Exciton Diffusion To Interfaces In Polymer Solar Cells

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Conjugated polymers are an important class of organic semiconductor, and are promising for a range of optoelectronic applications. They combine novel semiconducting properties with the simple processing properties of polymers, opening up the possibility of making semiconducting devices by simple techniques such as spin-coating or printing. Polymer light-emitting diodes and solar cells are being developed and in both cases interfaces play a crucial role in the device operation.

There are three key steps in the operation of a semiconducting polymer solar cell. The first is absorption of light, the second is charge separation, and the third is charge transport to the contacts. The second step is very important in conjugated polymers because their photoexcitations are mainly neutral species, and it is usually achieved at an interface with a strong charge acceptor. The resulting charge transfer leads to a quenching of luminescence. The rate of charge transfer can therefore be studied by time-resolved luminescence.

We report a systematic study of time-resolved luminescence in conjugated polymer structures relevant to solar cells. Samples were excited at 425 nm by the frequency-doubled output of a modelocked Ti:sapphire laser, and the photoluminescence (PL) was detected by a streak camera. We find that the rate of charge transfer is determined by exciton diffusion to the charge-accepting interface.

The exciton diffusion coefficient is therefore an important quantity for the understanding and optimization of solar cells. When combined with the measured lifetime (also measured by time-resolved luminescence measurements) it gives the exciton diffusion length i.e. the distance over which the exciton can diffuse to an interface and undergo charge separation. We report two approaches to measuring exciton diffusion lengths and apply them to poly(3-hexyl thiophene) and MEH-PPV.

In the first approach the photoluminescence decay kinetics are measured as a function of the film thickness for a polymer film on an indium tin oxide (ITO) or titanium dioxide substrate, which acts as a quencher. Polymer films on silica substrates were measured for comparison. The PL decay is faster on ITO and faster still for thinner films. The decays can be modelled in terms of exciton diffusion to the interface. For MEH-PPV, the lifetime is approximately 300 ps, and the diffusion coefficient leads to a diffusion length of approximately 30 nm.

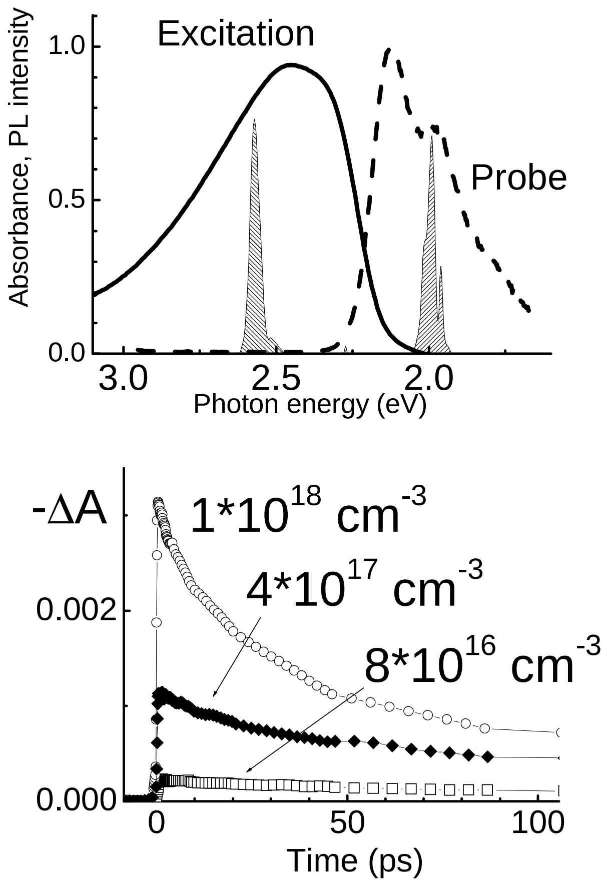

Figure 1: Upper panel – Steady state absorption and photoluminescence spectrum of MEH-PPV. Lower panel - time-resolved photoluminescence in MEH-PPV for a range of excitation densities.

At high excitation densities, exciton-exciton annihilation occurs, leading to a very rapid decay of PL. This provides a second approach to measuring exciton diffusion rates. We observe a faster decay at higher excitation density, and can fit the data to extract the exciton-exciton annihilation coefficient and hence the diffusion coefficient. The information that is obtained from these results complements the first approach. Exciton diffusion in different materials will be compared and related to complementary measurements including spectroscopic ellipsometry.