

## Ultrafast Energy Transfer Dynamics Between Block Copolymer and $\pi$ -Conjugated Polymer

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The quantum efficiency of the blended polymeric system consisting of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and a conjugated-nonconjugated multi-block copolymer (CNMBC), poly[1,3-propane-dioxy-1,4-phenylene-1,2-ethylene-(2,5-bis(trimethylsilyl)-1,4-phenylene)-1,2-ethylene-1,4-phenylene] (DSiPV) is several times higher than that of the constituent polymers, which is explained in terms of the Förster energy transfer theory[1]. But the ultrafast photoexcitation dynamics of MEH-PPV and of the blended polymer consisting of MEH-PPV and DSiPV using the time-resolved fluorescence and femtosecond transient absorption spectroscopic techniques[2] suggests that other mechanisms should be involved.

No apparent change in the absorption spectrum of the blended polymer (MEH-PPV:DSiPV = 6:4 mass ratio) compared to those of MEH-PPV and DSiPV indicates that neither chemical nor conformational change has occurred upon mixing. Their time-integrated photoluminescence (PL) spectra show that upon blending, the emission from DSiPV disappears while that from MEH-PPV predominates with a slight red-shift of the emission maximum (Fig.1). The red-shifted PL spectrum and the disappearance of the stimulated emission (SE) in the transient absorption spectrum (Fig.2) of the blended polymer clearly indicates that two different emissive states play roles in the relaxation process of the primary photoexcitations in MEH-PPV thin films. If the nature of the photoexcitations in blended polymeric system resulting from the exciton migration were the same as that in homopolymeric system, i.e., singlet polaronic excitons, a prominent SE signal would have been observed in the transient absorption spectra.

Fig.3(a) shows the temporal decay profiles of the transient absorption signals of MEH-PPV. The temporal profiles of bleaching and SE signals exhibit double exponential decay with detectable rise time at all probe wavelengths except at 440 nm, the emission maximum of DSiPV. The overall decay profiles of MEH-PPV:DSiPV (6:4) also represent double exponential decay (Fig.3(b)). However, an additional ultrafast decay component ( $\tau = 350$  fs) is clearly observed at 440 nm only, which corresponds to the SE of DSiPV, and consequently, the decay of the singlet polaronic excitons produced in DSiPV. This result suggests that the energy transfer from DSiPV to MEH-PPV in the blended polymer is one of the decay process of excitons generated in DSiPV units and that this energy transfer process is responsible for the observed ultrafast decay time constant.

Assuming that the energy transfer in blended polymer occurs thoroughly through Förster type