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New NIR Absorbing DPP-based Polymer for Thick Organic Solar Cells

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Sunlight covers a broad spectrum from ultra-violet to infra-red and low band gap materials are required to utilize the near infrared region (NIR) for better photon harvesting in organic solar cells. It has been shown that copolymers comprising diketopyrrolopyrrole based acceptors and simple donors (thiophene or furan) achieve absorption maximum around 800 nm. In this study, the selenophene based donor units coupled with diketopyrrolopyrrole acceptor unit based polymer (PFDDPSe) was synthesized with an absorption maximum at 830 nm and absorption onset of 930 nm. The optimized organic solar cells with PFDDPSe: PC₇₁BM active layer blends of 210 nm showed maximum PCE of 6.16 % (ave. 6.02 %) via solvent additive engineering with inverted device structure. Charge transport, recombination loss mechanism, and morphology are systematically studied. These results demonstrate that highly efficient NIR polymer can be achieved by the introduction of selenophene and a suitable solvent additive process suitable for NIR organic solar cells. PFDDPSe is also one of the rare examples of a polymer with a PCE over 6% that does not contain any thiophene-based unit in its backbone.

Introduction

The interest in organic solar cells (OSCs) grows steadily and 10% power conversion efficiency (PCE) barrier has recently been surpassed.¹⁻¹⁰ Additionally, the continuous progress in development of non-fullerene acceptors (NFAs) based OSCs brought a new level of excitement and opportunities to this lively research area,¹¹⁻¹³ which has pushed the efficiency over 13% with the structure design and device optimization.¹⁴⁻¹⁷ However, the absorption range of the active layer in fullerene and non-fullerene based solar cells is mainly between 300 nm and 800 nm.¹⁸ The utilization of near infrared (NIR) region of the solar spectrum is limited. Towards achieving this aim, a number of NIR-absorbing polymers were designed, synthesized and characterized.¹⁹⁻²² Additionally utilization of NIR absorbing NFAs for realization of high performance solar cells are recently getting significant attention.^{23, 24} Among donor polymers that have been evaluated, thiophene based diketopyrrolopyrrole (DPP) acceptor containing polymers showed promising results.^{22, 25} In addition to thiophene based DPP acceptors, their furan containing counterparts are also successfully utilized in organic solar cells. Frechet and co-workers showed that when furan based DPP acceptor (FDPP) copolymerized with a simple donor, thiophene, resulting polymer (PDPP2FT) has an absorption maximum at 789 nm and a PCE of 5% can be achieved utilizing this material in OSCs.²⁶ To further push the absorption towards NIR region, replacing thiophene with

selenophene is a valid strategy. The larger size of selenium compared to sulfur results in lower aromaticity of selenophene due to poor overlap of selenium orbitals and the π -system of carbon framework.²⁷⁻²⁹ This ultimately result in increased quinoidal contribution to the molecular energy levels, hence a red-shift in the absorption profile.³⁰ There are a number of examples in the literature where this approach results in red-shift in absorption and in some cases better photovoltaic performance was observed.³¹⁻³³

In this work, we designed a NIR polymer, PFDDPSe where furan based DPP was used as the acceptor and selenophene was used as the donor, marks the one of the rare examples of DPP based polymer where the polymer backbone does not include any thiophene or thiophene based unit (BDT, thienothiophene, etc.). With the construction of inverted structure device, we yielded a high performance over 6% with the introduction of diphenyl ether (DPE), a high boiling point solvent additive, which surpasses the as-casted devices, with an improvement of over 10 folds. Deeper morphological and electrical analysis demonstrated the beneficial effects on the morphology, charge transport and recombination, which resulted in much higher performance of the organic solar cells.

Results and Discussion

Synthesis

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Figure 1. Synthetic route for the polymers

First, we concentrated our efforts for the synthesis of the FDPP unit (**1**) (Figure 1). There are a number of approaches reported in the literature for the synthesis of this unit. Condensation of 2-furionitrile and diethyl succinate is the most common method due its convenience.²⁶ In this method the FDPP unit is attained as a salt which can be directly utilized in the subsequent alkylation reaction. However when this approach is used, the reported yields are generally low.²⁶ Alternatively, at the end of the same reaction, the solution can be acidified and the FDPP can be obtained in the neutral, protonated form. In literature acetic acid is commonly used for this purpose and the precipitated FDPP was collected by filtration and washed with methanol. However in our hands, very low yields were obtained after successive washing.³⁴ On the other hand when HCl was used instead of acetic acid, the target product was obtained in good yield.³⁵ Next the alkylation reactions were performed. Here two different alkyl chains were utilized: a linear C12 chain and a linear C18. The alkylations were performed successfully (utilizing both approaches mentioned above) to give compound **2**³⁵ and **3** albeit with relatively low yields. Then the attained alkylated FDPP units were brominated with NBS to give literature compound **4**³⁵ and compound **5**. Selenophene was stannylated from both 2 and 5-positions³⁶ and Stille coupling polymerizations were performed to obtain target polymers (PFDPPSe-12, PFDPPSe-18). As mentioned above it was stated in the literature that FDPP based polymers tend to have better solubilities compared to their thiophene analogues and a C12 linear chain or a C8 branched chain substituted FDPP-thiophene copolymers were shown to be soluble in common organic solvents. A significant difference was observed when donor unit thiophene in the polymer backbone is switched with selenophene; the resulting material, PFDPPSe-12, was completely insoluble, even in o-DCB. On the other hand both PFDPPSe-18 was highly soluble in CHCl₃, chlorobenzene and o-DCB. GPC analyses showed that PFDPPSe-18 have an *M_n* of 14.6 kDa and an *M_w* of 50.3 kDa with a PDI of 3.44. PFDPPSe-18 will be referred as PFDPPSe for simplicity.

Optical and Electrochemical Characterization of FDPPSe

Figure 2. a) Thin film UV-Vis spectrum and b) cyclic voltammogram of PFDPPSe c) band alignment of PFDPPSe in the proposed solar cell devices structure

A thin film of PFDPPSe was spin coated on to ITO glass slides and the UV-Vis spectrum was recorded. Two absorption maxima were observed similar to that of PDPP2FT (Figure 2a). The lower energy absorption maximum for PDPP2FT was reported to be 789 nm, and as expected, PFDPPSe showed significant red-shift and the absorption maximum was determined to be 832 nm. The onset of absorption also shifted substantially (880 nm vs 927 nm). The optical band gap was calculated from the onset and was found to be 1.34 eV. Cyclic voltammogram of PFDPPSe was also recorded and from the onset of oxidation and reduction potentials the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of PFDPPSe were observed at 5.46 eV and 3.81 eV respectively (Figure 2b). These values are comparable with the ones obtained for PDPP2FT.

Solar Cell Fabrication and Optimizations

Solar cells were fabricated using PFDPPSe as the electron donor and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as the electron acceptor with an inverted device structure, ITO/ZnO(~40nm)/PFDPPSe:PC₇₁BM(~210nm)/MoO₃(~7nm)/Ag(~100nm). The band alignment for the proposed device structure is given in Figure 2c. We first optimized the donor: acceptor blend ratio. In detail, the polymer: PC₇₁BM ratio was changed from 1:1 to 1:5 and the device performances were evaluated (Table 1). While the 1:1 ratio gave very poor results (PCE of 0.15%), increasing the PC₇₁BM loading resulted in significant enhancement (PCE of 0.93%) in device performance, due to increase in the fill factor (FF). Notably, the increase in PC₇₁BM ratio did not have a strong effect in the short

Table 1. Results of the polymer:PCBM ratio optimization (Film thickness of the active layer is 95 nm).

Ratio	J _{sc}	V _{oc}	FF	PCE
1:1	0.78	0.56	33.2	0.15
1:2	1.89	0.63	54.6	0.65
1:3	2.22	0.63	62.8	0.93
1:4	2.05	0.64	58.6	0.77
1:5	1.85	0.61	52.1	0.59

circuit current (J_{sc}). It is possible that due to the long alkyl chains of the donor unit large gaps are present in the morphology. The

Table 2. Comparison of device performance with no additive (CB) and DPE additive (CB+3%DPE) under optimized conditions. Active layer film thickness is 210 nm					
	Jsc	Voc	FF	PCE	Average PCE
CB	1.66	0.63	50.0	0.52	0.47
CB+3% DPE	16	0.64	60.4	6.16	6.02

increase in PC₇₁BM ratio helps filling of these gaps which results in higher FF.³⁷ However, the morphology still does not provide a pathway for efficient charge extraction, hence the low J_{SC}. The effect of additive was then introduced to see if the morphology can be improved for a better charge extraction.³⁸

Diphenyl ether (DPE) was chosen as the additive.^{25, 39} A strong additive effect was clearly observed in solar cell devices. With the optimization of film thickness via changing concentration of the polymer: PC₇₁BM solution and rotation speed for the spin coating, a high efficiency of 6.16% (average 6.02% over six devices) was achieved. The optimum film thickness was found to be 210 nm. It is important to note here that a decent FF was achieved with a thick active layer which is rare for NIR organic solar cells. To make a clear comparison, devices with optimized conditions were prepared with no additive and results are given below (Table 2). The devices processed with solvent additive result in almost 13 fold increase in the PCE. This is one of the highest enhancements using DPE as an additive for NIR organic solar cells. External quantum efficiency (EQE)

data for devices were also recorded and the integrated J_{SC} data (1.50 mA/cm² and 15.4 mA/cm²) was consistent with actual J_{SC} values (1.66 mA/cm² and 16.0 mA/cm²) from the devices, which is in good agreement with the J_{SC} values from J-V curves with the error smaller than 5% (Figures 3a and 3b). A significant difference in the photoresponses reflected in EQE curves after the introduction of DPE. The devices revealed a broad and high incident light response with maximum EQE approaching 60% with the help of DPE. In contrast, the device without DPE shows a low photoresponse (<10%) in all range from 300 nm to 930 nm (Figure 3b). According to a previous report, PDPP2FT derivatives (thiophene analogues of PDPPSe with a variety of alkyl chains) showed EQE values below 40% in the 700-850nm region because of the insignificant charge contribution. However, in our blend system, stronger contribution was achieved from the NIR region where EQE values were roughly higher than 40 % between 700 nm and 850 nm (Figure 3b). This data clearly shows that PDPPSe generates stronger contribution in the NIR region than the polymer with thiophene units.

Morphological and Electronical Characterization of FDPPSe:PC₇₁BM Blends

In general, the additive can efficiently help to obtain better micromorphology and phase separation, which is beneficial for the charge transport. The surface and inner morphology of blend films with/without DPE were studied by the characterization of atomic force microscopy (AFM) and transmission electron microscopy (TEM). As shown in Figure 3c, the AFM image of blend film without DPE clearly found many dots on the surface with root-mean-square (RMS) over 10 nm, whereas the blend film after the solvent additive treatment become smooth with a reduced RMS of 2.31 nm (Figure 3d).⁴⁰ The flat blend film is beneficial for the contact between active layer and top electrode. More importantly, the blend films with DPE indicated an interpenetrating nanoscale structure, which means an obvious phase separation has appeared. We utilized TEM technique to further study the inner morphology in a nanoscale. Similar with the AFM images, strong aggregation of PC₇₁BM was observed in the blend film without additive treatment (Figure 3e). Conversely, the incorporation of 3% DPE in solvent results in the significant change in morphology of the film. The interpenetrating network with optimal phase separation size is shown in Figure 3f, featuring an important sign of efficient charge generation and transport.⁴¹ Clearly, AFM and TEM images explain the order of magnitude increase in the J_{SC} and the improvements observed in the FF.

The charge carrier mobility in the blend film is critical, especially for carrier sweeping-out. In order to determine the electron and hole mobilities in the blend film with/without additive treatment, we measured the dark current density-voltage (J-V) characteristics of single carrier device and then analysed the data using space-charge-

Table 3. Comparison of hole and electron mobilities for the films coated from CB and CB with 3% DPE additive.			
	Hole Mobility	Electron Mobility	Ratio
CB	3.52 x 10 ⁻⁵	3.21 x 10 ⁻⁴	9.12
CB+3%DPE	3.44 x 10 ⁻⁴	2.68 x 10 ⁻⁴	0.78

Figure 3 a) the J-V curves of device with/without DPE, b) the EQE curve of device with/without DPE, c) and e) the topography image of AFM and TEM images of blend film without additive, d) and f) the topography images of AFM and TEM image of blend film with additive.

Figure 4 a) Hole mobilities of FPDPPSe-18 spin coated from CB and from CB+3%DPE, b) electron mobilities of PFDPPSe spin coated from CB and from CB+3%DPE, c) J_{sc} versus light intensity and d) V_{oc} versus light intensity measurements of solar cells with/without additive.

limited current (SCLC) method. The detailed equation and device fabrication are presented in Supporting Information. The fitting results in Figure 5a and Table 3 revealed that the increase in hole mobility with the introduction of DPE is in line with the conclusion of morphology analysis, in which the interpenetrating network formation when DPE is added into the solvent. Conversely, there is a decrease in electron mobility of blend film when the amount of additive changed from 0% to 3% (Figure 4b). We speculate that the distribution of over-aggregation fullerene domain may be the main reason for the decrease in electron mobility. More importantly, the electron and hole mobility are more balanced in the film processed with 3% DPE. The balanced carrier transport may be one reason that contribute to the higher device performance.⁴²

To further characterize the significant changes in current density and fill factor, we focused on the recombination loss in the blend films with/without DPE by collecting the J-V characteristics at different light levels to show the V_{oc} evolution as a function of light intensity. Particularly, the J_{sc} follows a power-law dependence on light intensity (P^{in}) as $J_{sc} \propto P^{in\alpha}$, where α represents the power-law exponent.⁴³ Normally, $\alpha = 1$ indicate bimolecular recombination become negligible, whereas $\alpha < 1$ suggest that bimolecular recombination is a limiting factor of device performance. As shown in Figure 4c, it is apparent that bimolecular recombination is one of the limiting factors which significant surpassed the charge transportation and/or extraction due to the moderate morphology in the film without additive because of the $\alpha = 0.83$. Interestingly, the α value is approaching unity ($\alpha = 0.98$) after the introduction of additive, which indicates that the bimolecular recombination is one reason surpassing the device performance. On the other hand, the relationship between V_{oc} and light intensity can give information about trap-assisted recombination by the following theoretical consideration. In detail, trap-assisted recombination is associated by a 2 kT/q in a semi-logarithmic plot of V_{oc} versus P^{in} , while the slope of the curves indicates a pure bimolecular recombination. Figure 4d demonstrated that trap-assisted recombination has a significant

decrease after the addition of additive in blend film. (1.56 kT/q in CB, 1.23 kT/q in CB+3% DPE).⁴⁴

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Conclusions

A new NIR absorbing copolymer, PFDPPSe, one of rare examples of a polymer that does not contain any thiophene-based unit in its backbone, was successfully synthesized and used as a donor in organic as solar cells with inverted device configuration. Compared to its thiophene containing analogues, PFDPPSe showed broader absorption in the NIR region due to the stronger electron-withdrawing property of selenophene unit, which translated to stronger response in the 700-900nm region by the corresponding EQE studies. Detailed device optimizations indicate strong additive influence to the blend morphology, whose PCE as high as 6.16% was recorded for PFDDSe (13 fold increase in PCE compared to the device without additive), which is favourably comparable to PCEs reported for a number of DPP-based polymers. More fundamentally, the NIR absorption ability of PFDPPSe shows the broad application prospects in the outdoor windows and semitransparent device applications. Additionally PFDPPSe is a good candidate for high band gap perovskite/NIR bulk heterojunction bilayer devices. The work on these lines are currently underway in our laboratories.

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A new NIR Absorbing DPP-based polymer for thick organic solar cells with PCE over 6%