Photovoltaic Properties of a Porphyrin-Containing Polymer as Donor in Bulk Heterojunction Solar Cells With Low Energy Loss

Léo Bucher, Loïc Tanguy, Nicolas Desbois, Paul-Ludovic Karsenti, Pierre D. Harvey,* Claude P. Gros,* and Ganesh D. Sharma*

A low bandgap D–π–A polymer (PPDPP; D = Zn-porphyrin, A = diketopyrrolopyrrole, π = ethynyle linker) has been synthesized and used as an electron donor for the fabrication of solution processed bulk heterojunction polymer solar cells (PSCs). PC71BM is used as the electron acceptor. After the optimization of the PPDPP: PC71BM weight ratio in 2-methyltetrahydrofuran (2-MeTHF), the PSC based on PPDPP: PC71BM (1:2) showed an overall power conversion efficiency (PCE) of 4.18% with $J_{SC} = 9.75 \text{ mA cm}^{-2}$, $V_{OC} = 0.78 \text{ V}$, and $FF = 0.54$. After the thermal annealing (TA) and subsequent solvent vapor annealing (SVA) of the active layer, the resulting device showed an overall PCE of 6.44% ($J_{SC} = 13.18 \text{ mA cm}^{-2}$, $V_{OC} = 0.74 \text{ V}$, and $FF = 0.66$) with a small voltage loss of 0.51 eV. The improvement in PCE after the TA and SVA treatment of the active layer is attributed to an enhancement of $J_{SC}$ and FF related to a more favorable nanoscale morphology for the exciton dissociation and charge transport as evidenced by the increased hole mobility.

1. Introduction

Organic solar cells (OSCs) are quite an emerging field within the broad photovoltaic (PV) technology. On one hand, they offer an alternative to classical solar cells (i.e., silicon-based technology), especially because they are advantageous in terms of Energy Payback Time (EPBT),[1] which represents the time needed for a PV device to produce as much energy as what is required for its own manufacture, installation, and recycling.[2] On the other hand, their intrinsic physical and mechanical properties, such as lightness and flexibility, allow for their use as complement to well-implanted PV technologies or for specific applications. Concurrently, beside the popular dye sensitized solar cells (DSSCs), one of the most promising candidates among the OPVs is bulk heterojunction solar cell (BHJ), which consists of a biphase blend between electron donor and electron acceptor materials.[3] The most commonly used acceptor is PC71BM, a soluble derivative of fullerene, and the donor may either be a conjugated polymer or a conjugated small molecule, both currently leading to power conversion efficiencies (PCEs) >10%.[4] Recently, the use of non-fullerene acceptors allowed reaching efficiencies as high as 13%.[5]

The porphyrin chromophore has been extensively explored for DSSC purposes because of its strong ability to absorb light then leading to efficient photoinduced electron transfer.[6] This chromophore has already shown very good results as donor in BHJ when used as complementary light harvesting unit located as planar pendant groups from the polymer chain.[7] Nevertheless, porphyrins did not enable the elaboration of efficient donor materials once included in the main conjugated chain of the polymer yet. Indeed, if several studies focused on developing porphyrin-containing polymers in this manner,[8] the best PCEs barely exceed 1%,[9] Noteworthy, small molecules (SM) based on porphyrin and diketopyrrolopyrrole (DPP) as donor (D)–acceptor (A) layouts have been quite widely studied and are among the most efficient donor materials in BHJ. Since 2013, A–D–A trimeric structures exhibited $\sim 5 > \text{PCE} > 9\%$, by engineering meso-substituents on the porphyrin moiety.[10] Recently, the reversed D–A–D analog has also shown good performances, yielding 8% PCE.[11] Noteworthy, these molecules have also been employed in efficient ternary blend BHJ OSCs[12] or in tandem solar cells as well.[13]

We now report the full photovoltaic characterization of a novel D–π–A polymer based on a porphyrin–diketopyrrolopyrrole (DPP) backbone, denoted as PPDPP exhibiting a low optical
behavior between the polymer and its small molecule analogs. After great interest in order to compare both photophysical and photovoltaic properties, as well as preliminary photovoltaic results, were described in an earlier communication.[14] This material acts as an hybrid of both D–A arrangements of small A–D–A and D–A–D molecules and is of great interest in order to compare both photophysical and photovoltaic behavior between the polymer and its small molecule analogs. After the optimization of the PPDPP/PC71BM weight ratios, the PPDPP:PC71BM (1:2) cast from 2-MeTHF showed the best photovoltaic performance with an overall PCE of 4.18% (Jsc = 9.75 mA cm−2, Voc = 0.78 V, and FF = 0.54). In order to improve the PCE, we have employed a two-step annealing process (TA), that is, thermal annealing (TA) followed by solvent vapor annealing (SVA) of the active layer. The resulting device showed an improved overall PCE of 6.44% with small voltage loss of 0.51 eV and Voc of 0.74 eV. The significant PCE improvement is due to the enhancement of Jsc and FF, resulting from a more favorable nanoscale morphology for exciton dissociation and charge transport.

2. Experimental Section

2.1. Device Fabrication

Polymer solar cells (PSCs) were fabricated using the conventional architecture for ITO/PEDOT:PSS/PPDPP:PC71BM/PFN/Al. Indium tin oxide (ITO) coated glass substrates were cleaned sequentially by ultra-sonication in detergent, deionised water, acetone, and isopropyl alcohol for 10 min each, followed by drying under a flow of nitrogen. The substrates were further dried at room temperature. PEDOT:PSS solution was filtered and spin coated onto the pre-cleaned ITO substrates at 3500 rpm for 30 s and annealed at 120 °C for 10 min. The blends of PPDPP and PC71BM (different weight ratios of PPDPP and PC71BM (1:1, 1:1.5, 1:2, and 1:2.5, total concentration 18 mg/mL) were dissolved in 2-MeTHF. The solutions were spin coated on top of the PEDOT:PSS layer at 2000 rpm for 60 s and the samples were dried under vacuum oven at 40 °C. The TSA treatment was done afterwards: the active layer was first thermally annealed at 110 °C for 2 min then cooled down to room temperature before being exposed to CS2 vapour for 2 min. A methanol solution of PFN (poly[(9,9-bis{3′-[N,N-dimethylamino] propyl]-2,7-fluorene)-alt-2,7-(9,9-diocetylfluorene)]) (containing 5 v% AcOH as additive) with a concentration of 1.5 mg mL−1 was spin coated on the top of active layer at 300 rpm for 30 s to give a 10 nm thickness. The aluminium (Al) electrode was deposited on top of the active layer by thermal evaporation under a vacuum of 10−5 Torr. The effective area of devices was 3 × 3 mm².

The current-voltage characteristics of the devices were measured using a computer-controlled Keithley 2400 source meter under stimulated AM1.5G at an intensity of 100 mW cm−2 provided by a solar simulator. The incident photon to current efficiency (IPCE) of the devices was measured by illuminating the device through the light source and the monochromator and the resulting current was measured using a Keithley electrometer under short circuit conditions.

The hole mobilities of the active layers were determined by fitting the dark current to the model of space charge limited current (SCLC) in the hole only device with the configuration ITO/PEDOT:PSS/active layer/Au. The active layers were deposited under the same conditions as for the corresponding solar cells.

3. Results and Discussion

3.1. Optical and Electrochemical Properties

PPDPP exhibits an absorption profile extending up to 1000 nm with an optical bandgap of 1.25 eV, which is lower than that for the small molecule analogs.[15] PPDPP and PC71BM were used as electron donor and acceptor, respectively. The absorption spectra of PPDPP:PC71BM (1:2) in thin film (Figure 1) showed a broad absorption spectrum covering from 350 to 1000 nm, which is the combination of the individual PPDPP and PC71BM absorption profiles. After the TA (110 °C for 2 min) and subsequent SVA, the absorption intensity of the active layer, particularly corresponding to PPDPP increased and also get redshifted as compared to as cast active layer, indicating the light harvesting efficiency of the active is enhanced, which is beneficial for the improvement in Jsc of corresponding PSC.

The HOMO and LUMO energies estimated from the cyclic voltammetry and absorption data are respectively ~−5.32 and −3.86 eV. In a BHJ PSCs, after the exciton dissociation at D/A interface, electrons are transferred from donor to acceptor and holes are transferred from acceptor to donor. Therefore, the HOMO offset and LUMO offset between the donor and acceptor should be sufficiently higher than the exciton binding energy. The HOMO offset between the PPDPP and PC71BM (HOMO and LUMO are −6.05 and −4.10 eV) are ≈0.73 eV above the threshold value of ≈0.30 eV indicating that efficient electron transfer from PPDPP to PC71BM at the donor/acceptor interface of the active layer is possible. Moreover, the more stable and deeper HOMO of PPDPP indicates that high value of Voc can be achieved for the BHJ PSCs using PPDPP and PC71BM as the donor and acceptor, respectively. The LUMO offset between the PPDPP and PC71BM is ≈0.24 eV, which is smaller than the suggested threshold value of 0.3 eV for efficient photo-induced charge separation.[16] However, despite the LUMO offset is small, it may not necessarily limit the charge separation property since an efficient photo-induced charge separation was also observed in some D/A systems used in PSCs with extremely low...
energy offset. This low energy offset also indicates a low energy loss, which is helpful for achieving a high $V_{oc}$.

To obtain information about the exciton dissociation and transfer in the OSCs, the photoluminescence (PL) spectra of pristine PPDPP, as cast PPDPP:PC$_{71}$BM (1:2, 10 mg/mL concentration) and TA and SVA treated PPDPP:PC$_{71}$BM thin films, were measured (Figure 2). By exciting at 720 nm (the absorption peak of PPDPP), the PL intensity of PPDPP is significantly quenched in as cast PPDPP:PC$_{71}$BM films, related to the dissociation of excitons generated in the PPDPP at D/A interfaces in the blend thin films, since at 720 nm the absorption of PC$_{71}$BM is poor and do not contribute to the exciton generation at this wavelength. Moreover, the degree of PL quenching in TA and SVA treated PPDPP:PC$_{71}$BM is more than that for as cast PPDPP:PC$_{71}$BM film may be due to the improved morphology of the blend that facilitates the exciton dissociation more efficiently, as discussed in the later part of the discussion. These results show that exciton dissociation and charge transfer are efficient in both blended active layers, in spite of the low value of the $E_{LUMO}$ offset.

3.2. Aggregation

One of the most interesting features going from SM to polymer is the observation of an additional intense band on the lowest energy side on the absorption spectrum of PPDPP in solution (i.e., 850 nm; Figure 3), no matter the concentration. A review of the literature reports different SM examples for which this band is absent in solution. However, this band appears in thin films. This low-energy feature is attributed to aggregation, which is common for conjugated polymers and SM where solid state organization is often π-stacking driven. Porphyrin aggregates are often of J-type readily identified by the bathochromic shift of the absorption band; an effect arising from interactions between transition moments of the chromophores.

In the PPDPP case, the polymeric chain in solution is assumed to be isolated from the other polymers, and yet it still behaves like J-aggregates, thus indicating this phenomenon could result from the parallel linear arrangement between chromophores within the conjugated chain. This hypothesis is further supported by Spano’s theory which states that H-aggregates are due to inter-chain interactions whereas J-aggregations come from intra-chain couplings.

The absorption spectra of PPDPP were recorded in different solvents (Figure 4a). The polymer solubilizes well in toluene, chlorobenzene, THF, and chloroform but not as well in ethyl acetate, benzonitrile, and DMF. There is a gradual decrease of the aggregation (i.e., amplitude of the low-energy band) from good to bad solvents, with a total disappearance of this transition in benzonitrile and DMF. The explanation for such a phenomenon could be that when the polymer is efficiently solubilized, inter-chain interactions are minimized, and intra-chain ones (J-aggregation) are promoted, whereas a poor solvent would fold up and bring polymer chains closer to each other, disrupting intramolecular interactions in favor of intermolecular interactions.
interactions. Absorption profile of PPDP in thin film was measured for several thermal annealing (TA) post-treatment times (Figure 4b). Initially, transitions attributed to ICT and optically active aggregates are strongly overlapping themselves, resulting in the very broad absorption from 600 to 950 nm. Again, J-aggregates band was decreasing with the time of TA, indicating a molecular reorganization in the solid state, from the less organized situation caused by rapid spin coating deposition to more favorable interactions. Noteworthy, both PPDP and its SM analogs exhibit this same behavior in the solid state. Indeed, this phenomenon was also noticed by Peng et al. with their SM, and they too, observed the disappearance of the low energy transition and the rise of a new band around 700 nm after treatment by thermal annealing.[18] This was then attributed to reorganization from J-aggregates to H-aggregates. The latter could correspond in our case to the absorption band noticed at 680 nm, which became more obvious for 40 min of thermal annealing but also in DMF solution discussed above (Figure 4a). These observations all suggest a J → H reorganization in the aggregation mode.

Noteworthy, the strong overlap between the different absorption bands coming from each chromophore, ICT and aggregates, does not allow to see whether the blue-shifted H-aggregates are present in solid state without TA. It is suspected that PPDP could feature both H- and J-aggregations, a phenomenon discussed in the literature and named HJ-aggregation.[20] The control of the amount of J-aggregates in order to transform it into H interactions by applying post-treatment such as TA may be possible. This could be beneficial to help finding a good balance between the optical and charge transport properties since the latter seems to be enhanced with H-aggregation whereas J-aggregation leads to a broad absorption bands.[21]

We previously reported the emission properties of PPDP.[14] The emission spectra is a combination of fluorescence from porphyrin and DPP monomers in solution, as well as ICT and even J-aggregates (Figure 5). Interestingly, PPDP in the solid state displays only the weak emission associated with aggregation at 900 nm. The time-resolved emission spectra (TRES) can be monitored in solution streak camera (Figure 6a). Decay-associated spectra extracted from the TRES exhibit three components (Figure 6b). The lifetimes, $\tau_p$, are consistent with the previously reported TCSPC results ($\approx 500$ and $\approx 200$ ps). The long $\tau_F$ (426 ps) is associated with an ICT fluorescence whereas the two short components (136 and 38 ps) are attributed to J-aggregates’ emission between 850 and 900 nm. These values are consistent with the 100[22] and 180 ps data for porphyrins J-aggregates reported as mono-exponential decays,[13], and with 320 and 80 ps reported as a bi-exponential decay.[24]

### 3.3. Photovoltaic Properties

The potential of PPDP in PSCs as electron donor, solution processed PSCs were examined with a device structure ITO/PEDOT:PSS/PPDP:PC$_7$BM/PFN/Al where PC$_7$BM is the electron acceptor. After device optimization, the best PPDP/
PC71BM weight ratio was 1:2 (total concentration of 16 mg/mL) and thickness of 95 nm showed the best photovoltaic performance. The current voltage characteristics ($J-V$) of the PSCs under illumination (100 mW cm$^{-2}$) are presented in Figure 7a and the corresponding photovoltaic properties are compiled in Table 1.

The PSC based on as cast PPDPP:PC71BM active layer gave an overall PCE of 4.18% ($J_{sc} = 9.75$ mA cm$^{-2}$, $V_{oc} = 0.78$ V, and FF = 0.54) with an energy loss of 0.47 eV (voltage loss is given as $E_g - V_{oc}$, where $E_g$ is the optical bandgap of PPDPP donor). Pyridine was tried as solvent additive, since this has led to strong enhancement of PCE for previously reported SM analogs.$[11,18a]$ However, this strategy did not appear to be effective for PPDPP and the PCE was not changed significantly. Therefore, we have used the combination of thermal annealing (TA) and subsequent solvent annealing (SVA) on the active layer to increase the PCE of our PSC. After of TA and SVA treatment (TA and SVA) that is, thermal annealing (TA) and subsequent solvent vapor annealing (SVA) of active layer before the deposition of PFN/Al electrode, the PCE of the resultant device improved up to 6.44% ($J_{sc} = 13.18$ mA cm$^{-2}$, $V_{oc} = 0.74$ V, and FF = 0.66) with the voltage loss of 0.51 eV. The IPCE spectra of the PSCs are shown in Figure 7b which is closely resemble with the absorption spectra of corresponding active layers (Figure 1). This indicates both PPDPP and PC71BM contribute to the photocurrent generation. The IPCE values for the device based on the TSA treated active layer were higher than that as cast counterpart which are indicative of highly efficient photon to electron conversion process in the TA and SVA based PSC which is in agreement with the absorption spectra of TA and SVA treated active layer where the absorption coefficient is higher than as cast active layer counterpart. The $J_{sc}$ values estimated from the integration of IPCE spectra are about 9.61 and 13.05 mA cm$^{-2}$ for the PSCs based on as cast and TA and SVA processed active layers, respectively, which are in agreement to the values obtained from $J-V$ characteristics of the PSCs under illumination.

Since the charge transport properties play important role in the generation of $J_{sc}$, we have measured hole and electron mobilities from the $J-V$ characteristics of the hole only and electron only devices in dark (as shown in Figure 8a and 8b) and fitting these curves in the space charge limited current model to get information about the effect of TA and SVA on the charge transport properties and the values are shown in Table 2. Both
the hole and electron mobilities were enhanced after TA and subsequent SVA treatment, but the degree of increase in hole mobility is quite high than that for electron mobility. The enhanced charge mobilities and better hole/electron balance in TA and SVA treated device reduce the charge recombination and contribute to higher $J_{sc}$ and FF values of the PSCs.\(^{[25]}\)

To understand the light absorption and charge extraction properties in the as cast and TA and SVA treated PSCs, we measured the variation of photocurrent ($J_{ph}$) with effective voltage ($V_{eff}$) for both devices and shown in Figure 9 ($J_{ph} = J_L - J_D$, where $J_L$ and $J_D$ are the current densities in under illumination and in dark, respectively).\(^{[26]}\) $V_{eff} = V_o - V_a$, [where $V_o$ is the voltage when $J_{ph} = 0$ and $V_a$ is the applied voltage] and under an applied bias, respectively) determines the electric field in the BHJ active layer that affects the charge dissociation and transport process. In the case of as cast device $J_{ph}$ is small and shows linear dependence on voltage without saturation, suggesting significant charge recombination loss and less efficient interfacial contact resulting to a low $J_{sc}$ and FF.\(^{[27]}\) At high $V_{eff}$, the photogenerated free carriers are driven more rapidly to the electrode and recombination loss is minimized, the saturation photocurrent ($J_{ph\text{sat}}$) is only limited by the incident photon absorption. For device with TA and SVA, $J_{ph}$ is higher than that for as cast counterpart, and showed linear dependence on $V_{eff}$ at low voltages of $V_{eff} (<0.5\ \text{V})$ and reaches $J_{ph\text{sat}}$ when $V_{eff}$ is 0.94 V, indicating that photogenerated excitons are dissociated into free charge carriers at the donor/acceptor interfaces and extracted by the electrodes more efficiently in TA and SVA treated active layer device. At high $V_{eff}$, the $J_{ph\text{sat}}$ Values for as cast and TA and SVA based devices are 11.96 mA cm\(^{-2}\) and 13.4 mA cm\(^{-2}\). Therefore, compared with as cast device, $J_{sc}$ in TA and SVA based device has an improvement of 18% which is mainly indorsed to the enhancement in light absorption. However, the overall improvement in $J_{sc}$ in TA and SVA treated device is 24.13%, therefore, the improvement in light absorption for TA and SVA based device is still not enough to account for the increase in $J_{sc}$, indicating that there should be some other factor

### Table 1. Photovoltaic parameters of the PSCs based on PPDPP:PC71BM active layers processed under different conditions.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$J_{sc}$ (mA cm(^{-2}))</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPDPP:PC71BM (as cast)</td>
<td>9.75</td>
<td>0.78</td>
<td>0.54</td>
<td>4.18 (4.11)(^{a})</td>
</tr>
<tr>
<td>PPDPP:PC71BM (TA and SVA)</td>
<td>13.18</td>
<td>0.74</td>
<td>0.66</td>
<td>6.44 (6.32)(^{a})</td>
</tr>
</tbody>
</table>

\(^{a}\)Average of 10 devices.

### Table 2. Hole and electron mobilities, series and shunt resistance of PPDPP:PC71BM active layers processed under different conditions.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>Hole mobility (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>Electron mobility (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>Series Resistance ($\Omega$ cm(^2))</th>
<th>Shunt Resistance ($\Omega$ cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPDPP:PC71BM (as cast)</td>
<td>$9.12 \times 10^{-5}$</td>
<td>$3.52 \times 10^{-4}$</td>
<td>12.03</td>
<td>7.16</td>
</tr>
<tr>
<td>PPDPP:PC71BM (TA and SVA)</td>
<td>$2.03 \times 10^{-5}$</td>
<td>$2.84 \times 10^{-4}$</td>
<td>735</td>
<td>959</td>
</tr>
</tbody>
</table>

Figure 8. Dark current-voltage characteristics of (a) hole only devices and (b) electron only devices processed with as cast and TA and SVA active layer.

Figure 9. Variation of photocurrent ($J_{ph}$) with effective voltage ($V_{eff}$) for the PSCs based on different active layers processed under different conditions.
contributing to the \( J_{sc} \) improvement. The possibilities of exciton dissociation into free charge carriers under the short circuit condition can be calculated by the ratio of \( J_{sc} \) and \( J_{phat} \) (\( J_{sc}/J_{phat} \)), which are 0.84 and 0.92, for as cast and TA and SVA treated devices, respectively. Moreover, under the maximum power conditions, these values are about 0.72 and 0.85, for as cast and TA and SVA. These results indicate that exciton dissociation and charge collection efficiency are much higher and bimolecular recombination suppressed in the device based on TA and SVA processed film.[28] Therefore, the TA and SVA treated PSC has not only enhanced light absorption but also efficient charge dissociation owing to the better nanoscale morphology.

In order to verify the influence of TA and SVA treatment on the morphology of blend film, transmission electron microscopy (TEM) measurement was employed and shown in Figure 10. It is well known that fine and small domain size is more efficient for exciton dissociation but harmful for charge transport. However, excessive phase separation or large domain size is favorable for charge transport but limits the exciton dissociation.[29] Therefore, there should be an optimized nanoscale phase separation morphology for active layer for efficient PSCs. The bright and dark regions observed in TEM images corresponds to donor rich (PPDPP) and acceptor rich (PC\(_{71}\)BM), respectively. As shown in TEM images, the as cast active layer showed a fine mesh network with small domain size indicating finely mixing between PPDPP and PC\(_{71}\)BM which limits the charge transport within the active layer, resulting low values of \( J_{sc} \), FF, and PCE. However, in TA and SVA treated films the domains were increased within the 10–20 nm size, and well phase-separated interpenetrating network is formed due to molecular aggregation, which is favorable for both efficient exciton dissociation into free charge carriers as well as charge transport in active layer toward respective electrodes. These combined effect hints to the improvement in both \( J_{sc} \) and FF, thereby enhancement in overall PCE of the PSC based on the PPDPP:PC\(_{71}\)BM film processed with TA and SVA treatment.

In order to understand the better charge transport properties of TA and SVA treated device, X-ray diffraction (XRD) characterization was performed to study the film structure of the blend films, including crystallinity and molecular packing and shown in Figure 11. PPDPP:PC\(_{71}\)BM blend film presented a strong and definite lamellar and \( \pi-\pi \) stacking peak at \( 2\theta = 3.76^\circ \) (\( d = 1.84 \) nm) and \( 2\theta = 23.16^\circ \) (\( d = 0.47 \) nm), respectively with a broad diffraction peak at \( 2\theta = 18.28^\circ \) corresponding the PC\(_{71}\)BM. The intensity of (100) diffraction peak was enhanced for blend film processed with TA and SVA indicating that the PPDPP may have more ordered molecular arrangement and improved crystallinity, leading to the efficient hole transport in the blend film. The crystallinity enhancement may be attributed to the enlarged size of crystallite which accords with the improved phase separation in the blend film upon TA and SVA treatment.[30] Moreover, the peak corresponding to \( \pi-\pi \) stacking get stronger upon the TA and SVA treatment as well as diffraction peak corresponding to (010) is shifted to longer value of \( 2\theta \), indicating the reduction in \( \pi-\pi \) stacking distance (from 0.42 to 0.38 nm). Since the carrier transport ability of conjugated polymer highly rely on the inter-chain packing properties, especially for their \( \pi-\pi \) stacking properties, we inferred that hole mobility improved due the reduction in \( \pi-\pi \) stacking distance in PPDPP upon TA and SVA treatment. It means the PPDPP and PC\(_{71}\)BM molecular redistribution in active layer can be simultaneously adjusted by TA and SVA treatment for better exciton dissociation and charge transport and collection.

The series \( (R_s) \) and shunt \( (R_{sh}) \) resistance of PSCs were estimated from the inverse of the slopes of \( J-V \) characteristics under illumination at \( V_{oc} \) and \( J_{sc} \), respectively to investigate the charge carrier transport and collection. The \( R_s \) of the PSC was significantly decreased for the active layer with TS and SVA treatment from 12.03 to 7.16 \( \Omega \) cm\(^2\). The decreased \( R_s \) may be beneficial for the charge transport in the active layer. Meanwhile, \( R_{sh} \) of PSC was increased from 735 to 959 \( \Omega \) cm\(^2\) upon TA and SVA treatment, indicating that leakage can be effectively suppressed due to the optimized morphology.[31]

We also investigated the difference in the charge recombination processes in the OSCs processed with TA and SVA treated active layers, by measuring the \( J-V \) characteristics at different illumination intensities. Figure 12b displays the variation of \( V_{oc} \) with illumination intensity \( (I_{in}) \) in the semi-logarithmic plot. The slope of these plots describes the degree of trap assisted Shockley-Read-Hall (SRH) recombination in BHJ OSCs.[32]

In the case of trap assisted recombination, \( V_{oc} \) strongly depends on light intensity with the slope close to \( 2kT/q \), where \( k \) is the
Boltzmann’s constant, $T$ is absolute temperature and $q$ is the electronic charge. The PSC based on as cast PPDPP:PC$_{71}$BM (1:2) active layer shows a slope of $1.48 \times \frac{kT}{q}$, indicating strong SRH recombination, while the TA and SVA cast PSC attains smaller slope of $1.28 \times \frac{kT}{q}$. The lower value of $\frac{kT}{q}$ indicates that PSC based on TA and SVA active layer exhibits less charge trapped recombination, which is reliable with the higher values of $J_{sc}$ and FF. The variation of $J_{sc}$ with $P_{in}$ is shown in Figure 12a and follows the relationship $J_{sc} \propto (P_{in})^{\gamma}$. The values of $\gamma$ estimated from the slope of the $J_{sc} - P_{in}$ plots for as cast and TA and SVA were about 0.91 and 0.96, respectively. The higher value of $\gamma$ for TA and SVA active layer based PSC indicates that the bimolecular recombination was insignificant for this device than the as cast counterpart. These results suggest that bimolecular recombination and space charge effect were suppressed for the devices based on TA and SVA treated active layer.

4. Conclusion

In summary, we have used a low bandgap D-$\pi$-A polymer consisting of Zn-porphyrin (donor unit) and DPP (acceptor unit), PPDPP, as electron donor material along with PC$_{71}$BM for the solution processed PSCs. After the optimization of PPDPP/PC$_{71}$BM weight ratio and annealing treatment conditions, the PSC processed with TA and SVA treated active layer showed overall PCE of 6.44% with $V_{oc}$ of 0.74 V and low voltage loss of 0.51 eV which is higher than that of as cast counterpart (PCE = 4.18%). The increased PCE was enabled by the favorable nanoscale morphology of the active layer, induced by the TA and SVA treatment, maintaining the high crystallinity of the active layer and more balanced charge transport. The PL quenching results indicate efficient electron/hole transfer between PC$_{71}$BM and PPDPP despite of small LUMO-LUMO offset, resulting low energy loss of 0.51 eV. Photovoltaic performances measured here are higher than every other donor materials containing porphyrins in their conjugated main chain reported so far. These results open new perspectives and show the true potential of this chromophore in order to design new donor materials for efficient BHJ solar cells. Aggregation related phenomena of PPDPP in the solid state and in solution were observed. The excited state associated to $j$-aggregates were examined using a Streak camera and $\tau_{ps}$ of $\approx$135 and 40 ps were extracted. The aggregation process was found to be solvent and temperature treatment dependent. Since organization in the solid state is of utmost importance for the optical, charge transport and photovoltaic properties, it would be imperative to control the aggregation mode “on demand” in order to design materials with tunable properties. Finally, because of its intense NIR absorption, PPDPP could also be considered as a third component (donor) for ternary blend PSCs to harvest photons of low energy wavelengths as well as for the tandem organic solar cells. More research is currently ongoing in our laboratories.

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Figure 11. X-ray diffraction pattern of as cast and TA and SVA PPDPP:PC$_{71}$BM (1:2) thin films.

Figure 12. Variation of (a) short circuit current ($J_{sc}$) and (b) open circuit voltage ($V_{oc}$) with incident illumination intensity for the polymer solar cells based on as cast and TA and SVA active layers.
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Conflict of Interest
The authors declare no conflict of interest.

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