

# Delayed emission of charge-transfer states in organic solar cells

F. Laquai, Max-Planck-Institute for Polymer Research, Mainz (December 2010)

## Introduction

Organic solar cells have recently attracted tremendous attention, as organic semiconductors can easily be processed from solution and thus allow low-cost production of large area photovoltaic elements. However, the photophysical processes leading to charge generation and in particular the efficiency-limiting charge recombination processes are not yet entirely understood.

The active layer of an organic solar cell is only 100 nm thin and usually consists of a blend of two components, an electron donor and an electron acceptor material, that create a so called bulk heterojunction. After excitation with light, the excited state (exciton) diffuses to the interface where charge transfer and subsequent charge separation occurs. The free charges contribute to the photocurrent of the solar cell. However, loss processes limit the efficiency. For example, the charge-transfer state generated at the interface can return to the ground state and free charges can recombine again, if they encounter each other. As these processes are partly emissive, they can be analyzed with time-resolved photoluminescence spectroscopy.

## Problem definition

By definition, an organic solar cell is supposed to absorb as much light as possible without emitting any. Each emitted photon corresponds to the loss of a charge carrier in the solar cell, and thus decreases the photocurrent. Actually it can be seen that particularly the charge-transfer states generated at the interface partially emit. However, the emission is weak and barely detectable under cw-excitation, as often the regular prompt photoluminescence of the organic materials is also detected.

With sensitive iCCD cameras that also cover the red spectral range, the longer lasting, delayed emission of the charge-transfer states can be monitored separated from the prompt luminescence of the materials. Furthermore, an analysis of the emission dynamics is possible with time-resolved systems.

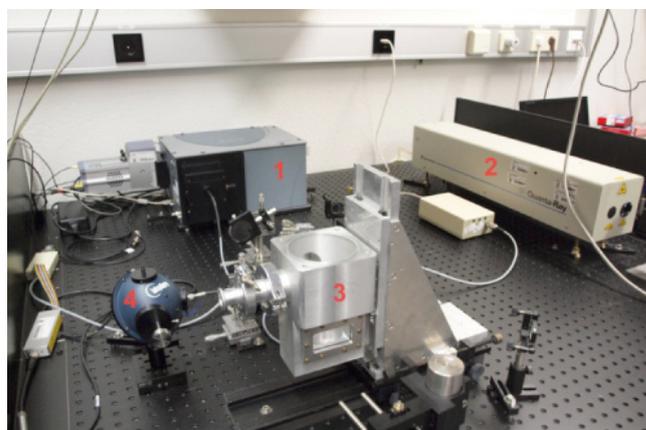
In the Max Planck Research Group for Organic Optoelectronics at the Max-Planck-Institute for Polymer Research, Dr. F. Laquai and his team members analyze the processes in organic solar cells with time-resolved optical spectroscopy. We use an Andor DH740-18U-73 iStar ICCD camera for the analysis of the emissive recombination of charge-transfer states.

## Application Note

The camera has convinced us by its wide spectral range, high time resolution and user-friendly handling.

## Test setup

A picture of the test setup is shown in pic. 1. To avoid a reaction with oxygen, the investigated samples (thin films of the organic material on quartz glass) are held under high vacuum in a self-built cryostat (3). The samples are either excited by a ns-pulsed Nd:YAG laser (2) or by the output of an optical parametric oscillator (OPO) that is pumped by the Nd:YAG and tunable in the visible range. The light emitted by the samples is collected by two achromatic lenses (telescope) and a system consisting of a spectrograph type Shamrock SR303i-B and ICCD camera (1) (both by Andor). Additionally, we can measure the photoluminescence quantum efficiencies of thin films with an integrating sphere and special fiber optics (4). We use the Andor software Solis for the data collection and Origin by OriginLab for the data analysis.



Pic. 1: The experimental setup for time-resolved photoluminescence spectroscopy.

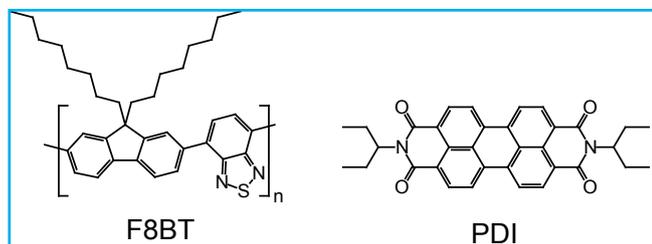
(1) Shamrock SR-303i spectrograph with Andor iStar DH740-18U-73 ICCD camera, (2) Nd:YAG laser (Spectra-Physics) with OPO (GWU, not shown), (3) self-built high-vacuum sample chamber, (4) integrating sphere (Labsphere) for quantum efficiency measurement with special fiber for Andor SR-303i spectrograph.

## Results

In this note, we will present selected results as an example of the experiments that we have recently published in collaboration with a partner [1, 2]. The experiments were performed on a donor polymer (polyfluorene copolymer) and a low-molecular electron acceptor (perylene diimide derivative, PDI). (See pic. 2a for the structures.)

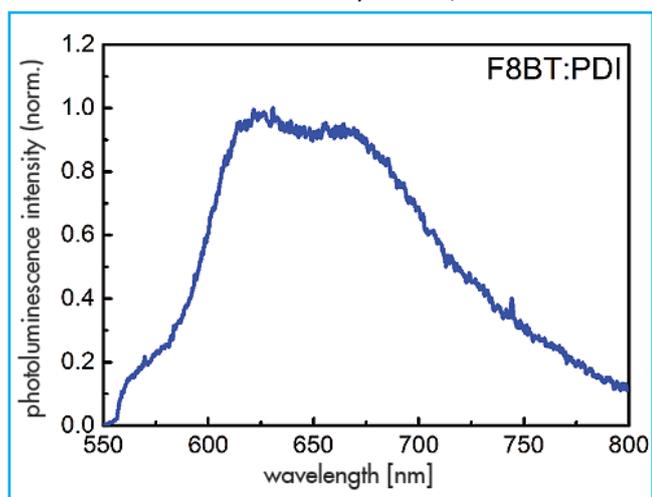
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Pic. 2a: Chemical structure of the polyfluorene copolymer (F8BT) and perylenediimide (PDI)

This system is of relevance for both organic solar cells and photodetectors [3]. We evaluated the prompt and delayed photoluminescence of the individual components and the blend of both components in thin films with our experimental setup (Shamrock SR303i-B and iStar DH740-18U-73 – both by Andor).

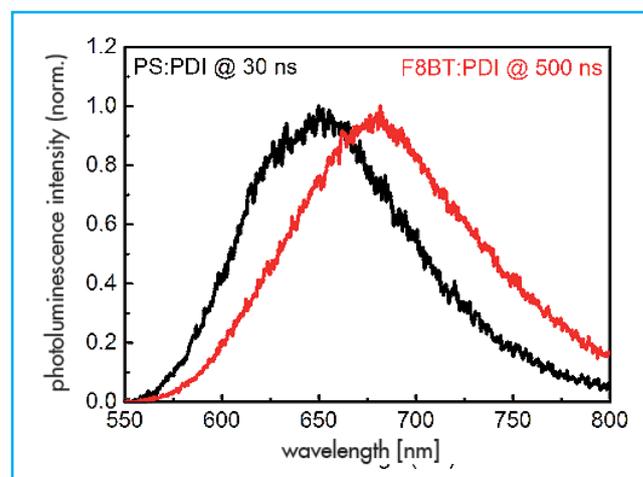


Pic. 2b: photoluminescence spectrum (not time-resolved) of a blend of both materials in thin film

Pic. 2b shows the cw-photoluminescence spectrum of the blend. The spectrum is broad and sparsely structured. It shows a broad tail in the red (>670 nm) of which we initially only assumed that it could be the emission of the charge-transfer states at the interface between polymer and acceptor. However, a precise determination of the emission in this spectrum is impossible, as the prompt fluorescence of the polymer interferes with other emissions. Furthermore, it is known that PDI aggregates in film causing a typical broad emission that can also be detected. Hence, in a cw-spectrum at least 3 different emission spectra overlap.

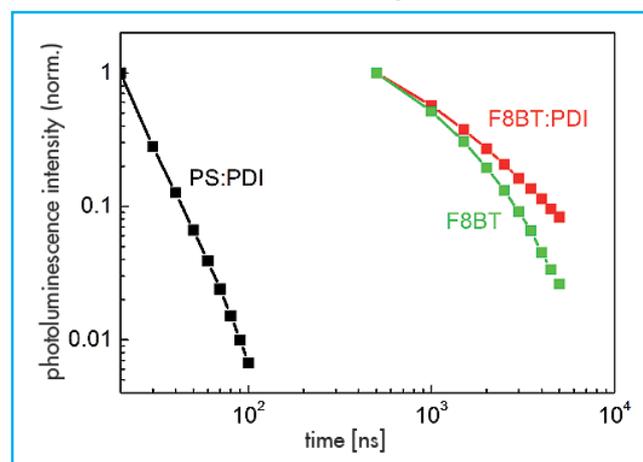
## Application Note

Time-resolved photoluminescence spectroscopy allows monitoring the emission of individual states, since the excited states have different lifetimes. The Andor iStar ICCD camera allows recording individual PL spectra with pre-defined delay times and selectable integration times. In the "kinetic mode", a series of (delayed) spectra can be recorded in certain time intervals to track the emission dynamics.



Pic. 2c: delayed photoluminescence spectrum of PDI in polystyrene (PS) (passive matrix) and PDI in F8BT (active matrix)

Pic. 2c shows delayed spectra of PDI in an electronically inactive matrix (polystyrene, 30 ns delay) and in the active matrix (polyfluorene copolymer, 500 ns delay). Clearly, the maxima are in different positions. Using a kinetic series the lifetime of the signals was determined.



Pic. 2d: chronological sequence of the photoluminescence of PDI in PS (black), PDI in F8BT (red) and F8BT as individual material (green) in comparison

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Pic. 2d shows the signal intensities as a function of time. The red-shifted signal that can be seen in the active matrix has a longer lifetime than the signal observed from the inactive matrix. For comparison, the pristine polymer was also measured, to exclude that the signal originates from the delayed fluorescence of the polymer itself.

The experiment clearly shows that the red-shifted emission of the blend of both components (F8BT:PDI) originates from charge-transfer states at the interface, as this type of emission could not be detected for the individual components. Furthermore, the emission was detected with comparatively long delays (longer than the lifetimes of charge transfer states initially generated) which means that it has to be the emission of charge-transfer states generated by the delayed recombination of free charges.

For the first time, these experiments allow an insight into the photo physical processes of the evaluated donor-acceptor system. The results are of high relevance for the understanding of loss processes in organic solar cells and photo detectors.

Last but not least we would like to point out that we are very happy with the performance of the Andor iStar DH740-18U-73 IDDC camera. It impressed us by its easy handling, very good time resolution and great sensitivity over a broad range. We are currently expanding our experiments to other donor-acceptor-systems.

## Application Note

### Literature

- [1] P.E. Keivanidis, V. Kamm, C. Dyer – Smith, W. Zhang, F. Laquai, I. McCulloch, D.D.C. Bradley, J. Nelson, "Delayed luminescence spectroscopy of organic photovoltaic binary blends: probing the emissive non-geminate charge recombination", *Adv. Mater.* 2010, 22 (45), 5183-5187.
- [2] I.A. Howard, F. Laquai, P.E. Keivanidis, R.H. Friend, and N.C. Greenham, "Perylene Tetracarboxydiimide as an Electron Acceptor in Organic Solar Cells: A Study of Charge Generation and Recombination", *J. Phys. Chem. C* 2009, 113 (50), 21225-21232.
- [3] P. E. Keivanidis, I. A. Howard, R. H. Friend, *Adv. Funct. Mater.* 2008, 18, 3189.

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