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Article

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The Role of Polymer Fractionation in Energetic Losses and Charge Carrier Lifetimes of Polymer: fullerene Solar Cells

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Abstract

Non-radiative recombination reduces the open-circuit voltage relative to its theoretical limit and leads to reduced luminescence emission at a given excitation. Therefore it is possible to correlate changes in luminescence emission with changes in open-circuit voltage and in the charge carrier lifetime. Here we use luminescence studies combined with transient photovoltage and differential charging analyses to study the effect of polymer fractionation in indacenoedithiophene-*co*-benzothiadiazole (IDTBT):fullerene solar cells. In this system, polymer fractionation increases electroluminescence emission at the same injection current and reduces non-radiative recombination. High molecular weight and fractionated IDTBT polymers exhibit higher carrier lifetime-mobility product compared to their non-fractionated analogues, resulting in improved solar cell performance.

Introduction

In polymer:fullerene solar cells, the open-circuit voltage (V_{oc}) is usually limited by recombination at the interface between donor and acceptor. Thus, it varies with the energy difference between the highest occupied molecular orbital of the donor ($HOMO_D$) and the lowest unoccupied molecular orbital of the acceptor ($LUMO_A$).[1-3] In practice the $HOMO_D$-$LUMO_A$ difference is insufficient to predict V_{oc} due to differences in non-radiative recombination.[4] The highest possible V_{oc}, denoted $V_{oc,rad}$, can be achieved when only radiative recombination occurs and the absorbed photon flux is balanced exactly by the emitted flux under open-circuit

conditions; this is called the radiative limit.[5-10] In a practical solar cell both V_{oc} and the LED quantum efficiency, Q_{LED}, are reduced relative to their thermodynamic limits by non-radiative recombination pathways, the degree of which can be quantified via a reciprocity theorem.[11-17] Therefore, it is of high interest in the field of organic photovoltaics to reduce these non-radiative recombination losses, thereby bringing the V_{oc} closer to the radiative limit. Recently, indacenodithiophene (IDT) copolymers have shown promising field-effect transistor mobilities and solar cell performance.[18-22] Enhanced co-planarity of the polymer backbone has been hypothesized to lead to reduced energetic disorder.[23,24] IDT-*co*-benzothiadiazole polymers have achieved up to 6.5% PCE with device optimization and material purification.[25] The role of polymer molecular weight on solar cell performance has been well studied[25-29]; however, the detailed analysis of the recombination processes in fractionated polymer devices remains comparatively unexplored.[29,30]

In this work, we describe how fractionation has an impact on energetic losses and charge transport in IDTBT: $PC_{70}BM$ bulk-heterojunction (BHJ) solar cells. In particular, we use the reciprocity relation between non-radiative recombination and electroluminescence to explain the reduced energetic losses in IDTBT-HM_w: $PC_{70}BM$ solar cells induced by fractionation and higher molecular weight by combining electroluminescence spectroscopy (EL) and Fourier-transform photocurrent spectroscopy (FTPS). The degree of non-radiative recombination, defined as the difference between $V_{oc,rad}$ and V_{oc} and denoted ΔV_{oc}, is found to reduce upon fractionation and with increasing molecular weight. Furthermore, for the same system, we analyze the origin of enhanced photocurrent in terms of charge carrier lifetime and mobility using transient photovoltage (TPV), differential charging, charge extraction (CE) at short circuit and photo-induced charge carrier extraction by linearly increasing voltage technique (photo-

CELIV) measurements. The combination of mobility and lifetime measurements shows that the mobility-lifetime product, which determines charge-carrier collection, is enhanced for the case of high molecular weight devices relative to devices made with low molecular weight and non-fractionated polymers.

Results and Discussion

We studied films and devices made from three IDTBT polymers; IDTBT-NF is not fractionated, and IDTBT-LM_w and IDTBT-HM_w are the low and high molecular weight fractions. The gel permeation chromatography traces and molecular weight information are presented in Figure S1 and Table S1, respectively.

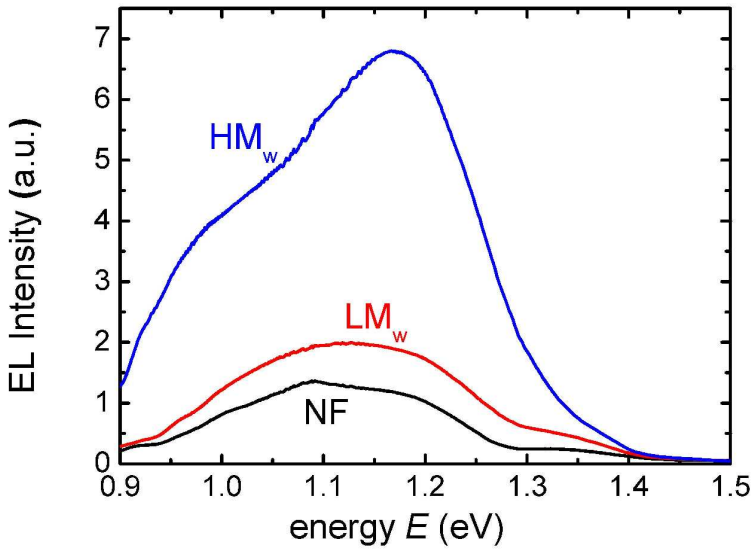

Figure 1 Electroluminescence spectra of IDTBT: $PC_{70}BM$ blend devices at the same current injection of 100 mA cm^{-2}.

Figure 1 shows the electroluminescence (EL) of IDTBT:$PC_{70}BM$ blend devices, with active layer thicknesses of 75 ±5 nm, was measured under a constant current injection density of 100 $mAcm^{-2}$; the spectral shape of some samples was checked for a range of injection currents down to 22 mA cm^{-2} and was found to be independent of current.[31] The EL intensity increased from the IDTBT-NF: $PC_{70}BM$ blend to the IDTBT-HM_w: $PC_{70}BM$ blend at the same current injection indicating a relatively higher emissive quantum yield for the charge transfer (CT) state for IDTBT-HM_w:$PC_{70}BM$ devices. It can be shown (see the Supporting Information for details) that the voltage loss ΔV_{oc} due to non-radiative recombination can be related to the LED quantum efficiency Q_{LED} via

$$\Delta V_{oc} = V_{oc,rad} - V_{oc} = -\frac{kT}{q}\ln[Q_{LED}]. \quad (1)$$

Here, $V_{oc,rad} \approx kT/q \ln(J_{sc}/J_{0,rad})$ is the radiative limit to the open-circuit voltage, J_{sc} is the device short circuit current density, $J_{0,rad}$ is the saturation current density for radiative recombination and T is the temperature (300 K). The radiative saturation current density ($J_{0,rad}$), is defined as the current due to blackbody radiation (ϕ_{bb}), and can therefore be calculated according to:

$$J_{0,rad} = q.\int_0^\infty EQE_{PV}(E).\phi_{bb}(E)dE \quad (2)$$

where EQE_{PV} is the photovoltaic external quantum efficiency. Similarly, J_{sc} is defined in terms of the solar flux density (ϕ_{sun}):

$$J_{sc} = q. \int_0^\infty EQE_{PV}(E). \phi_{sun}(E) dE \quad (3)$$

At the radiative limit, all the charges recombine radiatively, so the current at short-circuit must be balanced by the radiative current at open-circuit.

We investigated EQE_{PV}, the spectral photovoltaic external quantum efficiency, using FTPS measurements on the same devices in order to determine $V_{oc,rad}$ and hence ΔV_{oc} through the reciprocity relations outlined in the Supporting Information. Figure 2 depicts the experimental EQE_{PV} (solid lines) for blend devices made from IDTBT-NF (Figure 2a), IDTBT-LM_w (Figure 2b) and IDTBT-HM_w (Figure 2c) with $PC_{70}BM$. For comparison, ϕ_{EL}/ϕ_{bb}, the ratio of the emitted photon flux ϕ_{EL} obtained from electroluminescence for each device to the photon flux ϕ_{bb} expected for a room-temperature black body at the same photon energy, which by reciprocity is another measure of EQE, is also plotted (dashed lines). In all cases polymer absorption is visible at high energies followed by the distinct absorption shoulder of the $PC_{70}BM$ at around 1.8 eV. Below the fullerene absorption shoulder, there is a low energy absorption in the spectrum likely representing the CT state absorption at around 1.40-1.45 eV for IDTBT: $PC_{70}BM$ blends. EQE_{PV} at lower photon energies is estimated from ϕ_{EL}/ϕ_{bb}, which follows experimental EQE_{PV} faithfully at higher energies, as expected from reciprocity.

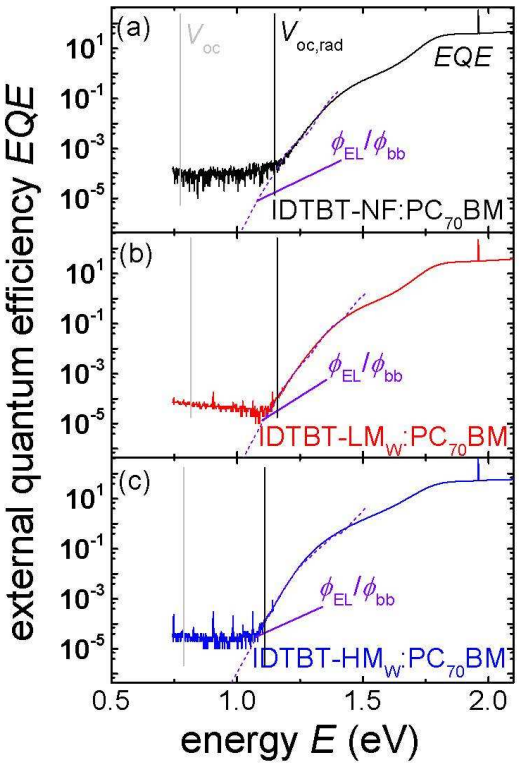

Figure 2 Semi-logarithmic plots of experimental photocurrent external quantum efficiency (EQE_{PV}, solid lines) and calculated EQE_{PV} from EL (dashed lines) as a function of energy for IDTBT-NF/LM$_w$/HM$_w$: PC$_{70}$BM blends (a,b and c respectively).

Table 1 summarizes the values measured and calculated from FTPS and EL measurements. Interestingly, the IDTBT-HM$_w$ device showed the lowest $V_{oc,rad}$ value of 1.11 V, with values of 1.15 and 1.16 V determined for –NF and –LM$_w$ devices respectively. It should be noted that the radiative open-circuit voltage depends on the energetic dependence of EQE_{PV} and so the value of $V_{oc,rad}$ on its own does not indicate merit, but rather the difference between this value and the experimental V_{oc} is pertinent. This ΔV_{oc}, defined by Eq. (1) using Eq. (2) and (3), is found to be 0.37, 0.35 and 0.32 V, for IDTBT-NF, -LM$_w$ and -HM$_w$, respectively. As seen from Table 1, the IDTBT-HM$_w$: PC$_{70}$BM blend yields the lowest radiative open-circuit voltage and the smallest

ΔV_{oc} compared to -LM_w and -NF blends. In addition, the non-fractionated IDTBT-NF: $PC_{70}BM$ system has the smallest measured V_{oc} and highest ΔV_{oc} indicating enhanced non-radiative recombination in the system. Note that according to Eq. (1), the EL quantum efficiency, obtained by integrating the EL spectrum, can also directly yield ΔV_{oc}: the system with the highest Q_{LED} value should correspond to the lowest ΔV_{oc}, since non-radiative recombination results in values of Q_{LED} less than 1. For polymer:fullerene solar cells the EL is dominated by CT emission with typical $Q_{LED} < 10^{-6}$, resulting in a loss in V_{oc} due to non-radiative recombination of over 0.36 V at room temperature.[32] In this experiment only relative EL flux densities were measured, so the differences in ΔV_{oc} between sets of two systems were calculated by dividing the two Q_{LED} values at the same current injection, i.e.

$$\Delta V_{oc2} - \Delta V_{oc1} = -kT \ln\left[{Q_{LED2}}/{Q_{LED1}}\right] \quad (2)$$

These values were found to agree well with the values calculated using FTPS and EL together (see Table S2).

The measurement of voltage losses indicates a decrease in non-radiative recombination upon increasing the molecular weight of the polymer, so we would expect this effect to be mirrored in the recombination lifetime. In disordered photovoltaic materials, charge recombination lifetime, like mobility, is charge carrier density dependent and therefore lifetimes must be probed as a function of charge density in order to compare different material systems. Therefore transient photovoltage (TPV) measurements in combination with differential charging were undertaken; the methods are described in detail elsewhere.[33-37]

Figure 3a displays the charge carrier lifetime from TPV as a function of the charge density obtained from differential charging, showing that carriers in the IDTBT-HM_w devices were much longer lived than carriers in the IDTBT-LM_w and IDTBT-NF devices at the same charge density (corresponding plot of the bimolecular recombination coefficient is shown in Figure S3). It should be noted that the devices measured were all made in the same device run, so any potential differences in the contacts, for example, are minimized; they were however different from the ones used for the EL/FTPS experiment, but showed similar characteristics (Table S4). Therefore, the finding of reduced ΔV_{oc} for IDTBT-HM_w can be assigned to reduced nongeminate recombination, as evidenced by the increase in charge-carrier lifetime. The external LED quantum efficiencies estimated from the values of ΔV_{oc} ($Q_{LED} \approx \exp(-q\Delta V_{oc}/kT)$[16] are in the range of 10^{-6} to 10^{-7} (Table 1). Thus, changes in radiative recombination have no effect on the total recombination rate and therefore on the charge carrier lifetime.

Table 1 Parameters used in calculation of non-radiative voltage losses[a]

Polymers with $PC_{70}BM$	**IDTBT-NF**	**IDTBT-LM_w**	**IDTBT-HM_w**
E_g (eV)[a]	1.7	1.7	1.7
J_{sc}(mA/cm^2) measured[b]	6.9	7.2	10.2
$J_{0,rad}$ (A/cm^2) calc.[c]	3.24×10^{-20}	2.02×10^{-20}	1.63×10^{-19}
$V_{oc,rad}$ (V) calc.[c]	1.150	1.160	1.110
V_{oc} (V) measured[b]	0.775	0.815	0.788
ΔV_{oc} (V)[d]	0.37	0.35	0.32
Q_{LED} at 100 mAcm^{-2}	5.91×10^{-7}	1.28×10^{-6}	4.10×10^{-6}

[a] The polymer band gap energy E_g was extrapolated from optical absorption, and is included to emphasize that differences in voltage are not due to the polymer energetics. [b] J_{sc} and V_{oc} were

taken from the *J-V* curve. [c] $J_{0,rad}$ and $V_{oc,rad}$ were calculated from EL and FTPS measurements and [d] ΔV_{oc} from $V_{oc,rad}$ - V_{oc}.

In order to evaluate the effect of charge carrier dynamics on solar cell performance, we compare the mobility-lifetime product ($\mu\tau$), a measure of charge carrier collection efficiency, for different systems under similar conditions.[38,39] Probing the mobility μ with charge extraction at short circuit,[40] we find only small differences in mobility for the different systems. Since the charge carrier lifetime τ was measured at open circuit and the carrier mobility was measured at short circuit, there is minimal overlap in charge densities between the two measurements. Mobility is not as strongly dependent on charge density as lifetime, so the mobility data were extrapolated over the charge density range of the TPV experiment, thus enabling a calculation of $\mu\tau$. Figure 3b clearly shows that HM_w devices exhibit significantly improved charge carrier collection relative to the NF and LM_w devices, in spite of slightly lower mobility. As a further probe of charge carrier dynamics we measured lifetime and mobility for a similar set of devices using photo-CELIV.[41,42] Also by this method a significantly higher $\mu\tau$ was observed for the highest molecular weight polymer (Table S5).

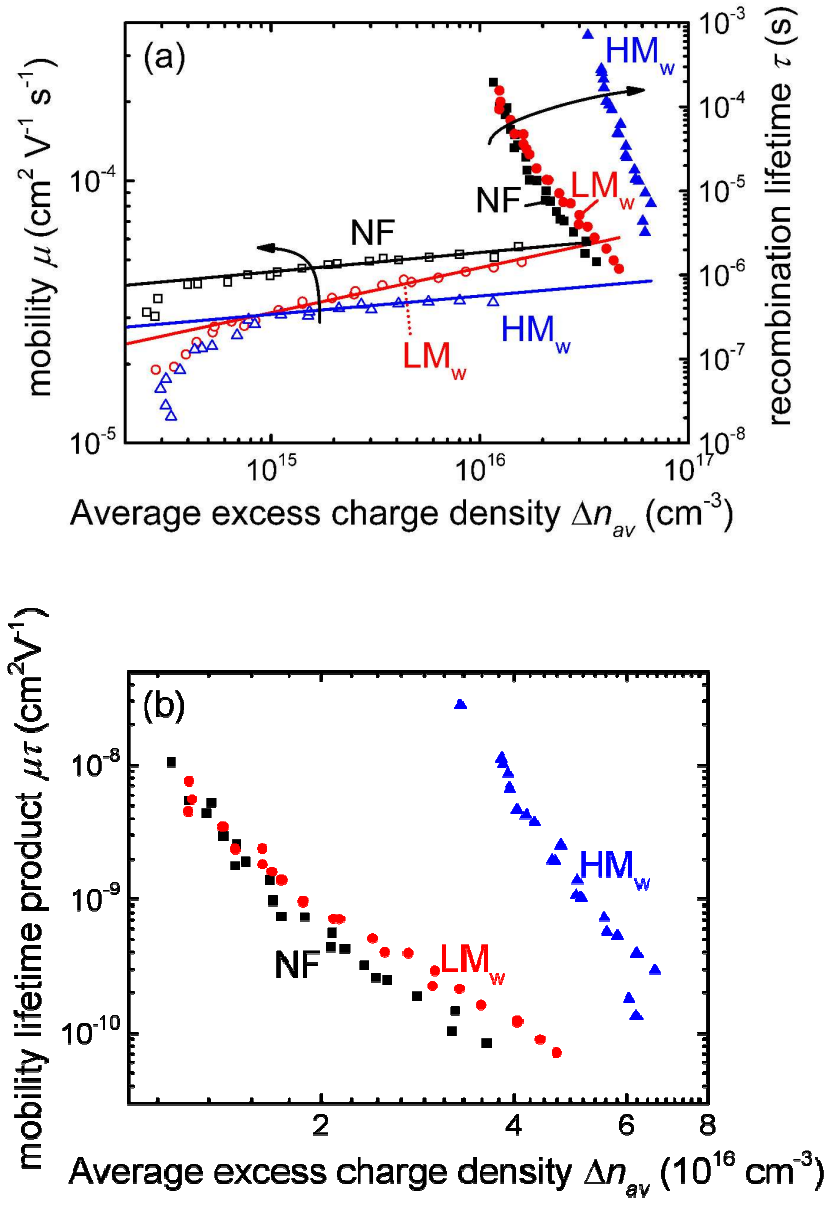

Figure 3 (a) Average carrier mobility, measured by charge extraction at short circuit (open symbols), and recombination lifetime, measured by transient photovoltage (solid symbols). The solid lines are the fits and resulting extrapolation of the mobility data over the charge density range of the transient photovoltage experiment. (b) Mobility-lifetime product, calculated over the charge density range of the lifetime data by extrapolating the mobility data.

The combined measurements of the degree of non-radiative recombination, charge carrier recombination lifetime and mobility for the three sets of devices provide a detailed explanation of the differences we observe in the current-voltage characteristics of solar cells made from these blends (Figure 4). Notably, the J_{sc} of the IDTBT-HM_w: $PC_{70}BM$ devices is significantly greater than that of the –NF and –LM_w devices. This photocurrent enhancement cannot be explained by the polymer optical properties: the absorption and photoluminescence (PL) spectra of the polymers are essentially identical (see Figure S2), as are the device film thicknesses (±5 nm). Furthermore, addition of $PC_{70}BM$ results in strong PL quenching in the visible region for all polymers, accompanied by intensified emission around 900 nm due to CT state emission. That said, the HM_w blend quenches approximately 50% more than the LM_w and NF blends, which is attributed to more efficient photo-induced charge separation between electron-donating and electron-accepting molecules.[42-45] Moreover, Mott-Schottky analysis of blend devices indicates no difference in the apparent doping concentration before and after fractionation (Figure S6). Therefore it appears that the short-circuit current increase in the HM_w blend is due to a higher efficiency of charge generation and/or charge collection, rather than any kind of optical effect. In addition, there are small differences in the V_{oc} between the devices, which is unexpected since the polymer itself does not change, and the device architectures are identical; however, these differences are explained through differences in the radiative and non-radiative recombination.

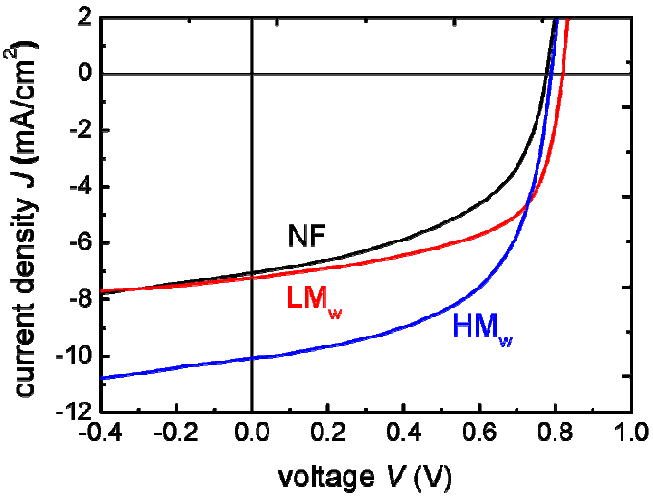

Figure 4 Current-voltage characteristics of the IDTBT-NF, -LM_w and HM_w devices used in this study to measure non-radiative voltage losses (black, red and blue lines respectively). All devices have an ITO / PEDOT:PSS / IDTBT:$PC_{70}BM$ / Ca / Ag architecture.

Conclusion

In summary, we have successfully demonstrated that non-radiative losses can be reduced with fractionation and higher molecular weight in indacenodithiophene copolymers. Analysis of charge dynamics in the bulk-heterojunction devices revealed that increasing the molecular weight of IDTBT polymers increases the carrier lifetime, as anticipated due to the reduced non-radiative voltage losses. The increased lifetime results in an increased mobility-lifetime product, and therefore enhanced carrier collection resulting in an increased J_{sc}. Therefore, this work demonstrates a methodical evaluation of the losses due to non-geminate recombination, and

provides a systematic explanation for the enhanced device performance with molecular weight observed in this system.

Experimental Details

Polymer materials. The polymer materials were synthesized according to Ref [25]. A portion of un-fractionated material, IDTBT-NF, was set aside and the rest was fractionated yielding high and low molecular weight fractions. The gel permeation chromatography traces for the materials are shown in Figure S1 and the corresponding molecular weight information is shown in Table S1.

Fabrication of Photovoltaic devices. All the devices were fabricated using the doctor-blade technique under ambient conditions. The devices for EL/FTPS and photo-CELIV were made at FAU Erlangen while the devices for TPV/CE were made at Imperial College. Pre-structured indium tin oxide (ITO) substrates were ultrasonic cleaned with acetone and isopropyl alcohol for 10 minutes each. After drying the substrates were coated with PEDOT:PSS (around 30 nm) and then 70-90 nm thick active layers based on IDTBT:$PC_{70}BM$ (1:3.5 wt fraction in 1,2-dichlorobenzene) were bladed. The total solution concentration used in Erlangen was 28 mg ml^{-1} while the concentration used at Imperial was 18 mg ml^{-1}; blade coating speeds were adjusted to compensate and achieve similar device thicknesses. To complete the fabrication of the devices 15 nm of Ca and 100 nm of Ag were thermally evaporated through a mask (device areas were 10.4 mm^2 (Erlangen) and 4.5 mm^2 (Imperial)) under vacuum (about 1-5x10^{-6} mbar). The *J-V* characteristics were measured using a source measurement unit from BoTest. Illumination was provided by a solar simulator (Oriel Sol 1A, from Newport) with AM1.5G spectrum at 100 mW cm^{-2}.

EL. EL measurements were performed by using a chopper and applying a constant current (100mA cm^{-2}) supplied by an external current/voltage source through the devices which have an active area of 0.104 cm^2. The emitted light was then collected by a monochromator and detected by liquid-nitrogen-cooled Ge detector. The spectrum was recorded by a standard lock-in technique. The system was wavelength calibrated.

FTPS. FTPS-EQE measurements were carried out using a Vertex 70 from Brucker optics, equipped with QTH lamp, quartz beam splitter and external detector option. A low noise current amplifier (DLPCA-200) is used to amplify the photocurrent produced upon illumination of the photovoltaic devices with light modulated by the FTIR. The output voltage of the current amplifier is fed back to the external detector port of the FTIR, in order to be able to use the FTIR's software to collect the photocurrent spectrum.

Transient photovoltage. The experimental details are as previously published.[33-34]

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Supporting Information Available. Containing additional experimental details and supporting figures. This information is available free of charge via the Internet at http://pubs.acs.org

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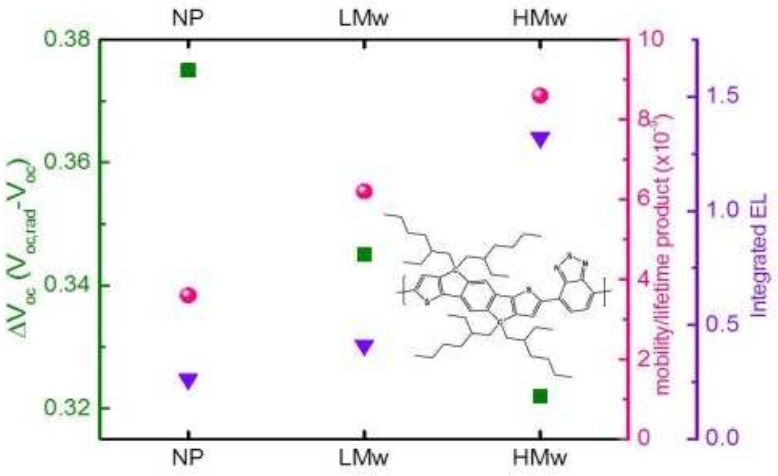
Table of Content Entry (TOC)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Integrated EL
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