

Probing time resolved charge-transfer-exciton recombination in organic solar cells by time-gated spectroscopy

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Application Note

Introduction

Organic solar cells are a promising technology for thin-film based photovoltaics, because of the low costs of production and the potential for high efficiencies. Solution processing and thermal evaporation are considered relevant with some of the best efficiencies scored by solution processed polymer/fullerene blends. This type of cells relies on the photoinduced charge transfer occurring between the light harvesting conjugated polymer and the strong acceptor fullerene. Among the different recombination mechanisms in organic solar cells the photoluminescence (PL) of charge transfer excitons (CTEs) has been identified as one of the most important, impacting both the open circuit voltage and the short circuit current [1]. While studies on recombination were performed using transient absorption spectroscopy, the recent observation of luminescence from CTEs or exciplexes at the polymer/fullerene interface allows for using a new probe to investigate recombination and its dynamics [2-4]. We expect that experimental facilities capable of probing the dynamics of this photoluminescence emission will give new insights for the development of more efficient organic solar cells. Here, we present a report on the dynamics of recombination in blends of the conjugated polymer poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) and the fullerene derivative [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM). We describe in detail the experimental facilities for time resolving the decay of the CTE PL.

Experimental Setup

Time resolved PL transients were obtained with an intensified charge coupled device camera (ICCD) Andor iStar detector DH740-18U-93 coupled to a single grating monochromator (Acton SP2300i) with three gratings blazed at 150 g/mm, 300 g/mm and 1200 g/mm. Laser excitation is provided by a pulsed nitrogen laser $h\nu = 3.68$ eV (337 nm), 500 ps, 50 Hz repetition rate or the second harmonic ($h\nu = 3.1$ eV (400 nm)) from a Ti:sapphire amplified laser with repetition rate of 50 kHz. Time resolved transients are obtained by triggering the iStar camera from the lasers and by time gating the detection with variable time-windows (from 2 up to 100 ns) and by sequentially delaying the detection in time in steps of 1 ns. Samples consisting of thin films are mounted in vacuum inside a cryostat. A scheme of the setup is shown in figure 1a. Figure 1b shows a picture of the camera coupled to the monochromator and the optical components to perform time resolved PL.

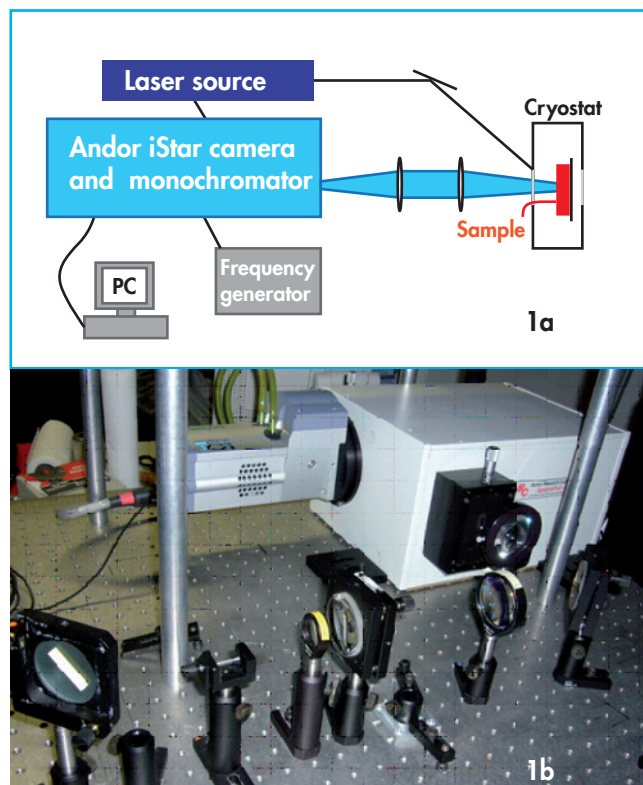


Figure 1 (a) Experimental setup scheme for time resolved PL spectroscopy of charge transfer excitons in organic solar cells. 1(b) picture of the setup showing the optical components for collection of PL and the monochromator/iStar CCD detection system.

Application in time resolved photoluminescence

Figure 2a shows an energetic scheme of the excitonic states in a polymer fullerene solar cells together with a representative PL spectrum of a MDMO-PPV/PCBM blend displayed on the right hand side. The singlet exciton levels are indicated as S1 and are expected to be localized in the domains of the pure polymer and fullerene. At the interface CTE states are formed and eventually can lead to radiative recombination. It has been shown that the energy of CTE transitions is correlated with the energy difference between the lowest unoccupied molecular orbital of the fullerene (LUMO) and the highest occupied molecular orbital (HOMO) of the polymer [1]. Therefore, PL emission bands are expected to appear in the NIR region of the spectrum where the iStar DH740-18U-93 has sensitivity. The PL spectrum of the blend shown in Fig. 2 exhibits three prominent peaks which have been assigned to the excitonic transitions of the pure materials and to the CTE emission (hatched green area) [4].

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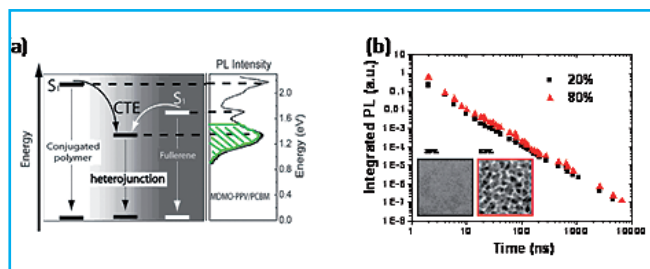


Figure 2. (a) Excitonic energy scheme for a blend of a conjugated polymer and a fullerene derivative. (b) Time resolved PL spectrum of CTE in two different blends of MDMO-PPV/PCBM differing in the weight percentage of PCBM, the inset show the morphology studied by electron microscopy.

In figure 2 we report the time evolution of the PL integrated in a photon energy interval from 1.1 to 1.4 eV, thus detecting emission from the CTE. The data points recorded with a time gated detection scheme are displayed on a double logarithmic plot. This type of representation is particularly useful for identifying power-law decays. The data span more than three orders of magnitude both in PL intensity and time, thus providing a clear evidence of a power-law decay, $I_{PL} \sim t^{-\alpha}$. This data can be obtained thanks to the high dynamic range of the camera even when detecting weak PL signals such as those from CTE in polymeric solar cells.

Conclusions

We have investigated the decay dynamics of CTE in MDMO-PPV/PCBM blends by means of a infrared sensitive iStar time gated camera. On a long time scale, which is relevant for the time scales of carrier extraction in solar cells, the decays are characterized by power-laws. The results are of interest in the design of materials with reduced recombination and therefore higher power conversion efficiencies.

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