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# Unlocking the potential of diketopyrrolopyrrole-based solar cells by a pre-solvent annealing method in all-solution processing

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In this work, we report a solution processible diketopyrrolopyrrole anthracene based diblock copolymer synthesized *via* a rapid direct C–H arylation coupling method. After optimizing the combination of solvent and thermol annealing process, we investigated the characteristics of this di-block low band gap copolymer used as a donor part in bulk hetero-junction solar cells. The influence of the polymer:fullerene ratio (PDPP-ANT:PC<sub>61</sub>BM) and annealing conditions on the photo active film nanomorphology and device performance has been studied in detail. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) reveal that the resulting film morphology strongly depends on the fullerene ratio before heat treatment. Power conversion efficiencies increase, more than four-fold, to 1.7% for regular architectures with high  $V_{oc}$  (0.73 V),  $J_{sc}$  (4.75 mA cm<sup>-2</sup>) and FF (49.0%), compared with the unannealed device 0.37% (with  $V_{oc}$  (0.54 V),  $J_{sc}$  (1.83 mA cm<sup>-2</sup>), FF (37.8%)). Furthermore, the two broad absorption bands of the PDPP-ANT materials show their potential to be applied in ternary polymer solar cells and tandem polymer solar cells.

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## 1. Introduction

Solar energy is one of the best available sources for alternative renewable energy. Therefore, scientists have shown much interest in the development of new-style solar cells, and in the past decade polymer solar cells (PSCs), as a new class of so-called ‘plastic’ photovoltaics,<sup>1</sup> based on organic materials have emerged and evolved as a promising cost-effective alternative to silicon-based solar cells. Due to their unique properties such as their low processing cost, ease of processibility, light weight, mechanical flexibility<sup>2,3</sup> and versatility of chemical structure,<sup>4,5</sup> and especially their high solubility, ease of spin-coating, ink-jet and roll-to-roll printing<sup>6</sup> for streamlined production of large area devices, their usable range has expanded to industrial production for niche applications in space, vehicles, marine industry, desert environment and residential buildings.<sup>7,8</sup> Recently, the power conversion efficiency (PCE) of ~10% (ref. 9 and 10) has been achieved for PSCs through combination of delicate molecular design and device optimization.<sup>11</sup>

The diketopyrrolopyrrole (DPP) unit, a well-known dye unit with many outstanding properties such as excellent light

absorption in long wavelength,<sup>12</sup> photochemical stability, preeminent charge carrier mobility, good solubility *etc.*,<sup>13</sup> has been widely used in polymer based functional devices such as organic thin-film transistors (OTFTs), organic photovoltaics (OPVs), chemical sensors, *etc.*<sup>14</sup> Moreover, this series of materials possesses efficient tunability in electronic characteristics through side chain substitution and solid state self-assemblies allowing for band gap tuning through hybridization of the highest occupied molecular orbital (HOMO) of the donor moiety with the lowest unoccupied molecular orbital (LUMO) of the acceptor moiety.<sup>15</sup> However, neither DPP-based organic polymer materials nor DPP-based film processing techniques are primitive leading to a strict device performance, therefore, the devices cannot meet the demands of real application yet. In order to further develop better DPP-based organic devices, several groups gain ground in this series of materials and devices. Ananth Dodabalapur group<sup>15</sup> synthesized PDPP-TNT materials, optimized OPV device fabrication processing and acquired high performance. Y. Chen group<sup>16</sup> reported two small molecules DOR2TDPP and DCAO2TDPP with a diketopyrrolopyrrole (DPP) unit for solution-processed bulk-heterojunction (BHJ) solar cells. R. Pacios group<sup>17</sup> reported diketopyrrolopyrrole-based polymer bulk hetero-junction solar cells with inverted and regular architecture and the influence of the polymer:fullerene ratio on the photoactive film nanomorphology. Y. Cao group<sup>18</sup> reported a highly soluble anthracene cyclic adduct with a thermally cleavable substituent in PSCs.

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However, the synthetic method of DPP-based materials, generally, shows complicated and low yield. Moreover, the PCE of PSCs, as inscape, is decided by three parameters, open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ) and fill factor (FF).<sup>19,20</sup> To improve the  $J_{sc}$  without sacrificing the  $V_{oc}$  and FF is one of the effective strategies to get high PCE for PSCs. As a matter of fact, there are many approaches to improve the  $J_{sc}$ , though the direct and fundamental method is to synthesis novel molecules with broad light absorption range and high harvest efficiency. An alternative approach is to compact the organic molecular arrangement to enhance the absorption of film<sup>21</sup> and a large amount of approaches such as active layer morphology controlling by adding additives,<sup>22–25</sup> thermal annealing,<sup>26</sup> solvent vapor annealing,<sup>27–29</sup> modification of buffer layer,<sup>30–32</sup> applying anti-reflection coating<sup>19,33</sup> and light harvesters methods.<sup>34</sup> Hence, for the purpose of unlocking the promising DPP-based PSCs potential, it is worthwhile to boost the synthesis method and device fabrication processing.<sup>35,36</sup> In Alan J. Heeger's group, optimized thermol annealing procedure of PSCs prompted their PCE from ~1% to ~5%.<sup>37</sup> In Yang yang's group, the maximum efficiency obtained for slow-grown film was ~4.4% which is three time more than that of fast-grown film (~1.36%) by solvent vapor annealing.<sup>38</sup> We are inspired by these research findings. Slow-grown film may improve the performance and further unlock the potential of PSCs, therefore, we introduce a solvent vapor annealing procedure before the conventional thermal annealing procedure in fabrication devices.

Here we applied a palladium-complex catalysed direct C-H arylation polymerisation method to synthesize DPP-anthracene di-block copolymer, further fabricate and investigate polymer bulk hetero-junction solar cells with all solution processed regular architecture. The influence of the polymer:fullerene (PDPP-ANT:PC<sub>61</sub>BM) ratio and annealing condition on the photo active film nanomorphology and device performance has been studied in detail. Especially, we combined solvent annealing before thermal treatment method and optimized the device fabrication process, improving PCE significantly to 1.7% (with  $V_{oc}$  (0.73 V),  $J_{sc}$  (4.75 mA cm<sup>-2</sup>) and FF (49.0%)), comparing with the unannealed device 0.37% (with  $V_{oc}$  (0.54 V),  $J_{sc}$  (1.83 mA cm<sup>-2</sup>), FF (37.8%)), which unlocked the performance barrier of DPP-based PSCs by developed annealing method. In order to emphasize the effects of combined annealing method on photovoltaic properties of the PDPP-ANT:PC<sub>61</sub>BM blend system, we further investigated the absorption spectra, energy levels, thermostability and film morphology.

## 2. Experimental details

### 2.1 General

All the chemicals were purchased from Sigma Aldrich and used without further purification. All reactions were carried out using Schlenk techniques in an argon or nitrogen atmosphere with anhydrous solvents.

### 2.2 Instrumentation and characterization of PDPP-ANT

<sup>1</sup>H NMR measurements were performed on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to residual CHCl<sub>3</sub> in CDCl<sub>3</sub>.

Thermogravimetric analysis (TGA) was carried out using a TA Instrument TGA Q500 at a heating rate of 10 °C min<sup>-1</sup>.

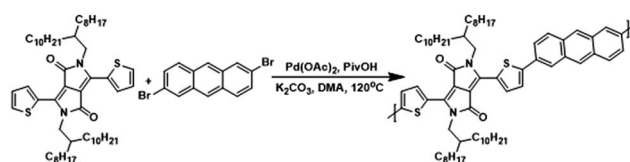
### 2.3 Electrochemical properties of PDPP-ANT

The electrochemical properties of the polymer were studied using the cyclic voltammetry (CV) technique and its HOMO and LUMO energy levels were calculated. Cyclic voltammograms of the polymer were recorded by spin coating the polymer solution on a glassy carbon (GC) disk electrode with 0.1 M tetrabutylhexafluorophosphate in CH<sub>3</sub>CN as the electrolyte at a scan rate of 100 mV s<sup>-1</sup>. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was measured under the same conditions and it was located at 0.11 V relative to the Ag/AgCl electrode. It was assumed that the redox potential of Fc/Fc<sup>+</sup> has an absolute energy level of -4.80 eV under vacuum. Cyclic voltammetry experiments were performed using a Shanghai Huchen (model CHI620E) by Echochimie. The HOMO energy level was calculated using the equation:  $E_{HOMO} = -(E_{ox-onset} + 4.8 \text{ eV})$ , where  $E_{ox-onset}$  is the onset potential for oxidation relative to the Ag/AgCl reference electrode.<sup>39</sup>

### 2.4 Synthesis of DPP-Thi-anthracene

Synthetic routes to polymer DPP-anthracene are depicted in Scheme 1. DPP-Thi (200 mg, 0.24 mmol), 2,6-dibromoanthracene (77.96 mg, 0.24 mmol), and palladium acetate (Pd(OAc)<sub>2</sub>) (2.67 mg, 0.01 mmol) were added to a 38 mL Schlenk flask. DMA (4 mL), PivOH (7.34 mg, 0.07 mmol) and a nitrogen degassed aqueous solution of 2.5 M K<sub>2</sub>CO<sub>3</sub> (160.08 mg, 1.16 mmol) were added and stirred for 15 min under nitrogen. The mixture was heated at 120 °C for 16 h and monitored *via* thin layer chromatography (TLC) for reaction completion. During the reaction, the color of the reaction mixture was changed from red to purple after 10 h and with a 94% yield in 16 h.

The crude polymer was filtered off, washed with water, diluted acid chloride, water, acetone, methanol and subsequently it was subjected to Soxhlet extractions with acetone, methanol, and hexane to remove the impurities and oligomers. Finally, it was subjected to extract by Soxhlet with chloroform. The chloroform fraction was collected, concentrated, and precipitated from methanol to yield dark fiber-like polymer. Yield: 68%.  $M_w/M_n$ (GPC) = 25 000/17 600. Chemical shifts are reported in parts per-million (ppm) and are referenced to the residual solvent peak (chloroform,  $\delta^1\text{H}$  = 7.26 ppm,  $\delta^{13}\text{C}$  = 77.0



Scheme 1 Synthesis route of DPP-Thi-anthracene polymers.

ppm),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm), 9.31–6.66 (br, 12H), 3.85 (s, 4H), 1.89–0.66 (m, 78H).

## 2.5 Nanomorphology characterization

Scanning electron microscopy (SEM) images were acquired using a ZEISS MultiSEM 505 digital electron scanning microscope. Atomic force microscopy (AFM) measurements were performed on polymer thin films obtained by spin coating a polymer solution in chloroform on ITO coated glass substrate (PDPP-ANT:PC<sub>61</sub>BM/PEDOT:PSS/ITO). AFM images were recorded with a Nanoscope V microscope (Veeco Inc., Santa Barbara, CA) operated in tapping mode at room temperature in air, using micro fabricated cantilevers (spring constant of  $30 \text{ N m}^{-1}$ ). Thermal annealing was carried out on thin film samples at  $130^\circ\text{C}$  for 25 min in nitrogen. The thickness of the device layers was measured by J.A.Woollam M-2000 ellipsometer.

## 2.6 PSC device fabrication

OPV devices were fabricated on ITO glass substrates with a configuration of ITO/PEDOT:PSS/PDPP-ANT:PC<sub>61</sub>BM/Ca/Al. All devices were fabricated on glass substrates with patterned indium-tin-oxide (ITO) anode having a sheet resistance of  $15 \Omega$  per square. The substrates were subjected to a routine cleaning process with rinsing in deconex 12Pa-A, deionized water, acetone, isopropanol *via* ultra-sonification for 15 min each and then dried with nitrogen gun and finally treating in a UV-ozone chamber for 15 min. A layer of PEDOT:PSS ( $\sim 30 \text{ nm}$ ) was spin coated on the substrate at 1500 rpm using an aqueous solution of PEDOT:PSS (Clevios PV P AI4083) and then annealed at  $130^\circ\text{C}$  on a hot plate under nitrogen. The PDPP-ANT:PC<sub>61</sub>BM blend layer was then deposited by spin-coating a solution ( $15 \text{ mg mL}^{-1}$ ) of PDPP-ANT (66, 50, 33, 25 wt%) and PC<sub>61</sub>BM (American Dye Source) (34, 50, 67, 75 wt%) in a mixture of chloroform and *o*-dichlorobenzene (4 : 1 by volume) at 5000 rpm on top of the dried PEDOT:PSS layer. The thickness of the active layer used in these OPV devices was around 150 nm. Combined solvent annealing before thermal treatment method was carried out on film samples placed in a closed Petri dish till film drying in nitrogen, then heating at  $130^\circ\text{C}$  for 25 min for firming smooth films<sup>13</sup> in nitrogen while it is known that  $230^\circ\text{C}$  annealing temperature<sup>18</sup> may damage film crystal structure leading to lower PCE of PSCs. An aluminium cathode and calcium buffer layer were deposited to reach 100 nm and 20 nm, respectively, by thermal evaporation through a shadow mask under a pressure of  $\sim 10^{-5} \text{ m bar}$  to complete the device fabrication, which was finally packaged with glass cover-plate by epoxy glue, in nitrogen, with a square device area of approximately  $9 \text{ mm}^2$ .

## 2.7 Optoelectronic characterization

UV-vis spectra were recorded on a Shimadzu model UV-2450-PC.  $J$ - $V$  characteristics of the encapsulated devices were taken using a Keithley 4200 source unit under 1 SUN AM1.5G illumination from a xenon lamp based Oriel 9600150 W Sun Simulator.

# 3. Results and discussion

The synthetic approach to the solution processable donor polymer PDPP-ANT is outlined in Scheme 1 and molecular structure of the PDPP-ANT polymer and PC<sub>61</sub>BM fullerene derivative used in this study is shown in Fig. 1. Thermal properties of the polymer were investigated using thermal gravimetric analysis and were carried out under nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ . PDPP-ANT exhibited good thermal stability with the onset decomposition temperature ( $T_d$ ) being  $350^\circ\text{C}$  (Fig. 1) which is much higher than annealing temperature. The HOMO and LUMO energy levels of the PDPP-ANT thin film were characterized by cyclic voltammetry (CV) using  $0.1 \text{ M CH}_3\text{CN}$  electrolyte solution in dry acetonitrile. The cyclic voltammogram of this polymer shown in the inset of Fig. 2 clearly indicates a reversible oxidation and a partially reversible reduction processes. The magnitude of the current measured during the oxidation process is higher than that of the reduction process, indicating the p–n bipolar type characteristics of this polymer. The onset potential is determined from the intersection of two tangents drawn at the rising current and the baseline charging current of the CV scans. The calculated HOMO value of PDPP-ANT is  $\sim -5.5 \text{ eV}$  from the oxidation onset ( $+0.7 \text{ V}$ ). The LUMO estimated from the reduction on-set potential ( $\sim -0.9 \text{ V}$ ) is  $+4.80 - 0.9 = +3.9 \text{ eV}$ , the electrochemical band gap is found to be  $-1.55 \text{ eV}$ .

The absorption properties of PDPP-ANT were characterized in solid state (thin film on glass) by UV-vis-NIR spectroscopy. The PDPP-ANT polymer showed two broad absorption bands in the 300–500 nm and 500–800 nm regions as shown in Fig. 3, while the P3HT showed the strong absorption bands in the 350–650 nm. It is providing the possibility of creating a novel ternary polymer solar cell or tandem polymer solar cell. The absorption maxima ( $\lambda_{\text{max}}$ ) in solid state are located at 701 nm in PDPP-ANT film. The optical band gap ( $E_g^{\text{opt}}$ ) calculated from the solid state absorption onset is  $1.55 \text{ eV}$ , which is a little narrower than earlier reported polymer PCOAODDPP ( $E_g^{\text{opt}} = 1.6 \text{ eV}$ ).<sup>15,18</sup> PDPP-ANT forming after  $230^\circ\text{C}$  heating to remove hydroxys, the device performance is suffered from non-complete transformation of PCOAODDPP to PDPP-ANT and the defects are

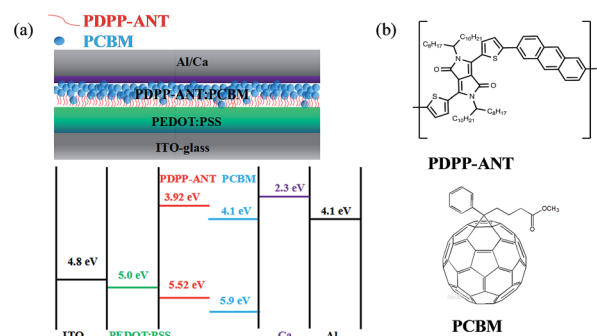


Fig. 1 The device configuration and energy level diagrams with respect to vacuum level for the materials used in the (a) regular architecture and (b) molecular structure of the PDPP-ANT polymer and PC<sub>61</sub>BM fullerene derivative used in this study.

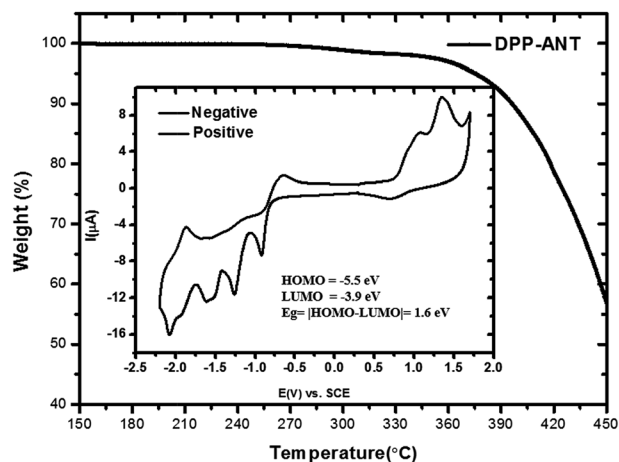


Fig. 2 Thermogravimetric (TGA) profiles of the DPP-ANT with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under a  $\text{N}_2$  atmosphere. Inside graph is voltammogram of PDPP-ANT thin films on platinum electrode showing the first cathodic and anodic cycles at a scan rate  $100\text{ mV s}^{-1}$ . The electrolyte was  $0.1\text{ M}$  tetrabutylammonium hexafluorophosphate in anhydrous.

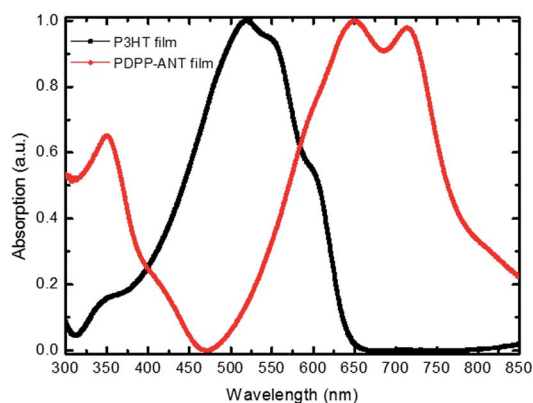


Fig. 3 Absorption spectra of P3HT and PDPP-ANT pure polymer film on a glass substrate.

generated in the active layer films during the exorbitant high temperature heating process.

In the perspective of designing PSCs, recently, amount of the reported DPP-based organic solar cells present regular architectures based on ITO/PEDOT:PSS as the high work function electrode, and either Ca or LiF together with Ag or Al as the low work function electrode.<sup>17</sup> Low work function materials combined with PEDOT:PSS are well known to be all-solution processed. Therefore, previously designed and tested architecture for the PDPP-based: PCBM system was applied to the fabrication of these new generation DPP-based polymer solar cells. In order to do so, we have reported the following configuration and device energy level diagrams: ITO/PEDOT:PSS (30 nm)/PDPP-ANT:PC<sub>61</sub>BM (150 nm)/Ca (10 nm)/Al (100 nm) (Fig. 1). We used PDPP-ANT as an electron donor in combination with [6,6]-phenylene-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as an electron acceptor for the fabrication of polymer BHJ solar cells. A solution of PDPP-ANT

and PC<sub>61</sub>BM (1 : 3 by weight) in a mixture of chloroform and *o*-dichlorobenzene (4 : 1 by volume) was used to deposit the photoactive layer. PDPP-ANT has limited solubility in *o*-dichlorobenzene, so that PDPP-ANT readily crystallizes from solution during spin-coating. The best-performing devices were spun from a relatively dilute  $15\text{ mg mL}^{-1}$  solution (in comparison, P3HT:PCBM cells are often made from  $30\text{ mg mL}^{-1}$  solutions) at a high speed of 5000 rpm. Due to the low vapor pressure of *o*-dichlorobenzene and its preferential PCBM solvation, a PCBM concentration gradient may be induced during spin-coating, *i.e.* the blend film is PCBM-rich towards the cathode, but PDPP-ANT rich towards the anode.

According to a previous article on the P3HT:PCBM active layer system, self-organization 'solvent' annealing of polymer blends is one of most effective method to boost the PCE of PSCs.<sup>38</sup> The article systematically researched on the self-organization and annealing varied by controlling the film growth rate, it was found that the slow-grown films already have a high degree of ordering which helps to improve the PCE of PSCs, and so far no researcher has applied self-organization 'solvent' annealing method in DPP-based active layer PSCs.<sup>40</sup> As illustrated in Fig. 4, here, we combined solvent annealing before thermal treatment method to optimize the device fabrication process. Solvent annealing disposes off solvent and makes the film in good order. Further, annealing makes the arrangement of molecules more compact and reduces the defect states to enhance the charge generation and transport. A similar process has been reported in the PTB7:PCBM blend system combining pre-annealing and post-annealing processing.<sup>41</sup> Since charge generation and transport mechanisms strongly depend on the light absorption profile, moreover, on the electron and hole mobility and the nanodomains formation of both components in the photoactive film,<sup>42,43</sup> the first step to optimize efficient solar cell fabrication is the readjustment of the polymer: fullerene ratio.<sup>44</sup>

As seen in Fig. 5, the absorption spectra of the different fullerene concentration films with and without combined annealing method were tested to evaluate the different fullerene concentration and combined annealing method effect on the absorption of light. The polymer: fullerene ratio is important in order to maximize the light absorbance, at the same time, obtaining balanced electron and hole transport, which should be reflected in a rather large FF. This strategy of controlling the polymer:fullerene ratio is an effective attempt to balance light absorption and charge transport.<sup>45</sup> Therefore, high efficient polymer:fullerene solar cell is a matter of finding the best compromise between light absorption and charge transport. Fig. 5 shows the absorption spectra of 150 nm thick films for different polymer:fullerene ratios (*i.e.* 2 : 1, 1 : 1 and 1 : 3 with or without annealing). Although all films exhibit similar absorbance for two broad absorption bands in the 300–500 nm and 500–800 nm regions, significant differences can be detected in the absorbance of thin films with different polymer:fullerene ratio, where the absorbance decreases as the fullerene ratio in the films increases. Moreover, the light absorbance significantly boosts after combined annealing for all the films leading to

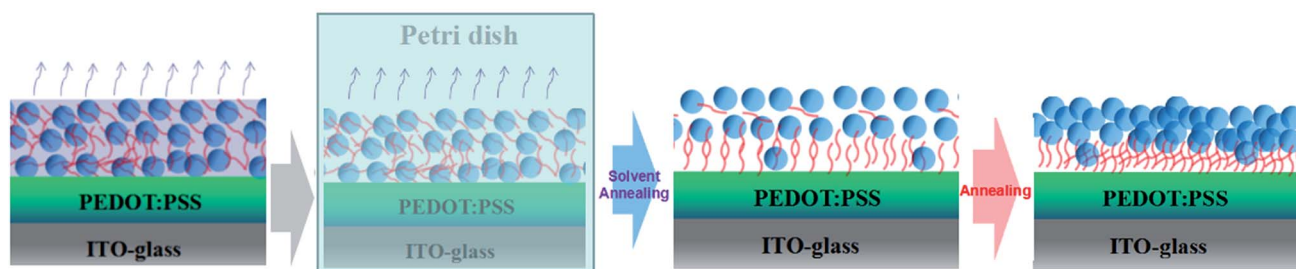


Fig. 4 A combined annealing method in all-solution fabrication processing.

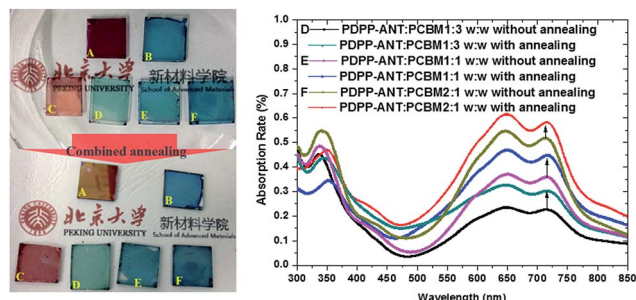


Fig. 5 Absorption spectra of blend film PDPP-ANT:PCBM in  $x:y$  weight ratio. (A. P3HT B. PDPP-ANT C. P3HT:PCBM D. PDPP-ANT:PCBM (1:3) E. PDPP-ANT:PCBM (1:1) F. PDPP-ANT:PCBM (2:1)).

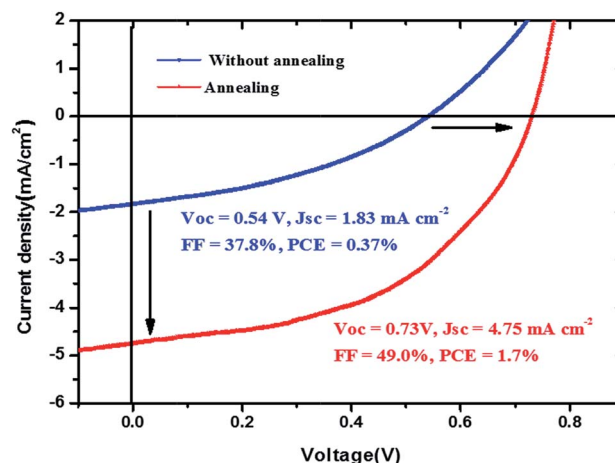


Fig. 6 Current density–voltage curves of the best PDPP-ANT:PCBM-based solar cell under dark and simulated AM1.5 conditions with and without combined annealing.

deeper colors of the films on ITO glass substrates as shown in the photograph in Fig. 5.

Control of the blend structure at the nanoscale is, in fact, one of the most effective ways to significantly enhance the organic solar cell efficiency.<sup>46</sup> In this contribution we have investigated PDPP-ANT:PCBM blend systems in the conventional devices by applying the different fullerene concentrations with and without combined annealing method. The rationale for this was to be able control the formation of microscale phase separation through the natural entanglement of random polymer chains, while allowing the formation of crystallites at the nanoscale in the voids left by the Fig. 6 shows the  $J-V$  characteristics of the best analyzed ratios of PDPP-ANT:PCBM while Table 1 summarizes the photovoltaic performance of the solar cells measured over 30 individual samples with efficiencies ranging from 0.002–1.7%. The solar cell comprising the ratio 1:3 presents the highest photovoltaic performance. It delivers both the highest photocurrent ( $4.75 \text{ mA cm}^{-2}$ ) and the highest fill factor (0.49) leading to a promising 1.7% power conversion efficiency. Despite the lower photovoltaic performance of the 2:1, 1:1 and 1:2 blend compositions, they show meaningful performance that can help us to understand the charge generation and transport processes for polymer:fullerene solar cells. For instance, the solar cell with 1:3 ratio and combined annealing presents a FF of 0.49, this is indicative of an efficient transport since it is larger than that measured for 1:3 blend composition without annealing, suggesting annealing as an improved charge

transport method. In summary, it can be said that blend ratios below the optimum composition of 1:3 present larger absorption of solar light and an efficient charge transport. On the contrary, ratios 1:3 present an improved charge transport but lower solar light harvesting than ratios 1:2 with the photocurrent of  $5.71 \text{ mA cm}^{-2}$  and a FF of 0.39. However, devices based on 1:3 blend composition exhibit the best balance between light harvesting and the charge generation and transport processes as a function of the suitable fullerene ratio acceptor.

Control of the blend structure at the nanoscale is, in fact, one of the most effective ways to significantly enhance the organic solar cell efficiency.<sup>46,47</sup> In this contribution we have investigated PDPP-ANT:PCBM blend systems in the conventional devices by applying the different fullerene concentrations with and without combined annealing method. The rationale for this was to be able control the formation of microscale phase separation through the natural entanglement of random polymer chains, while allowing the formation of crystallites at the nanoscale in the voids left by the diluted polymer matrix.<sup>48</sup> As shown in the SEM photographs in Fig. 7, with the increase of PCBM ratio, the precipitated phase of the crystallites diminishes after annealing. In order to confirm what the crystallites are, we prepared

Table 1 Performance data for PDPP-ANT:PCBM (w/w) solar cells

| Active layer (w/w)                                 | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF (%)            | PCE <sup>a,b</sup> (%) | Annealing     |
|----------------------------------------------------|---------------------------------|--------------|-------------------|------------------------|---------------|
| PDPP-ANT:PC <sub>61</sub> BM (2 : 1)               | 0.11                            | 0.13         | 27.3 ± 1.1        | 0.003 ± 0.001          | 130 °C        |
| PDPP-ANT:PC <sub>61</sub> BM (1 : 1)               | 4.77                            | 0.46         | 37.7 ± 1.1        | 0.84 ± 0.11            | 130 °C        |
| PDPP-ANT:PC <sub>61</sub> BM (1 : 2)               | 5.71                            | 0.5          | 38.3 ± 1.1        | 1.02 ± 0.11            | 130 °C        |
| <b>PDPP-ANT:PC<sub>61</sub>BM (1 : 3)</b>          | <b>4.75</b>                     | <b>0.73</b>  | <b>47.8 ± 1.2</b> | <b>1.58 ± 0.12</b>     | <b>130 °C</b> |
| PDPP-ANT:PCBM (1 : 3)                              | 1.83                            | 0.54         | 36.8 ± 1          | 0.34 ± 0.03            | No            |
| Pcoahdpp:PC <sub>71</sub> BM (1 : 3) <sup>18</sup> | 7.78                            | 0.76         | 36.32             | 2.15%                  | 230 °C        |

<sup>a</sup> Average PCE of ten devices fabricated under identical conditions ± 3 standard deviation ( $\sigma$ ). <sup>b</sup> Maximum lies outside ± 3 $\sigma$  (standard deviation).

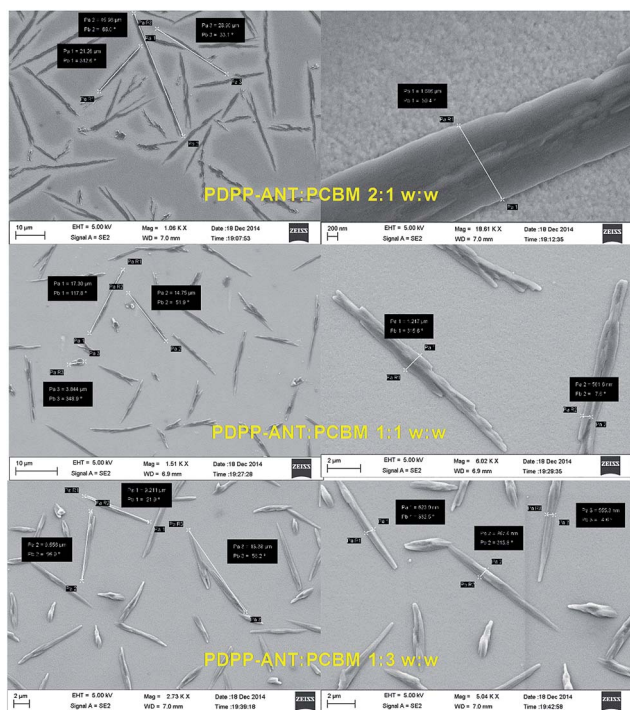


Fig. 7 Scanning electron microscope of PDPP-ANT pure polymer film and blend film PDPP-ANT/PC<sub>61</sub>BM in  $x : y$  weight ratio.

thesamplesontheITOGlass with the configuration: glass/ITO/PEDOT:PSS/PDPPANT:PCBM, and carried out the energy dispersive spectrometry on the film. As shown in Fig. 9, we obtained four data (1, 2, 3, 4) on the different regions of the film, showing the high carbon content of nearly 40% on the crystallites as compared to 25% on the smooth surface, which intensify our verdict that the crystallites are PCBM crystallites after combined annealing. The size and spatial distribution of both polymer and fullerene nanodomains will define whereabouts in the film, like where the light is mostly absorbed and hence charges are mainly generated, the charge generation rate, and the charge transport properties of the film. Therefore, a detailed nanomorphological characterization is required for understanding the behavior of this type of solar cells. The crystalline nature of PCBM formations after annealing has been reported in polymer/fullerene solar cells system.<sup>49,50</sup>

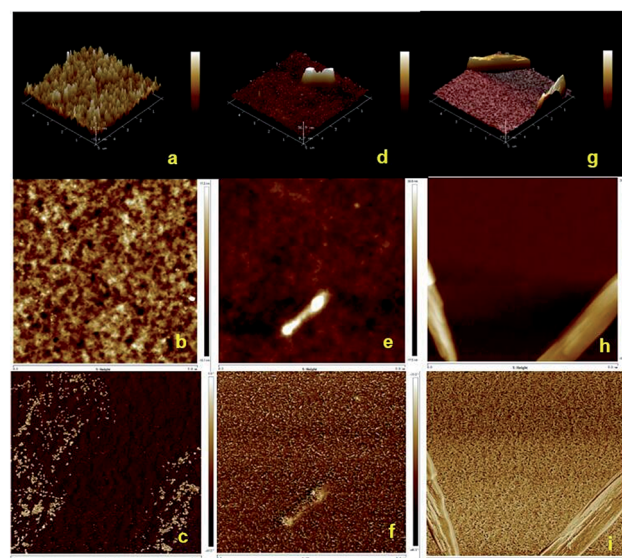


Fig. 8 AFM 3D images (up), height (middle) and phase images (down) of PDPP-ANT:PCBM (without annealing (left), after annealing 1 : 1 (middle), after annealing 1 : 3 (right)) blend films. All the micrographs were scanned in range of 5  $\mu\text{m} \times 5 \mu\text{m}$  scale.

To get further insights into the effect of combined annealing on the film morphology, atomic force microscopy (AFM) measurements were undertaken to visualize the morphological changes with respect to the fullerene ratio and with or without annealing. As shown in Fig. 8, all the micrographs were scanned in the range of 5  $\mu\text{m} \times 5 \mu\text{m}$  scale and the rms surface roughness values of the films are found to be 4.47 (b), 2.26 (e) and 3.8 (h) for without annealing 1 : 1, after annealing 1 : 1 and after annealing 1 : 3, respectively. No clear contrast features are detected for 1 : 1 ratio showing in (f). This observation suggests a polymer fullerene phase separation within the range of or below 10 nm. However, fine phase separation can be detected for the films with 1 : 3 ratio showing in (i). Meanwhile, for films made up of 1 : 2 ratio of PDPP-ANT:PCBM, the phase separation is dominated over range of 50–100 nm range. As it can be seen from these AFM images (i), the PDPP-ANT:PCBM blend films show large crystalline domains, which leads to inefficient exciton splitting. For the other two substituted DPP-based films, smaller PCBM crystals are observed, indicating an increased intermolecular

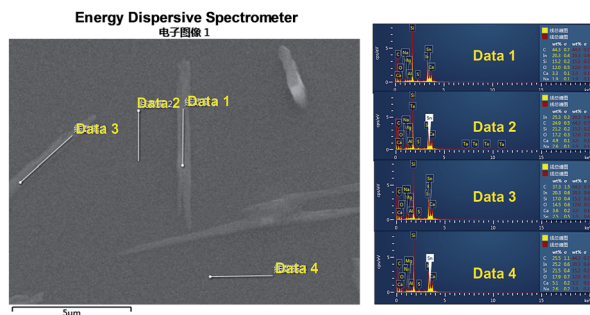


Fig. 9 Line scanning energy dispersive spectrograph on glass/ITO/PEDOT:PSS/PDPPANT:PCBM film samples after annealing.

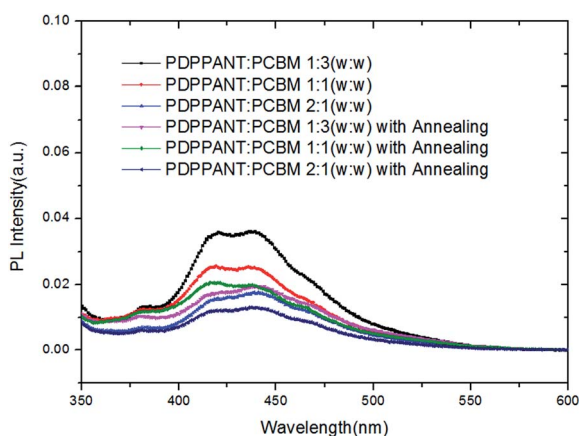


Fig. 10 The photoluminescence (PL) spectrum of PDPPANT:PCBM  $x : y$  (w/w) with or without annealing all excited at 330 nm.

interaction in these blend films. In particular, the PDPP-ANT:PCBM blend film shows the smoothest surface with RMS roughness of 3.8 nm. Suitable crystalline domains and phase separation of the blend film are beneficial to achieving a high  $J_{sc}$  and PCE. This result is consistent with the highest device performance for the PDPP-ANT:PCBM based devices.<sup>51</sup> Large crystals are observed yielding unfavorable phase separation, whereas in PDPP-ANT:PCBM system, much more homogenous film morphology is found, suggesting an excellent intermixing for these two compounds. However, well defined interpenetrating networks were formed in PDPP-ANT:PCBM film, which is a direct consequence of the high performance of PDPP-ANT:PCBM film based solar cells. PDPP-ANT will tend to phase segregate within the film formation process.<sup>†</sup>

<sup>†</sup> The photoluminescence (PL) spectrum of PDPPANT:PCBM  $x : y$  (w/w) as seen in Fig. 10, present emission at approximately 400–500 nm in the PDPPANT:PCBM blends films when the films are excited with 340 nm light. This can be assigned to the emission from the PCBM singlet state.<sup>36</sup> The peak at 400–500 nm indicates that the main energy level structure of blend films is unchanged with different ratios of PDPPANT and PCBM, and whether annealing was done or not, albeit the PL emission band intensity enhanced when the ratio of PCBM increased. Surface morphology and phase segregation of blend active layers may play the key role in the performance of PSCs.

## 4. Conclusions

A novel synthetic route diketopyrrolopyrrole-based donor material is demonstrated for its application in polymer photovoltaic cell. We combined solvent annealing before thermal treatment method to optimize the device fabrication process. This annealing method of the thin polymer film induces better ordering and improves charge transportation across the channel, higher absorption in the UV-vis-NIR region, and appropriate HOMO and LUMO energy levels of PDPP-ANT, which are desirable characteristics for an electron donor component in bulk heterojunction solar cells (BHJs). Such a composition is often beneficial for improving device performance spectrum of our best ITO/PEDOT:PSS/PDPP-ANT:PCBM/Ca/Al solar cell. The extracted figures-of-merit are: a short-circuit current  $J_{sc}$  of  $4.75 \text{ mA cm}^{-2}$ , open-circuit voltage  $V_{oc}$  of 0.73 V, fill factor FF of 0.49 and power conversion efficiency PCE of 1.7% in comparison with the unannealed device 0.37% (with  $V_{oc}$  (0.54 V),  $J_{sc}$  ( $1.83 \text{ mA cm}^{-2}$ ), FF (37.8%)), by a developed combined annealing method in all-solution processed fabrication. Higher short circuit current of the OPV devices is due to the low band gap nature and high charge carrier mobility of the polymer. The open circuit voltage value of the device is also quite high, which is due to the lower HOMO energy level of polymer. These results are comparable to those obtained by previous research work on DPP-based PSCs.<sup>12,13,16,17,19,52</sup> Further, morphological studies explain photovoltaic performance as a function of the blend composition and this diketopyrrolopyrrole material shows strong absorption in the wavelength range of 600–750 nm different from general polymer materials, which shows its potential to be applied as a novel donor material in state-of-art ternary polymer solar cells<sup>53</sup> or tandem polymer solar cells.<sup>54,55</sup>

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