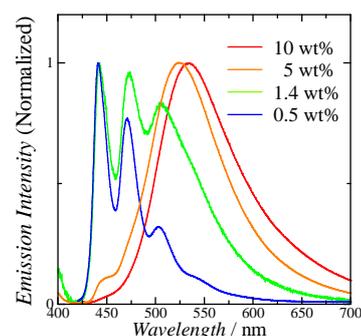


Figure 1. Emission spectra for perylene/PMMA films with various perylene density ($\lambda_{\text{ex}}=405$ nm)

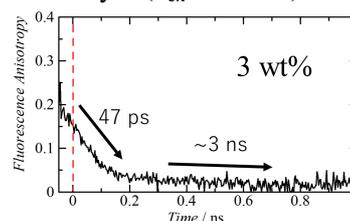


Figure 2. Temporal profiles of fluorescence anisotropy for monomer excitons for 3 wt%

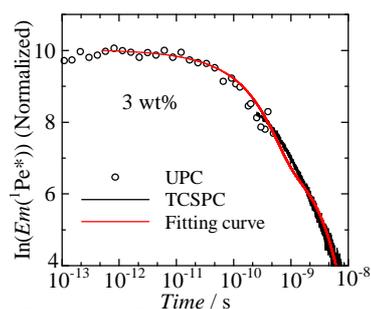


Figure 3. Temporal profiles of emission intensity of perylene monomer in a 3 wt% film and fitting curve using the Smoluchowski's model.