The Influence of Nanocrystal Aggregates on Photovoltaic Performance in Nanocrystal–Polymer Bulk Heterojunction Solar Cells

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CdSe nanocrystals (NCs) can be used as an electron acceptor in solar cells, employing organic ligands to passivate their surface and make them processable from solution. The nature and abundance of impurities present after NC ligand exchange from oleic acid to n-butylamine are identified. A further purification step using hexane as a selective solvent is described, which excludes NC aggregates from solution. The influence of NC aggregates on photovoltaic device performance is studied in a CdSe:poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) bulk heterojunction solar cell. The exclusion of NC aggregates leads to a four-fold increase in device power conversion efficiency (PCE) in optimized devices. A superior blend morphology leading to improved charge generation and a better NC percolation network is identified as the main causes of this increased solar cell performance.

1. Introduction

Nanocrystal-polymer hybrid bulk heterojunction solar cells offer a promising way to overcome limitations of all-organic heterojunctions. In particular, the inorganic component offers a high dielectric constant, which translates into effective charge carrier screening.[1] Furthermore, the possibility of tuning the band gap by adjusting the nanocrystal (NC) dimensions offers a way to align energy levels at the bulk heterojunction.[2] In a hybrid bulk heterojunction with a polymer, the advantageous properties of NCs are complemented by the high absorption cross-section of the organic material, which allows efficient light harvesting.[3] Because both components are solution processable, this provides an avenue towards low cost solar cells.

Since the introduction of hybrid organic-inorganic solar cells incorporating cadmium selenide (CdSe) NCs blended with polymers,[2] a comprehensive understanding of the influence of NC size and shape,[4–5] NC-polymer blend morphology and weight ratio,[6,7] and the choice of ligand species[8] on relevant solar cell parameters has been established. For instance, replacing long and insulating NC surface ligands by short ones allows more efficient charge transfer from polymer to NCs and subsequent electron transport via the NC network.[9,10] However, it has been pointed out by Owen et al. that these post synthetic ligand replacements are strongly dependent on the binding mode of the ligand to the NC surface: while anionic X-type ligands bind strongly to the positively charged Cd surface atoms, neutral L-type ligands can only provide weaker dative bonds to the NC.[11] Since most native ligand species are X-type, their replacement is often challenging and incomplete.[12,13] An additional consequence of post-synthetic ligand exchange reactions is the inevitable introduction of impurities in the guise of aggregated NCs, residual native and exchange ligands, traces of solvents, and high-molecular-weight species formed by the oligomerisation of free ligands.[8,11,13] While it is widely accepted that post-synthetic ligand exchange treatments are not 100% efficient,[12,13] little is known about residual impurities. Radychev et al. have shown that free ligand dimer formation occurring during ligand exchange reactions on CdSe NCs can be suppressed when pyridine is chosen as the initial L-type ligand. This is most likely due to the reduced reactivity of the sp² hybridized nitrogen in pyridine compared to the more reactive sp³ hybrid in most alkyl amines. Morris-Cohen et al.[11] have reported that CdSe NCs with a mixture of X- and L-type ligands release unbound L-type ligands over time once they are dispersed in hexane. Additionally, they identified dimer formation of reactive free ligand species that persist throughout multiple purification procedures and cannot be removed from the NC dispersion. Ligand exchange in general bears the risk of producing agglomerated clusters of NCs, as the initial removal of the native ligand creates surface dangling bonds that are likely to combine with similar reactive sites on NCs in close proximity.[11,14] Once imple-
ment in optoelectronic devices, some of the identified impurities may act as electron\cite{15,16} and hole\cite{14,15,17} trap sites. However, a detailed picture of the direct influence of these impurities on PV performance has not yet been provided.

Here we study the influence of aggregated and poorly passivated NCs on photovoltaic device performance in the model system of a bulk heterojunction solar cell consisting of colloidal CdSe NCs and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV). The application of an additional purification steps after a post-synthetic ligand exchange treatment using hexane as a selective solvent\cite{11,13} allows us to separate well-passivated NCs from aggregated and poorly ligated NCs in solution. Here, we identify and quantify the impurities and the relative ligand coverage before and after purification, and show a marked improvement in PV performance after purification. We investigate the differences in blend morphology, charge generation, recombination and extraction that are responsible for the improved PV performance.

2. Results and Discussion
2.1. Post-Synthetic Ligand Exchange and Purification

The ligand exchange reaction from oleic acid (OA) to \( n \)-butylamine following standard procedures\cite{7} is expected to produce aggregated NCs, residual native and exchanged ligands, and traces of solvents\cite{11,13} as impurities. In order to minimize the amount of residue, we apply a post-ligand-exchange purification using hexane as a selective solvent for well-passivated NCs, as proposed by Morris-Cohen et al.\cite{18}. In the remainder of this work we will refer to this procedure as hexane treatment. In contrast to the strongly binding X-type alkylphosphonates used in ref. [13] we employ NCs with weaker binding native X-type OA ligands in order to obtain a more complete removal of native ligands. Furthermore, we use \( n \)-butylamine as exchange ligand species, which is highly miscible in the precipitation solvents used in this work, compared to the relatively insoluble hexadecylamine (HDA) used in ref. [13]. We therefore do not expect any free \( n \)-butylamine to be present after precipitation. As a by-product of the ligand exchange reaction, free OA and \( n \)-butylamine may dimerise to an amide or ammonium salt species. Most of the ammonium salt should be removed from the dispersion upon flocculation with polar solvents like methanol. Furthermore, we do not expect the formation of any amides, as it has been shown that the present carboxylic acid and amine species do not form amides without the aid of a catalyst at room temperature.\cite{19–21} Considering the choice of ligands and purification method, we anticipate the final NC dispersion to only contain well-passivated, \( n \)-butylamine-ligated NCs and negligible amounts of ammonium salt. A schematic depiction of the expected products after the ligand exchange reaction and subsequent hexane treatment is shown in Figure 1.

We first use proton nuclear magnetic resonance spectroscopy (\( ^{1} \)H NMR) to verify if OA is still attached to the NC or has been removed from the NCs upon ligand exchange. In Figure 2a, the large resonance at 2.4 ppm can be accounted for by residual toluene that could not be removed from the dispersion. The signal at \( \approx 5.35 \) ppm in both OA-containing samples can be identified as the resonance for the olefin double bond of OA. As expected for the sample containing OA bound onto NCs, this signal is broader and shifted compared to the sample with unbound OA. In fact, the rotational mobility of the bound ligand is reduced compared to the unattached ligand, and this leads to an observable broader resonance compared to the clear multiplet fine structure for free ligands.\cite{22} The peak at 2.7 ppm in both \( n \)-butylamine samples represents the two protons in \( \alpha \)-position to the amine functionality. The extreme broadness of the signal in the \( n \)-butylamine capped NCs sample again supports the binding of \( n \)-butylamine onto NCs. Pure \( n \)-butylamine does not have an olefin bond in its backbone and therefore lacks an olefinic resonance at 5.35 ppm (see Figure 2a). Since we do not observe any signal at 5.35 ppm for the sample containing \( n \)-butylamine capped NCs we can conclude that no OA, in the guise of free OA or as an attached species, is present in the sample, i.e., the applied ligand exchange from OA to \( n \)-butylamine successfully removed the OA molecules from the NC surface.

Treating amine-ligated CdSe NC dispersions with hexane has been shown to partially remove impurities from the original NC synthesis\cite{8} or the post-synthetic ligand exchange.\cite{11} We note that the analyses in ref. [8,13] are based upon strong, native X-type ligands that can still cover up to 80% of the NC surface after purification, thus maintaining dispersability of the NC.\cite{18} The ligand exchange presented here, however, produces NCs without any original, X-type ligand coverage (see Figure 2a). As a consequence, the fraction of temporarily unpassivated NC surface is greater, leading to a higher risk of NC agglomeration, due to a more likely encounter of unpassivated surface sites of NCs in close proximity. We expect, however, that the presented
post-ligand exchange hexane treatment only selects NCs that are well-covered with n-butylamine, and leaves out aggregated and poorly passivated NCs. In order to confirm this hypothesis, we employ X-ray photoelectron spectroscopy (XPS) to analyze the nitrogen content as an indicator of the relative n-butylamine coverage. The direct comparison of nitrogen signal in the two n-butylamine containing samples is complicated by the overlapping Se LM Auger peak and N1s signal (see Figure 2b). We therefore reconstruct the N1s signal, by subtracting the Se LM Auger peak obtained from the nitrogen-free OA sample from the superimposed signal of both n-butylamine samples. Having reconstructed the N1s signal, we compare the nitrogen content in the two n-butylamine samples by considering the nitrogen-to-cadmium ratio. As mentioned above, free ligands and dimer species are either excluded from solution during flocculation or have only been formed in negligible amount, i.e., any nitrogen signal is indicative of attached n-butylamine. The measured greater abundance of nitrogen in the hexane-treated sample compared to its non-hexane-treated analogue therefore implies a higher relative n-butylamine coverage by ≈30%, after subtraction of the Se signal. We note that this is a lower limit, since any attenuation of the Se signal by OA compared to the shorter n-butylamine would increase the relative coverage estimate.

At this point we can conclude that the ligand exchange presented here to replace native OA ligands with n-butylamine produces NCs that are completely stripped of OA molecules. Furthermore, we identify hexane treatment as a method to enrich the NC ligand shell with n-butylamine by at least 30%. Next, we investigate the influence of this higher n-butylamine surface coverage on solar cell performance in the model system of a NC:polymer bulk heterojunction solar cell.

2.2. Photovoltaic Performance

Figure 3 shows the device performance of bulk-heterojunction solar cells of MDMO-PPV blended with both hexane-treated and non-hexane-treated CdSe NCs. We observe a dramatic difference in the current-voltage characteristics under AM1.5G illumination conditions, namely an increase in short-circuit current ($J_{SC}$) by a factor of 2.9, whereas the open-circuit voltage ($V_{OC}$) is reduced by about 50 mV. The external quantum efficiency (EQE) shows increased contributions from both polymer (400–600 nm) and NCs (600–660 nm) in solar cells incorporating hexane-treated NCs. The power conversion efficiency (PCE) increases from 0.4% to 1.0%. Although we have achieved up to 1.7% PCE for hexane-treated NCs by optimizing the active layer thickness (see Supporting Information S3), we restrict our analysis to the two devices shown in Figure 3, as they contain NCs from the same synthesis, and the layer thickness and absorption are very similar (see next section and Supporting Information S4), allowing a direct comparison. In the remainder of this work we study the mechanism by which the hexane treatment leads to superior device performance.

2.3. Morphology

The results of AFM and TEM analysis are shown in Figure 4. Panels a and b show the film surface of non-hexane and hexane-treated blend films, as measured by AFM. A cross-sectional height profile of the two films is shown in panels c and d. While the hexane-treated film appears smooth, the non-hexane-treated film shows features several µm wide and >100 nm high, embedded in a continuous blend film. Averaging over
the continuous film thickness excluding aggregates in the AFM image (see Supporting Information S4), we find that the non-hexane film has an average height of 62.9 nm ± 3.9 nm, compared to 59.5 nm ± 3.9 nm for the hexane-treated film. Likewise, the absorbance of both films as measured using a UV-vis spectrometer is very similar (see Supporting Information S5), ruling out differences in absorption as a cause for the observed performance difference. We note, however, that blends containing hexane-treated NCs show a higher contribution from NCs (600–660 nm), but a lower contribution from the polymer (400–600 nm), which may indicate a difference in film composition. Although both hexane-treated NCs and non-hexane-treated NCs containing films were spun using solutions of identical NC to polymer ratio (9:1 by mass), it is possible that some aggregated NCs fell out of solution during processing, leading to a slightly higher NC loading in hexane-treated films.

As mentioned before, non-hexane-treated NCs display a less passivated surface compared to the hexane-treated analogs and hence are more prone to aggregation.\[23\] It is therefore likely that the observed particulates in the non-hexane-treated film are NC aggregates. TEM images of hexane and non-hexane-treated blend films are shown in Figure 4e–h. While individual NCs can be recognized in the hexane-treated film, the non-hexane-treated film shows significantly larger NC aggregates. The size and number of NC aggregates on the surface of non-hexane-treated films implies a significantly lower NC loading in the underlying blend. As a consequence, the NC percolation network within the blend will be sparser.\[23\] Indeed, Figure 4e,f reveal only short-range connectivity of the NC network, in contrast to well-connected NC domains for hexane-treated samples. Furthermore, larger polymer domain sizes are recognizable in the hexane-treated film, the non-hexane-treated film shows significantly larger NC aggregates. The better connected NC network and the smaller polymer domains in samples containing hexane-treated NCs is likely to have a beneficial impact on charge carrier pathways and may be the origin for the observed higher photocurrent. In order to investigate charge extraction and recombination we next study the transient photocurrent and transient photovoltage decay in both devices.

2.4. Charge Evolution on the Microsecond Time Scale

Charge carrier extraction and recombination dynamics on the microsecond timescale were studied by investigating the transient photocurrent (TPC), where the current is monitored after the light is turned off, and transient photovoltage (TPV), where the voltage decay is measured following a small perturbation light pulse under variable white light bias.

The decay of the photocurrent yields a measure of the charge extraction timescales in photovoltaic devices. In Figure 5a the photocurrent decay of hexane and non-hexane-treated devices after a 2 ms light pulse (λ = 500 nm) is shown, in absence of white light bias. We note that a measurement artefact appears at the onset of the TPC transient, the origin of which is explained in the Supporting Information S6. The hexane-treated device clearly shows faster current decay, especially at short times (<1 µs). We attribute this to an improved charge extraction, as recombination in these devices occurs on longer timescales, as probed by TPV and discussed below. The observed improvement in connectivity of the NC network is likely to improve charge extraction.\[7,24\]

Since there is no current flowing under open-circuit conditions, the decay of the photovoltage perturbation ΔV at V_{OC} provides a direct measure of the recombination of photogenerated charge carriers.\[25\] Devices containing hexane-treated NCs show faster photovoltage decay than their non-hexane-treated analogs over a wide range of white light biases. The evolution of τ, defined as the time it takes for the additional photovoltage ΔV to decay to 1/e of its initial value, with increasing white light bias is shown in Figure 5b. We note that recombination is much slower than typical TPC decay timescales, indicating that the TPC decay is indeed dominated by extraction rather than recombination.

Nelson,\[26\] Heinemann et al.\[27\] and Rauh et al.\[28\] have proposed the presence of recombination that is limited by the
de-trapping of one carrier. This could be the case for a trapped charge that is spatially removed from the heterojunction interface, for instance in a cluster of NCs. In hexane-treated samples, the finer morphology could prevent trapping in NC clusters, which explains the faster TPV decay observed. An increase in recombination rate is likely to lead to a reduction in $V_{OC}$. However, only a modest reduction of 50 mV is observed under AM1.5G illumination (see Figure 3). This supports our earlier observation that charge extraction can successfully outcompete recombination under operating conditions. We note that the recombination rate is likely to be density dependent, such that an improvement in charge generation will also reduce the value of $t$. 

Next we employ transient absorption (TA) spectroscopy in order to investigate charge carrier generation in the nanosecond region.
2.5. Excitons and Free Charges on the Nanosecond Time Scale

Figure 6 shows the near-IR TA spectra of hexane and non-hexane-treated devices, excited at 532 nm at a pump fluence of 1.6 µJ and measured 3 ns after the pump pulse. At 3 ns, neither non-geminate recombination nor charge extraction is expected to play a significant role, especially at the relatively low excitation fluence used. Hexane-treated devices were found to show a much larger photoinduced absorption than non-hexane-treated devices at the same excitation density. MDMO-PPV polarons are well known to have an absorption peak between 860 nm and 920 nm. We thus attribute the negative TA signal to the photoinduced absorption of the hole polaron residing on the polymer. Contributions from NC trapped or free charges have been shown to be more than an order of magnitude weaker than the polaronic contribution and thus can be neglected.

We find that hexane-treated devices show a superior charge carrier generation by a factor of 2.2 compared to their non-hexane-treated counterparts (see Figure 6). This marked difference in charge generation indicates that the higher Jsc of hexane-treated devices is mainly due to improved charge generation. Time-resolved photoluminescence measurements (see Supporting Information S7) indicate similar exciton quenching rates for devices consisting of hexane and non-hexane-treated NCs. This was further confirmed by similar photoluminescence quantum efficiencies for both blends. We show elsewhere that excitons generated in the polymer domain of CdSe:MDMO-PPV blends are quenched efficiently by either Förster resonance energy transfer or electron transfer to the nanocrystal. Furthermore, we identified that only an initial charge transfer from the polymer to the NC domain is capable of producing free charges efficiently. Excitons quenched by energy transfer have to undergo a subsequent hole back transfer in order to create free charges. This second process takes place on timescales on which competing recombination mechanisms occur, rendering this mechanism inefficient for the generation of free charges. We note that charge and energy-transfer processes operate on different length scales. While charge transfer relies on a close spatial proximity between donor and acceptor energy transfer is considered a longer-range interaction.

Considering the unchanged absorption in both devices (see Supporting Information S5) and the finer blend morphology in devices consisting of hexane-treated NCs (see Figure 4) we attribute the improvement...
in charge generation to a larger fraction of excitons on the polymer being quenched by charge transfer. With energy transfer operating over larger length scales than electron transfer, only excitons generated in close proximity to the interface will lead to electron transfer. As we identified larger polymer domains for devices consisting of non-hexane-treated NCs (see Figure 4), excitons generated within the polymer domain will on average be further from the interface than in their hexane-treated analogs. As a consequence, exciton quenching will be dominated by energy transfer, making charge generation in devices containing non-hexane-treated NCs inefficient. We note that we cannot monitor charge separation within the CdSe-NC network, as this population would not contribute to the polaronic signal measured here.

We therefore conclude that the reduced polymer domain size in devices consisting of hexane-treated NCs most likely affects the balance between energy and electron transfer yields. As only electron transfer from the polymer to the NC domain leads to efficient free charge generation, we propose that a higher electron transfer yield in devices containing hexane-treated NCs leads to superior charge generation. This improvement in charge generation is the main cause of the marked improvement in $J_{SC}$ with improved carrier extraction contributing to a lesser degree.

3. Conclusion

We have presented a CdSe NC ligand exchange method from long and insulating oleic acid capped to shorter and more conductive n-butylamine capped NCs. In contrast to known ligand exchange strategies our approach is capable of removing all native OA molecules from the NC surface. Furthermore, we found that using hexane as a selective solvent in a post-synthetic purification procedure allowed us to expel aggregated and poorly passivated CdSe NCs. To study the effects of impurities and aggregates on charge dynamics, bulk heterojunction solar cells were prepared using either purified or non-purified NCs as the electron acceptor and MDMO-PPV as the donor material.

4. Experimental Section

Synthesis of CdSe Nanocrystals (NCs): NCs were synthesized using a modification of previously reported methods [35]. All chemicals were purchased from Sigma Aldrich, if not stated otherwise, and were anhydrous if available.

Briefly, CdO (0.748 g, 5.8 mmol), oleic acid (28.7 mL, 90.6 mmol) and 1-octadecene (ODE, 19 mL, 59.4 mmol) were degassed in a three neck flask under vacuum ($10^{-2}$ mbar or better) at $110 \degree C$ for 2 h. For formation of the Cd-oleate complex the flask was flushed with N$_2$ gas and the temperature was increased to $230 \degree C$. Water residues present from formation of the Cd-oleate complex were removed by degassing again under vacuum ($10^{-2}$ mbar or better) at $110 \degree C$ for 1 h. Subsequently, the flask was set under N$_2$ atmosphere and heated to $230 \degree C$. Two identical Se precursor solutions, containing Se (Alfa Aesar, 0.345 mL, 4.4 mmol) dissolved in trietylphosphine (TOP, 4.6 mL, 10.0 mmol), were prepared in a nitrogen filled glove box. The first Se precursor was injected rapidly into the Cd precursor at $230 \degree C$ under nitrogen atmosphere to initiate crystal nucleation. In order to replenish the depleted Se content in the reaction flask the second Se precursor was injected after 15 min and the solution was left at $230 \degree C$ for another 45 min. To quench crystal growth, the flask was placed into a water bath and 5 mL methanol was injected. The NCs formed were isolated from the reaction mixture by flocculating to turbidity using 2-propanol and methanol. After redispersion in toluene and a second precipitation the NCs were finally dispersed in toluene and filtered through a PTFE filter (pore size 0.2 µm). The synthesis yielded particles with a diameter of $5.9 \pm 1.3$ nm (see Supporting Information S2).

Butylamine Ligand Exchange: Nanocrystals (600 mg) were transferred into a nitrogen filled glovebox and dispersed in anhydrous toluene to yield a concentration of 50 mg mL$^{-1}$. n-butylamine (3 mL, 30 mmol) was added and stirred for 11 h at room temperature. The exchange solution was flocculated with a mixture of 2-propanol and methanol, and the NCs were redispersed in chlorobenzene and filtered through a syringe filter with a pore size of 0.2 µm to yield a final concentration of 50 mg mL$^{-1}$.[7] As will be shown later, these samples contained a large density of aggregates.

For samples containing a reduced density of dispersed aggregates, the exchanged NCs were precipitated with a mixture of 2-propanol and methanol and re-dispersed in hexane. The dispersion was centrifuged in order to exclude aggregated and poorly passivated NCs. NCs that remained in the supernatant were precipitated using a mixture of 2-propanol and methanol, and were finally redispersed in chlorobenzene. Prior to device fabrication, the NCs were filtered through a syringe filter with a pore size of 0.2 µm to yield a concentration of 50 mg mL$^{-1}$.

Determination of NC Concentration: NC mass concentrations were measured gravimetrically by drying of 100 µL solution on an electronic scale.

Absorbance Measurements: For absorbance measurements, films were spin-cast on Spectrosil quartz substrates. The spectra were collected using a Hewlett-Packard 8452 UV-vis spectrometer.

Atomic Force Microscopy (AFM): Samples identical to those fabricated for absorbance spectra were prepared for AFM analysis and annealed at 140 °C for 10 min in a N$_2$ atmosphere. Imaging was performed using a Veeco Dimension 3100, operated in tapping mode.

Proton Nuclear Magnetic Resonance Spectroscopy ($^1$H NMR): NC samples were diluted to a concentration of ~2 mg mL$^{-1}$ and dispersed in d-chloroform. NMR spectra were recorded using a Bruker AVS-500 spectrometer. $^\delta$H values are reported relative to the internal standard CDC$_3$ ($^\delta$H = 7.26 ppm).

Transmission Electron Microscopy (TEM): Pristine QDs were diluted to a concentration of ~1 mg mL$^{-1}$ in chlorobenzene and drop cast on a TEM Grid (200 Mesh Cu, Agar Scientific) in a nitrogen-filled glove box. As an independent control, NC:polymer blends were spun onto PEDOT:PSS (Heraeus Clevios) coated indium tin oxide (ITO) patterned glass substrates and annealed at 140 °C for 10 min in a N$_2$ atmosphere. Subsequently, the blend film was transferred to a TEM grid by a lift-off technique. TEM images were taken on a FEI Philips Tecnai 20 at an electron acceleration of 200 keV in bright field mode.

X-Ray Photoemission Spectroscopy (XPS): XPS samples were prepared by spin-coating from 50 mg mL$^{-1}$ solution of NCs in chlorobenzene onto silicon wafer substrates. The samples were then transferred to an ultrahigh vacuum (UHV) chamber (ESCALAB 250Xi) for XPS measurements. XPS measurements were carried out using a XR6 monochromated AlKα X-ray source ($h\nu = 1486.6$ eV) with a 900 µm spot size and 20 eV pass energy.

Preparation and Characterization of Solar Cells: Solar cells were prepared on ITO patterned glass substrates, cleaned in an ultrasonic
bath with ethanol, acetone and isopropanol, respectively. The substrates were then treated with oxygen plasma for 10 min at 250 W, after which they were coated with a 50 nm layer of PEDOT:PSS and dried under \( N_2 \) flow at 230 °C for 30 min. The active layer was spin-coated from a 17.5 mg mL\(^{-1}\) blend solution of MDMO-PPV and CdSe NCs in chlorobenzene, in a 9:1 (NC:PPV) ratio by weight. The devices were then annealed under \( N_2 \) at 140 °C for 10 min, before thermally evaporating a 60 nm aluminium electrode under vacuum.

For external quantum efficiency (EQE) measurements, a 100 W tungsten halogen lamp dispersed through a monochromator was used as the light source and a Keithley 2635 source measure unit (SMU) was used to measure the short-circuit current at various wavelengths. Current-voltage characteristics were measured under AM 1.5G equivalent conditions using an Abet Sun 2000 solar simulator, at an intensity equivalent to 100 mW cm\(^{-2}\), after correcting for spectral mismatch. Both the dark and light current-voltage characteristics were measured using the Keithley 2635 SMU.

**Transient Photovoltage Decay and Transient Photocurrent Decay:** For the transient photovoltage and photocurrent measurements, a high-brightness 525 nm green LED (Kingbright, L-7104VC-G-H) was used as the light source and a Hewlett Packard (HP) 8116A function generator was used as the power supply for the LED. A ring of six white high-brightness LEDs was used for constant background illumination and a set of lenses was used to focus the incident light (both from the pulse light source and background light source) onto a single pixel of the device. The intensity of the background illumination was calibrated by comparing the short-circuit current density \( J_{SC} \) with the values previously obtained from the solar simulator. Open-circuit voltage transients were recorded by connecting the device under test in series with an Agilent DS06052A digital oscilloscope with input impedance of 1 MΩ. Short-circuit current transients were recorded by connecting the device under test in series with an Agilent DS06052A digital oscilloscope with input impedance of 50 Ω.

**Transient Absorption Spectroscopy (TA):** In time-resolved transient absorption spectroscopy, the change of absorption after an initial excitation is monitored as a function of time. Here we use a frequency-doubled Q-switched Nd:YVO\(_4\) laser (AOT-3Q5SPX, Advanced Optical Technologies) as the excitation source. A narrowband 1 kHz repetition rate Ti:Sapphire amplifier system (Spectra-Physics, 90 fs pulse width) was used to power a home-built non-parametric amplifier. The resulting broadband band near IR pulse (850–1050 nm) of 300 fs width was used as the probe beam. The probe beam was subsequently split in two, with the second "reference" beam probing a region of the device that is not excited. In this way the fluctuations of the laser system can be compensated and the overall noise reduced. Pump and probe beam are overlapped on the device. Both probe and reference beam were subsequently dispersed into an Andor Shamrock SR-303i spectrometer and detected using a pair of 16-bit 1024-pixel linear image sensors (Hammatsu, S8381–1024Q), which were driven and read out by a custom-built board from Stresing Entwicklungsbuero. The polaronic signal of the hole charge on MDMO-PPV was measured by exciting the sample at 532 nm at a pump fluence of 1.6 µJ cm\(^{-2}\) and probing in the near IR (850–1050 nm).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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