Mapping the Competition between Exciton Dissociation and Charge Transport in Organic Solar Cells

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ABSTRACT: The competition between exciton dissociation and charge transport in organic solar cells comprising poly(3-hexylthiophene) [P3HT] and phenyl-C61-butyric acid methyl ester [PCBM] is investigated by correlated scanning confocal photoluminescence and photocurrent microscopies. Contrary to the general expectation that higher photoluminescence quenching is indicative of higher photocurrent, microscale mapping of bulk-heterojunction solar-cell devices shows that photoluminescence quenching and photocurrent can be inversely proportional to one another. To understand this phenomenon, we construct a model system by selectively laminating a PCBM layer onto a P3HT film to form a PCBM/P3HT planar junction on half of the device and a P3HT single junction on the other half. Upon thermal annealing to allow for interdiffusion of PCBM into P3HT, an inverse relationship between photoluminescence quenching and photocurrent is observed at the boundary between the PCBM/P3HT junction and P3HT layer. Incorporation of PCBM in P3HT works to increase photoluminescence quenching, consistent with efficient charge separation, but conductive atomic force microscopy measurements reveal that PCBM acts to decrease P3HT hole mobility, limiting the efficiency of charge transport. This suggests that photoluminescence-quenching measurements should be used with caution in evaluating new organic materials for organic solar cells.

KEYWORDS: organic solar cells, charge transport, exciton dissociation, scanning confocal photoluminescence microscopy, scanning photocurrent microscopy

INTRODUCTION

Thin-film organic solar cells (OSCs) have attracted much attention due to their potential application as low-cost, high efficiency, and flexible solar energy-conversion devices. Early OSCs were fabricated via sequential stacking of thin films of a polymeric electron donor and a derivatized fullerene electron acceptor, forming a planar-heterojunction (PHJ) active layer. However, PHJ OSCs have low interfacial areas between the electron donor and acceptor, limiting exciton-dissociation and therefore power-conversion efficiency. To enhance exciton-dissociation and power-conversion efficiencies in OSCs, bulk-heterojunction (BHJ) active layers were introduced. In the BHJ architecture, the photoactive layer comprises an electron donor and an electron acceptor that is intermixed at the nanoscale, creating a more extensive donor−acceptor interface that increases the exciton-dissociation efficiency in comparison to the active layers in PHJ devices.

To evaluate the exciton-dissociation efficiency in OSCs, which operate far below the radiative limit as exciton-dissociation is followed by rapid, nonradiative recombination through a manifold of charge transfer states, photoluminescence (PL) quenching measurements are commonly used. PL quenching measurements indirectly infer that a reduction in the radiative recombination of electrons and holes arises from an increase in charge transfer and therefore macroscopic photoconductivity. Indeed, researchers have observed that higher PL quenching generally induces higher photocurrent in thin films having various donor and acceptor concentrations in photoactive layers of solar cells. However, the relationship between PL quenching and PC has not been precisely established as they are typically probed in different...
devices. It is therefore questionable whether PL quenching is a suitable predictor for the performance of OSCs comprising new materials.

Here, we study the relationship between PL quenching and PC by simultaneously mapping and correlating their signals in the same device through a combination of scanning photocurrent microscopy (SPCM) and scanning confocal photoluminescence microscopy (SPLM). SPCM and SPLM have been utilized to understand the structure, phase, and composition of organic solar cells. Using these techniques, we first probed a BHJ OSC of poly(3-hexylthiophene) [P3HT] and phenyl-C61-butyric acid methyl ester [PCBM]. In contrast to the generally accepted relationship that a reduction in PL is reflective of higher PC, we observe PL quenching to be inversely proportional to PC. To elucidate the origin of this unexpected observation, we designed a model structure in which we laminated a PCBM thin film atop a portion of a uniform P3HT thin film, leaving the remaining portion of P3HT exposed. SPCM and SPLM were conducted across this same laminated interface. We find PL quenching and PC to be inversely proportional at the boundary between the P3HT-only region and the P3HT/PCBM stack, where PCBM has diffused into P3HT upon thermal annealing such that this stack resembles a BHJ. We carried out conductive atomic force microscopy (C-AFM) to map the hole mobility. These experiments reveal that the competition between charge transport and charge separation is responsible for this inverse relationship between PC quenching and PL and implicates PL quenching to not necessarily be an accurate indicator of OSC performance.

■ EXPERIMENTAL SECTION

To study the relationship between PL and PC, we first fabricated a P3HT:PCBM BHJ inverted solar cell with an efficiency of 2.0%. We have opted to build our devices in the inverted architecture because the gold contacts employed in this architecture are more stable than the aluminum contacts that would have been used in the conventional architecture. In our hands, P3HT:PCBM bulk-heterojunction devices of both the conventional and inverted architectures yield comparable power-conversion efficiencies of 2−3%. To construct OSCs with a BHJ architecture, prepatterned ITO substrates (15 Ω/sq.; Colorado Concept Coatings) were cleaned with acetone, isopropyl alcohol and deionized water by sonication. After drying in a nitrogen stream and further cleaning by UV/ozone for 10 min, we spin-coated a solution of 1 wt % titanium isopropoxide in isopropyl alcohol on the ITO substrates at 3000 rpm for 30 s. The precursor films were allowed to hydrolyze in air for 1 h at room temperature followed by 10 min at 170 °C to yield 40 nm thick titania electron transport layers. A co-solution was prepared by dissolving P3HT and PCBM at an equimass ratio to form a 2.4 wt % solution in chlorobenzene. Then, the co-solution of P3HT and PCBM was deposited by spin-coating on the titania-coated ITO substrates at 500 rpm for 60 s and thermally annealed at 150 °C for 1 min. Thermal evaporation of gold through a stencil mask completed the construction of P3HT:PCBM BHJ OSCs with active areas of 0.18 cm². The fabricated devices were subsequently sealed by epoxy under a cover glass slip in a nitrogen glovebox to limit possible oxidation upon air exposure during measurements.

SPCM and SPLM measurements were carried out by illuminating the OSC through the transparent ITO top window of the device with 488 nm light from an Innova 70C spectrum Ar:Kr laser focused to a 1 μm diameter spot using a 0.3 NA objective lens. Figure 1A depicts the experimental setup used to simultaneously measure and map PC and PL. The device was mounted on a stage with stepper motors (Thorlabs BSC102) and, at zero applied voltage and under focused illumination, was scanned across a 100 μm × 100 μm area with a step size of 0.5 μm while simultaneously measuring PC and PL. The short-circuit photocurrent (PC) was recorded by a source measure unit (Keithley 2400). PL was collected through the same objective lens as the excitation, filtered by a 488 nm super notch filter, captured confocally by a fiber, relayed to a monochromator, and recorded by a

Figure 1. (A) Schematic of the correlated scanning photocurrent microscopy and scanning confocal photoluminescence microscopy setup. (B) BHJ solar cell structure and (C) line scan (along x direction in panel B) mapping the microscopic PC and PL across a BHJ solar cell.
CCD camera. Forward and reverse scans were conducted to rule out possible aging or bias stress effects.

RESULTS AND DISCUSSION

Figure 1B is a schematic of the OSC device, and Figure 1C shows the PC and PL intensity as a function of position as the device is scanned along the x-axis, as illustrated in Figure 1B. As seen in Figure 1C, the region that yields higher PC generally shows higher PL. This is in direct contrast to the expectation that higher PL quenching arises from more efficient charge separation and should therefore yield higher PC.

Because it is possible for this unexpected commensurability between PC and PL in the PCBM/P3HT BHJ solar cell to result from local differences in light absorption and exciton generation, we probed a model system. The model system comprises a PCBM/P3HT PHJ on half of the device and a P3HT single junction on the other half, shown in Figure 2A and B. In the model system, we expect comparable light absorption and exciton generation across the device because the amount of P3HT, which is the main light absorber in this materials pair, is the same over the entire sample. To fabricate the model system comprising a P3HT/PCBM PHJ and a P3HT single junction, we spin-coated PEDOT:PSS (Clevios P) at 2000 rpm for 120 s on prepatterned ITO substrates and annealed the samples at 150 °C for 20 min. Then, 1 wt % P3HT in chlorobenzene was deposited by spin-coating at 1000 rpm for 1 min. We laminated and transferred a thin layer of PCBM (45 nm) partially onto the P3HT film to create a bilayer step junction. P3HT was chosen as the underlayer to provide film uniformity across large areas. The PCBM thin film was prepared by spin-coating a 0.5 wt % PCBM solution in chloroform at 3000 rpm for 60 s onto a UV/Ozone-treated Si wafer. A PDMS stamp was prepared, by mixing the PDMS precursor (Sylgard 184A) and curing agent (Sylgard 184B) at a 10:1 weight ratio, and curing it at 80 °C for 4 h. The cured PDMS stamp was placed in direct contact with the PCBM/Si assembly. Then the assembly was immersed in water. The water penetrated the interface between the hydrophobic PCBM and the hydrophilic UV/Ozone-treated Si wafer, allowing the Si wafer to be removed from the PCBM/PDMS stack and the PCBM layer to be transferred onto the PDMS stamp. We then selectively laminated PCBM on half of the P3HT layer on the PEDOT:PSS-coated ITO substrate, forming a P3HT/PCBM planar-heterojunction on the left (L)-side and leaving P3HT exposed on the right (R)-side of the step junction. After removing the PDMS stamp, we evaporated 80 nm thick aluminum through a stencil mask to complete the fabrication of the patterned OSC device. We studied this model system before and after annealing at 130 °C for 3 min. The device performance of a PCBM/P3HT PHJ and P3HT-only Schottky junction solar cell are shown in Figure S1. We denote the PCBM/P3HT PHJ side by the L-side, the P3HT-only layer by the R-side, and the interfacial region (in which interdiffusion of P3HT and PCBM occurs during thermal annealing) by the I-zone.

To confirm the model system is constructed as expected, we examined it using energy dispersive X-ray (EDX) elemental analysis. EDX mapping (Figure 2) is shown (Figure 2C) before and (Figure 2D) after annealing. Before annealing, a dramatic change in carbon content is seen across the interface because PCBM is substantially more carbon-dense than P3HT. The interfacial width over which the carbon content decreases is...
approximately 5 μm. After annealing, interdiffusion of PCBM and P3HT occurs over ∼10 μm and an extended I-zone forms across the mapped region from −5 to 5 μm. Interdiffusion of PCBM occurs over very long micron-scale distances within a few minutes of annealing at 100–150 °C, resulting in the carbon concentration gradient seen in the EDX measurements. Therefore, the I-zone structurally resembles a BHJ, though with a gradient of donor:acceptor composition across the zone.

We mapped the PC and PL across the junction along the x-axis, as depicted in Figure 2A. Figure 3 shows representative line scans (Figure 3A) before and (Figure 3B) after thermal annealing tracking the PC (black) and PL (red) across the interface. The PL spectra of the samples are shown in Figure S2. Before thermal annealing, the R-side shows lower PC and higher PL than the L-side, consistent with photoexcitons recombining radiatively rather than undergoing dissociation in the absence of PCBM. In the presence of PCBM on the L-side, PL quenching and charge separation are, in comparison, more efficient. After annealing, a similar phenomenon is observed on the L-side and on the R-side away from the junction, that is, higher PL is correlated with lower PC.

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However, the behavior of PC and PL is interesting in the I-zone. Before thermal annealing [Figure 3A], the amplitudes of the PC and PL signals are inversely proportional to one another in the I-zone. In Figure 3B, we observe that the annealing extends the I-zone over a larger region across the junction and in contrast, the PC and PL signals are now directly proportional to one another. As the device is translated from −5 to 5 μm [Figure 3B], the PCBM content decreases gradually [Figure 2D], and the PL increases as the probability of charge separation is reduced. However, in this region the PC also increases even though more excitons decay. Although PL quenching is commonly accepted as a measure of charge separation and therefore one would expect a concomitant increase in PC in organic heterojunction thin films, here we observe that increases in PC need not come at the expense of PL; the signal amplitudes of both can increase simultaneously.

To understand why the left side of the I-zone with higher PCBM content and PL quenching shows relatively low PC compared to right side of the I-zone, we turn to the contributing processes of photon-to-electron conversion efficiency (η_elec): (1) light absorption (η_abs), (2) exciton dissociation (η_diss), (3) charge transport (η_ct), and (4) charge collection at the electrodes (η_cc).27,28

\[ \eta_{elec} = \eta_{abs} \cdot \eta_{diss} \cdot \eta_{ct} \cdot \eta_{cc} \]

Since Ohmic contacts are formed at both the ITO anode and Al cathode,29 we exclude effects of charge-collection efficiency at the electrodes and assume η_cc is the same. We next compare light absorption in both the L-side and R-side. The absorption on both sides of the junction should be comparable since P3HT is the dominant light absorber of the materials pair and PCBM contributes negligibly to light absorption, as seen in Figure 3.
absorption spectra (Figure S3). Therefore, we can also exclude the
effect of absorption and assume $\eta_{ph}$ to be constant across
the interface. We are left to focus on the contributions of exciton
dissociation and charge transport to the overall
efficiency of the OSCs.

To quantify the transport properties, we carried out C-AFM,
as seen in the inset in Figure 4A. For this measurement, we
prepared the same patterned device comprising a PCBM/
P3HT PHJ on half of the device and a P3HT only layer on
the other half as described above, but without depositing the
cathode. We used a Pt–Ir tip in the C-AFM experiments as the
top electrode and measured the current passing through the
depth of the active layer as we recorded current–voltage
characteristics at multiple positions along the sample. The high
work function of the electrical contacts ensures hole-only
transport. Using the space-charge limited current model with a
correction to account for the tip–sample geometry, we
extracted the hole mobility as a function of position. As noted
in Figure 4, the position at $0 \mu m$ denotes the interface between
P3HT only and P3HT:PCBM regions, with positive values
indicating the P3HT-only region, as seen in the inset of Figure
4A. We were unable to extract the hole mobility in the $x < 0$
region of P3HT:PCBM region, as PCBM blocks hole transport.

Before annealing [Figure 4A], the hole mobility in the P3HT
region is low, around $1 \times 10^{-4} \text{cm}^2/(\text{V s})$, and is invariant with
position. After annealing [Figure 4B], the mobility increases to
$5 \times 10^{-4} \text{cm}^2/(\text{V s})$ on the R-side (low PCBM:P3HT ratio),
and then decreases as we move toward the interface, down to a
value of $1 \times 10^{-4} \text{cm}^2/(\text{V s})$ at the interface (high PCBM:
P3HT ratio). Thus, we expect hole mobilities lower than $1 \times
10^{-4} \text{cm}^2/(\text{V s})$ on the L-side where the PCBM:P3HT ratio is
even higher. This observation is consistent with a previous report
that as PCBM content decreases, the hole mobility increases
due to greater crystallinity of the P3HT.

As PC is defined as $\sigma_{ph} = e(n\mu_e + p\mu_h)$, the mobility is an
important factor in determining the overall photovoltaic
performance, where $\sigma_{ph}$ is photoconductivity, $e$ is electric
charge, $\mu_e$ and $\mu_h$ are the electron and hole mobilities, $n$ and $p$
are electron and hole concentrations, respectively. In the
unannealed sample, the hole mobility is constant and therefore
charge separation governs device efficiency. However, after
annealing, we hypothesize that while on the left side of the I-
zone (higher PCBM:P3HT ratio) the efficiency of charge
separation is higher, the lower mobility for hole transport limits
charge transport and therefore the overall photon-to-electron
conversion efficiency. On the right side of the I-zone (lower
PCBM:P3HT ratio), charge separation is less efficient, but the
hole mobility is at least five times higher than the mobility on
the left side. This observation is consistent with the observation
that the PL and PC signals are high relative to their signals on
the left side. The spatial variation of charge separation and hole
mobility thus shows that donor and acceptor intermixing has
competing effects on the charge separation and transport
processes, limiting the photon-to-electron conversion efficiency.
It should be noted that the proportionality between PC and PL does
not stem from variations in film thickness as both signals are
continuous over the scanned area and are inversely proportional
prior to annealing.

This conclusion is further supported by previous work
showing that, among samples with different ratios of P3HT and
PCBM or other similar blends, the greatest PL quenching
does not always show the highest device efficiency. This
assertion also agrees well with our observation that the
PCBM:P3HT gradient in the I-zone creates a gradient in
carrier mobility, resulting in a change in PC that is proportional
to PL. Therefore, in BHJs, the correlation between PC and PL
is attributed to the distribution of local mobility that results
from the local variations in the PCBM:P3HT ratio. This idea of
local heterogeneities affecting local charge transport efficiencies
agrees with literature reports that suggest charge separation
may not be the limiting factor of the photovoltaic performance.
While we have simplified the model and further study is
needed to completely understand the quantitative contributions
of exciton dissociation and charge transfer with respect to
structural development that takes place on annealing, we
believe this study explains the uncommon correlation between
PC and PL observed in our experiments. It should be noted
that the proportional behavior between PC and PL quenching
is macroscopically observed in many donor–acceptor
systems. More detailed analysis on other OSC systems having
different charge transfer states has to be conducted to extend
our findings.

CONCLUSIONS

In conclusion, we studied the behavior of photoexcited carriers
using a correlated spatially resolved photoconductivity and
photoluminescence mapping technique and further investigated
charge transport using conductive atomic force microscopy. We
prepared bulk-heterojunction solar cells and patterned devices
to study the fate of photoexcited carriers in OSCs. Unlike the
conventional expectation where PC and PL are inversely
proportional, we observe that PC and PL may be proportional
to one another in BHJs. That is, regions with higher PCBM
show more PL quenching due to efficient charge separation, but
lower PC arising from the lower hole mobility in P3HT. We
found this phenomenon to be consistent with intermixing of
the donor and acceptor leading to competition between charge
separation and transport. We conclude that in well-blended
bulk-heterojunction active layers, PL quenching cannot be
directly used as a measure of PC or OSC efficiency, and that for
efficient photon-to-electron conversion, all factors including
charge separation and mobility need to be carefully considered.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the
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Device performance of solar cells and photoluminescence
and absorption spectra (PDF)

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Notes
The authors declare no competing financial interest.

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