Enhanced Charge Separation Efficiency in DNA Templated Polymer Solar Cells

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The insertion of a DNA nanolayer into polymer based solar cells, between the electron transport layer (ETL) and the active material, is proposed to improve the charge separation efficiency. Complete bulk heterojunction donor–acceptor solar cells of the layered type glass/electrode (indium tin oxide)/ETL/P3HT:PC70BM/hole transport layer/electrode (Ag) are investigated using femtosecond transient absorption spectroscopy both in the NIR and the UV–vis regions of the spectrum. The transient spectral changes indicate that when the DNA is deposited on the ZnO nanoparticles (ZnO-NPs) it can imprint a different long range order on the poly(3-hexylthiophene) (P3HT) polymer with respect to the non-ZnO-NPs/DNA containing cells. This leads to a larger delocalization of the initially formed exciton and its faster quenching which is attributed to more efficient exciton dissociation. Finally, the temporal response of the NIR absorption shows that the DNA promotes more efficient production of charge transfer states and free polarons in the P3HT cation indicating that the increased exciton dissociation correlates with increased charge separation.

1. Introduction

Bulk heterojunction (BHJ) solar cells in which an oligothiophene polymer acts as a photoabsorber and electron donor (D) and a fullerene derivative acts as an acceptor (A) have been intensely investigated in recent years.[1] The reason being that high power conversion efficiencies (PCEs) have been achieved for these cells largely thanks to the efficient exciton formation and subsequent dissociation at the D/A interface.[1,2] Together with solar cell engineering, including efficient electron and hole transport layers, PCEs higher than 11% have been achieved.[3] This type of cell is particularly versatile as the thin film can be deposited on numerous substrates including, for example, flexible transparent plastics making them ideal for certain applications such as building integrated photovoltaics.[4]

A great deal of research has been invested in optimizing the performance of these cells by tailoring the chemical structures of the donors and acceptors (e.g., ref. [5]), optimizing the nanomorphology of the polymer:fullerene blend,[6] and the electron and hole transport layers (ETL and HTL) to improve charge transport and injection to the electrodes (e.g., ref. [7]) as well as tuning the work function of the ETL.[8]

Clearly, in order to optimize the conversion efficiency of a solar cell it is necessary to have a detailed understanding of the dynamics of charge formation from the photoabsorption all the way through to the charge collection at the electrodes. The generally accepted time line can be summarized as follows[9]:

i) photogeneration of the exciton in the polymer; ii) exciton diffusion to the polymer:fullerene interface; iii) charge transfer to the fullerene and formation of a charge transfer state (CTS, also sometimes called a bound polaron pair) at the polymer:fullerene interface; iv) complete charge separation (dissociation into free polarons); v) diffusion of the resulting polarons to the ETL/HTL and subsequent injection into the electrodes. If the exciton is generated close to the interface with the fullerene, the second step of this time line (i.e., the exciton diffusion) does not occur and an ultrafast mechanism takes place instead of a diffusive one.[10] The ultrafast mechanism takes place on a timescale of <100 fs while the diffusive mechanism requires a picosecond timescale (the precise time depends on where the exciton is formed and on polymer grain size).[11] Figure 1 reports a schematic of the above described time line for both the diffusive and ultrafast mechanism. It is clear that the extent of delocalization of the exciton[11–14] and regioregularities[15–18] and morphology[6,17,19] of the polymer part of the blend are important in determining the relative efficiency of these processes. These effects strongly influence the optical and electrical properties...
of the solar cells with a resulting knock-on effect on their efficiency.[10,20–22]

In this paper we demonstrate that the addition of a DNA nanolayer on top of the ETL of an inverted indium tin oxide (ITO)/ZnO-NPs (ETL)/P3HT:PC70BM/MoO3(HTL)/Ag cell (schematically shown in Figure 2a) has multiple effects on the dynamics of the processes involved in photocharge generation (see Figure 1) and in turn on their efficiency. DNA has been widely investigated as a potential template for the realization of different DNA-templated layers or nanostructures as it is a readily available, well characterized, controllable and easily adaptable material.[23] DNA and its derivatives have also been used to improve the performance of organic electronic devices including organic light emitting diodes,[24] organic field effect transistors[25] and organic polymer solar cells.[8,26] Whereas the main explanation for the effects seen upon incorporation of DNA in these organic semiconductor devices has focused on the electronic properties of the contact, the effect of DNA on the morphology and order of the polymer has largely remained unexplored.

We aim to show that when the DNA is deposited on the ZnO nanoparticles the subsequent spin coating of the polymer:fullerene blend allows the DNA to imprint a different long range structure on the polymer with respect to the solar cells not containing ZnO-NPs/DNA. The resulting structure is more efficient at extracting the initially formed excitons into separated polarons. These aspects have been extracted from a detailed analysis of the UV–vis and NIR transient absorption (TA) spectra of complete solar cells following photoexcitation.

2. Results and Discussion

The discussion is structured as follows: first we present the device performance information where it is shown that there is an improvement in the performance of the cells in which the DNA layer is coated on top of the ZnO-NP ETL layer; then

Figure 1. Schematic illustration of the time line for the different processes involved in charge generation for the ultrafast mechanism (left) and diffusive mechanism (right): i) photogeneration of the exciton in the polymer (orange cloud) or close the polymer:fullerene interface (green cloud); ii) exciton diffusion to the interface; iii) charge transfer to the fullerene and formation of a charge transfer state at the interface; iv) complete charge separation; and v) diffusion of the resulting polarons to the ETL/HTL and injection into the electrodes. In the ultrafast mechanism step (ii) does not occur.

Figure 2. a) Schematic diagram of the glass/ITO/ETL/P3HT:PC70BM/MoO3/Ag with ETL = nothing, ETL = DNA, ETL = ZnO-NPs, and ETL = ZnO-NPs/DNA solar cells. b) Steady state absorption of the solar cells examined in this work.
the discussion gives a description of the features of the static UV/vis absorption of the cells; and finally the most significant part is dedicated to the transient absorption data of the solar cells. The analysis of the spectral content of the TA spectrum at a given delay is discussed in order to demonstrate the change of the poly(3-hexylthiophene) (P3HT) morphology due to the presence of the DNA layer and to show that the exciton initially formed is more delocalized in these cells. The temporal analysis, on the other hand, allows us to show that the DNA containing cells lead to a higher charge separation efficiency both by monitoring exciton populations and the formation of free polarons in the P3HT layer as a function of time. Before discussing the spectroscopic analysis of the cells we briefly describe their performance characteristics. The average values of photovoltaic parameters, including short circuit current ($I_{sc}$), fill factor (FF), open circuit voltage ($V_{oc}$), and power conversion efficiency are summarized in Table 1. The cells with a nanolayer of DNA on ITO deliver average PCE $= 3.2\%$, higher than that of ITO-only case (PCE $= 1.17\%$). The ZnO-NPs layer based devices gave an even better PCE $= 3.4\%$. When DNA was deposited over ZnO-NPs ETL (ITO/ZnO-NPs/DNA) the increment was significant (21% enhancement of PCE in relative terms compared to ITO/ZnO-NPs devices) yielding a high average value of PCE $= 4.09\%$. Further details on the device measurements can be found in the Experimental Section.

2.1. Static UV/Vis Absorption

The UV/vis absorbances of cells of the type Glass/ITO/ETL/P3HT:PC$_{70}$BM/MoO$_3$/Ag with ETL = nothing, ETL = DNA, ETL = ZnO-NPs, and ETL = ZnO-NPs/DNA measured by a static absorption spectrometer together with an integration sphere are shown in Figure 2b.

The absorption in the visible range is dominated mainly by the $\pi-\pi^*$ absorption of the P3HT polymer. In the case of pristine regioregular-P3HT ($rr$-P3HT) films there are three peaks\cite{27} which are centered at 610 ($A_1$), 570 ($A_2$), and 520 nm ($A_3$) but are strongly overlapped, similar to what is observed here in Figure 2b. There are various models present in the literature which are used to describe the absorption peaks.\cite{27–31} The details of these models are fascinating but they are not central to the present work as the most important point to be taken from these discussions is that the wavelengths of the $A_2$ and $A_3$ peaks are dependent on the degree of long range order and conjugation length of the polymer chains while the position of the $A_1$ peak is quite insensitive to these parameters. This point is strongly supported by empirical evidence reported in literature.\cite{27,32}

There are only small differences in the static UV–vis spectra (see Figure 2b) between the different solar cells and thus it is not possible to extract information of the morphologies of the P3HT crystals in the blend from this data. This is not true in the case of the TA spectra as will be described below.

2.2. Transient UV/Vis and NIR Absorption

Ultrafast optical spectroscopy has been used extensively to determine the time scales and efficiencies of the above described processes in BHJ devices.\cite{7,10,32–43} The particular form of ultrafast spectroscopy used in this work is TA spectroscopy in which an optical pump excites the sample and a white light continuum probes the photoinduced effects at a variable delay time.

The optical pump pulse used in this work (405 nm, 3.06 eV) principally excites the P3HT thus generating an exciton which then eventually leads to partial charge separation at the polymer:fullerene interface, complete charge separation in free polarons and, finally, collection at the electrodes following the steps outlined in the introduction (see Figure 1). Some excitons will also be formed in PC$_{70}$BM but for the remainder of this discussion we will concentrate on the fate of the P3HT excitons as these are the species that we follow spectroscopically.

The false color NIR and UV–vis transient absorption maps for the Glass/ITO/ETL/P3HT:PC$_{70}$BM/MoO$_3$/Ag cells are shown in Figure 3. These maps show the wavelength of the probe white light pulse on the $y$-axis and the time between the pump and the probe on the $x$-axis.

The principal features one can observe in these maps are i) photoinduced absorption (positive AA) in the region between 620 and 1300 nm which can be further divided into features $\Pi A_1$ to $\Pi A_5$ (see, for example, Figure 3a,c), and ii) photoinduced bleaching (negative AA) in the wavelength region 470–620 nm (2.0–2.75 eV) which can be further divided into the features labeled $PB_1$, $PB_2$, and $PB_3$ as shown in Figure 3c–f. These features are common to the TA spectra of all blended P3HT polymers and we rely on the comprehensive literature to make an assignment of each of these features.\cite{10,34,37,44} The photoinduced bleaching in the visible region, $PB_1$, $PB_2$, and $PB_3$ which correspond reasonably well with the energies of the $A_1$, $A_2$, and $A_3$ transitions in the static UV–vis spectra discussed in the previous section, are generally assigned to ground state bleaching.\cite{44} However, if this were indeed the case the time dependence of the $PB_1$, $PB_2$, and $PB_3$ signals should reflect the population of the ground state and therefore should all be equal. This is clearly not the case as can be seen from visual inspection of Figure 3c–f where it is clear that the $PB_2$ and $PB_3$ typically have shorter lifetimes than $PB_1$. We therefore attribute at least part of these signals to photoinduced emission or transition blocking due to state filling of the excited state. In either case, the intensities of the signals $PB_1$, $PB_2$, and $PB_3$ depend on the populations of the corresponding excited states which, having different lifetimes, can confer different temporal behaviors on these signals.
The photoinduced absorption features, on the other hand do not have corresponding features in the static absorption. It is found that the PIA 1 to PIA 4 features are generally assigned to a number of overlapping features due to absorption of the CTS (also called a bound polaron pair), and the delocalized and localized hole polaron in the P3HT [7,37] while the PIA 5 is commonly associated with absorption of the initially excited singlet exciton.[38,41] The PIA 2 and PIA 3 are the same feature just spectrally situated on either side of 800 nm and thus present in both the UV–vis and NIR spectra.

### 2.2.1. Spectral Analysis

We start with the spectral analysis in the visible range by making a spectral cut of the TA spectra shown in Figure 3 at a time delay of 800 fs. Cuts at other time delays lead to similar conclusions and are shown in Figure S1 (Supporting Information). The 800 fs time-delay cuts are reported in Figure 4, where the intensity of the signals has been normalized to the minimum of PB 1. The first point to note is that the PB 1 signal at 610 nm (2.1 eV) exhibits very little spectral changes on the modification of the ETL. From the above discussion on the steady state absorption of P3HT it was noted that this peak in general is largely insensitive to the degree of order of the P3HT. The region of the TA spectra containing the PB 2 and PB 3 features, on the other hand, exhibits significant variation in the peak wavelength behaviors of the signals with varying composition of the ETL including a strong spectral shift of the PB 2 to the blue which is particularly visible in the cell with the ZnO-NPs/DNA ETL while the other cells show much smaller shifts. This suggests that the ZnO-NPs/DNA has an effect on the regularity of the intrachain order of the P3HT. Furthermore, the conjugation length and long range order play a role in the degree of intrachain coupling. So the suggestion is that the DNA layer imprints a different conjugation length and long range order when the P3HT:PC 70 BM blend layer is applied on top of the DNA. In the case of PB 3 a new feature at 510 nm appears in the ETL = ZnO-NPs/DNA cell (PB 3*) in addition to the original PB 3 of the other cells at 470 nm. The overlap of these signals makes it difficult to assess the spectral and temporal behaviors of the individual components therefore we concentrate on PB 1 and PB 2 for the remainder of the text.

NIR probing[10,32,38–43] has been of great use in the investigation of the dynamics of PSCs. In this work, the TA in the NIR has been measured for the PSCs with ETL = ZnO and ETL = ZnO-NPs/DNA and both are dominated by three areas of PIA (see Figure 5). The two features (PIA 3 and PIA 4) evident at

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**Figure 3.** False color NIR transient absorption maps for the glass/ITO/ETL/P3HT:PC 70 BM/MoO 3/Ag cells with a) ETL = ZnO and b) ETL = ZnO/DNA. Pseudocolor UV–vis transient absorption maps of c) ETL = ZnO-NPs and d) ETL = ZnO-NPs/DNA, e) ETL = nothing, and f) ETL = DNA solar cells. It should be noted that there is a change from linear to log scale on the temporal axis at 10 ps.
longer delay times in Figure 5b, are centered at 840 and 980 nm, respectively. These have been assigned to overlapping features due to the bound polaron pair and the separated polaron in P3HT.[10] These appear to have the same spectral content in both cells but with a very slightly higher intensity of the polaron signal in the ZnO-NPs/DNA cell at long times (see Figure S2 in the Supporting Information). The largest signal at short times is in the range 1200–1250 nm (PIA5) and has generally been attributed to the excited state absorption of the singlet exciton.[38,41] An interesting point to note is that while the central wavelength of PIA 5 in the ZnO-NPs cell is at 1214 nm that of the ZnO-NPs/DNA cell is shifted to longer wavelengths at ≈1250 nm. This red shift has been associated with a larger delocalization of the exciton,[41,45] which in turn is related to an increase of the intrachain order of the P3HT.[10] This larger delocalization of the exciton can lead to a higher charge separation efficiency.[46,47]

The effect of the DNA intralayer may result from both its morphological and chemical interactions with the ETL and with the polymer:fullerene blend. In a previous paper by some of the authors,[8] it was shown by AFM and STM on the ITO/ZnO-NPs and ITO/ZnO-NPs/DNA substrates that the latter is smoother and contains elongated regular structures on the surface not visible on the ITO/ZnO-NPs substrate. These elongated structures, with an average lateral distance of 1–6 nm, contain several DNA strands. Furthermore, Sönmezoglu et al.[48] have reported highly efficient dye-sensitized solar cells with a DNA modified ITO photoanode, in which the double-helix of the DNA acts as linker bridging unit between the active layer and the ITO. Thus we postulate that when the P3HT polymer is spin coated on our ITO/ZnO-NPs/DNA, the elongated strands of DNA chemically interact with the polymer strands leading to a more ordered layer as the solvent evaporates. The conclusions from the spectral analysis are therefore that the DNA layer changed the morphology of the P3HT grains in the blend and that this leads to a larger delocalization on the initially excited exciton. The temporal analysis presented in the next section addresses the fate of the exciton in the first tens of picoseconds after formation.

2.2.2. Temporal Analysis

The temporal response has been extracted from the TA data by fitting the part of the spectrum containing PB1 and PB2 by two Gaussian functions and then plotting the amplitude of the fits as a function of time (see Figure 6). The significant difference (and more directly related to the efficiency of the cells) is in the temporal evolution of the PB2 signal as is clearly seen in Figure 6. The main difference in the PB2 evolution between ETL = ZnO-NPs and ETL = ZnO-NPs/DNA cells is that there is a smaller contribution of the long-time tail and the appearance of two decay times of 5 and 100 ps (in addition to the 1 ps timescale present in all cells) in the ETL = ZnO-NPs/DNA cells (see Table S2 in the Supporting Information). Furthermore, it can be seen that there is a general trend for a smaller contribution of the long-time tail to the PB2 signal on going from ETL = nothing to ZnO-NPs/DNA (see Figure S3 and Table S2 in the Supporting Information). The overall effect correlates well with the PCE of the cells and therefore we propose that the long time scale is due to trapping of the exciton states into defects in the P3HT crystalline phase. The appearance of two intermediate timescales in the ETL = ZnO-NPs/DNA cells can be interpreted as additional charge separation mechanisms which are possible due to the longer lifetime of the untrapped excitons in these cells. Clearly the smaller the contribution of the signal at long time delays the higher the fraction of excitons extracted...
from the P3HT phase into CT states at the interface, the higher the amount of separated charges and thus the higher the efficiency of the cell. It should be noted that the short timescale decay of 1 ps which is due to bimolecular recombination as demonstrated by power dependence studies (see Figure S4 in the Supporting Information) is not significantly affected by the ETL (see values for $\tau_1$ in Table S2 in the Supporting Information).

The temporal evolution of the PIA$_3$, PIA$_4$, and PIA$_5$ signals are shown in Figure S1 (Supporting Information). The PIA$_3$, PIA$_4$, and PIA$_5$ bands have been assigned to overlapping features due to the bound and free hole polarons in P3HT while the PIA$_3$ band is due to the singlet exciton. The lack of a significant difference in the temporal behavior of the singlet exciton (PIA$_3$), is somewhat surprising considering the above discussions where it was shown that the dissociation of excited/hot excitons is more efficient in the ZnO-NPs/DNA containing cells compared to the ZnO only cells. This is taken as evidence that the more efficiently quenched excited excitons in the ZnO-NPs/DNA containing cells is in the long timescale of the polaron signal while more polarons are observed in the ZnO-NPs/DNA containing cells than in the ZnO only cells. This is taken as evidence that the more efficiently quenched excited excitons in the ZnO-NPs/DNA containing cells are more efficiently converted into free charges.

The temporal analysis of the TA spectra allows us to conclude that the ZnO-NPs/DNA containing cells lead to more efficient exciton dissociation and subsequent formation of free polarons in the P3HT part of the blend.

3. Conclusions

We have measured the femtosecond transient absorption spectra in the UV-Vis and NIR ranges of a series of complete working polymer:fullerene blend solar cells as a function of the composition of the cells. Spectral variations of the transient response in the visible range indicate a change in the long range intrachain order of the P3HT polymer when a layer of DNA is placed between the polymer and ZnO nanoparticles of the electron transport layer. This suggests that the DNA can “imprint” a different long range order of the polymer when the blend is spin coated on top of the DNA containing ETL. Examination of the temporal traces corresponding to the excited exciton state populations show additional intermediate timescale decays (5 and 100 ps) and longer time trapping of the ZnO-NPs/DNA containing cells for the excited state. This has been interpreted as being due to more efficient dissociation of the initially formed exciton. Confirmation is obtained from a higher yield of the long lived P3HT cation polaron as observed in the NIR TA spectra. These observations of higher exciton dissociation into polarons in the ZnO-NPs/DNA containing cells are consistent with their measured PCEs. In view of the above results we propose an interesting approach to improve the BHJ solar cells performance, which consists of the insertion of a nanolayer between the ETL and the active blend, in this case a DNA nanolayer. This layer not only determines a change in the electronic properties of the contact but also, importantly, exerts control on the P3HT morphology (but possibly also on other polymers). Indeed, starting from these results different kinds of templating layers can be envisaged and tailored to optimize the P3HT morphology (or in general the electron donor polymer) and thus to improve the PCE.

4. Experimental Section

Materials: DNA sodium salt from salmon testes, double chain, molecular mass of $1.3 \times 10^6$ Da ($\approx$2,000 base pair) was purchased from Sigma Aldrich. Zinc oxide, dispersion nanoparticles (ZnO-NPs) of the average particle size less than 40 nm and with 20 wt% concentration in water was also purchased from Sigma Aldrich. P3HT (20 mg mL$^{-1}$ in orthodichlorobenzene) and PC$_{70}$BM$_2$, [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (99.99%) were purchased from Solarmer and Solenne BV, respectively. Molybdenum oxide (MoO$_3$, 99.98% powder), orthodichlorobenzene and silver (Ag, wire Z 99.99%) were purchased from Sigma Aldrich.

Figure 6. The intensities of the a) PB$_1$ and b) PB$_2$ signals as a function of delay time between the 400 nm optical pump and the visible probe for the glass/ITO/ETL/P3HT:PC$_{70}$BM/MoO$_3$/Ag with ETL = ZnO-NPs and ETL = ZnO-NPs/DNA solar cells.
Solar Cell Preparation: In the process of inverted solar cell device fabrication, the ITO glass-covered substrates (Kintec, −8 Ω cm−2), are patterned with wet-etching in hydrobromic acid (HBr) and cleaned in an ultrasonic bath in acetone and isopropanol for 10 min with each solvent. For the fabrication of ITO/ZnO-NPs/DNA/P3HT:PC70BM/MoO3/Ag solar cells the ZnO-NPs solution for the thin film deposition was prepared by dissolving 200 µL ZnO-NPs dispersion in 20 mL ethanol which was further stirred overnight at room temperature. The ZnO-NPs thin film was deposited onto ITO-coated glass substrate by spin-coating at spin speed of 3000 rpm over the ZnO-NPs thin film. The prepared ITO/ZnO-NPs/DNA samples were left in vacuum overnight for drying. The active layer P3HT:PC70BM (1:0.7) was dissolved in chloroform and isopropanol for 10 min with each solvent. The solution becomes transparent and then 4.5 mL of methanol was added to dilute it to be 1 mg mL−1 concentration.[16] After overnight stirring at room temperature, the DNA solution was filtered using a 0.2 μm Polycaplylilene fluoride (PVDF) filter (NB: it is important to use this type of filter to obtain the films discussed in this article; the use of PTFE or polypropylene filters with the same pore size instead, resulted in DNA films with different optical and thickness properties) and then spin-coated onto ITO-coated glass substrate at spin speed of 3000 rpm over the ZnO-NPs thin film. The prepared ITO/ZnO-NPs/DNA samples were left in vacuum overnight for drying. The active layer P3HT:PC70BM (1:0.7) was dissolved in ortho-dichlorobenzene and stirred at 75 °C temperature overnight. Next, the blend solution was filtered using 0.22 μm pore sized PTFE filter and spin coated at 500 rpm which was followed by annealing at a temperature of 130 °C for 10 min in order to obtain thickness of 150 nm which was confirmed by profilometer (Dektak 150). In the End all substrates were transferred in the metal evaporator where the MoO3 (hole extracting interlayer) and the silver top contact were thermally evaporated through a shadow mask at pressures below 10−6 mbar for a final thickness of 5 and 150 nm, respectively. Each substrate contained 6 devices of 0.1 cm2 area.

Device Measurements: Solar cell electrical characteristics were measured in air with a Keithley2420 source meter under an AM1.5G Class A ABET solar simulator at an intensity of 1000 W m−2 calibrated with an ECO Pyranometer MS-602 at room temperature. The voltage step, scan speed and delay time for data point scans were fixed at 20 mV, 1 s, and 200, ms respectively. Forward and reverse sweeps gave negligible hysteresis. Cells were masked with 0.1 cm2 black tapes to ensure that cell degradation would not have any effect on the measurements. Furthermore, the PCEs of the cells were measured before and after the measurements. All solar cells were assembled/produced at the Laboratorio di Scienze Fotoniche, Roma, Italy.

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Figure S5 in the Supporting Information reports the dark J–V curves of the best P3HT:PC70BM solar cell devices with various interlayers such as DNA, ZnO-NPs, and ZnO-NPs/DNA together with that without any interlayer, measured under AM1.5G, 1000 W m−2 solar illumination. The on/off current ratios (from +1 V/−1 V) for ITO/ZnO-NPs/DNA ETL based devices were calculated, yielding values of 1.5 × 103 which were higher than that of ITO/ZnO-NPs which was 8.0 × 102.

The energy level diagram of the complete cell is reported in Figure S6 in the Supporting Information, and clearly shows that the presence of DNA does not inhibit charge transfer between layers of the cell. To test the shelf life stability over a duration of 30 d, the inverted P3HT:PC70BM solar cell devices fabricated using different interlayers, were kept in ambient air without any encapsulation. As reported in Figure S7 in the Supporting Information, the PCE decrease was only ~20% for the ZnO-NPs/DNA solar cells after 30 d in air compared to ~39% lower for the ZnO-NPs devices.

Transient Absorption Measurements and Data Analysis: The transient absorption measurements were performed by exciting the solar cells with the second harmonic of a 35 fs 810 nm Ti:Sapphire laser with an intensity of 180 μJ cm−2. All of these measurements were performed in a commercial FemtoFrame II TA spectrometer (IB Photonics) on the complete devices described in the previous sections. The experiments were performed in a pseudo-reflectivity mode in which the focused pump beam (spot size diameter 500 μm) passes through the cell from the glass side, reflects from the Ag electrode and exits again through the glass with an incidence angle of 4° (see Figure 2a for a schematic view of the pump–probe geometry). The probe beam for the UV–vis TA experiments is generated by focusing ~3 μJ of 800 nm light into a CaF2 crystal thus generating a white light continuum in the range 350–800 nm (the results here only show the range 450–750 nm), while the NIR continuum (800–1600 nm) is generated in a similar manner in a YAG crystal. In the case of the UV/vis white light probe the beam is split into two with half passing through the optically pumped cell and analyzed by a first spectrometer and half used as a reference and analyzed by a second spectrometer, both equipped with CCD detectors. In the case of the NIR a single spectrometer with an InGaAs detector array was employed with the on/off pump signal achieved by mechanically chopping the pump beam. The variable time delay in each case was achieved by varying the length of the optical path of the probe pulse. Further details can be found in previous work.[31]

An important aspect of this work is the use of a comparative technique in which the TA spectra of different solar cells are compared by varying the ETL components. As a result the absolute values of the time decay constants are not discussed in detail but only the relative values on changing the composition of the ETL. The fitting procedure to extract the time constants of the temporal behavior of the PB1, PB2, PIA1, PIA2, and PIA3 signals is described fully in the Supporting Information. Furthermore, all time constants and weighting parameters are reported in Tables S1–S5 (Supporting Information).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

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