Synthesis and photovoltaic properties low bandgap D-A copolymers based on fluorinated thiadiazoloquinolinoxaline

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ABSTRACT

In this communication, we report the design a low bandgap D-A copolymer consist of fluorinated thiadiazoloquinolinoxaline (TDQ) as strong acceptor and benzothiophene (BT), denoted as P(fflTDQ-x-BT) exhibiting broad absorption profile covering from 350 nm to 1000 nm with optical bandgap of 1.26 eV. P(fflTDQ-x-BT) showed highest occupied molecular orbital (HOMO) energy level of ~5.46 eV which is deeper than that for nonfluorinated counterpart copolymer. The photovoltaic properties were evaluated using conventional devices with a structure of ITO/PEDOT:PSS/P(fflTDQ-x-BT):PC71BM/Al. After the optimizations of the P(fflTDQ-x-BT) to PC71BM weight ratios, and concentration of the solvent additive (DIO), the devices showed overall power conversion efficiency of 7.27%. The higher value of PCE of this device is higher than that of nonfluorinated copolymer (5.80%) is attributed to the higher values of both Jsc and FF, related to the higher hole mobility and better exciton dissociation efficiency. Moreover, employing a low boiling point solvent additive, i.e. o-chlorobenzaldehyde (CBA) (boiling point 132 °C) for active layer deposition and after the optimization of concentration of CBA, the resulted PSC showed overall PCE of 8.10%, which is higher than the PSC based on active processed with DIO/CB, related to the better balanced charge transport, induced by the fast removal of residues of solvent. To our best of our knowledge, PCE of 8.10% is also the highest for the PSCs with low bandgap of below 1.30 eV.

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1. Introduction

Polymer solar cells (PSCs) based a bulk heterojunction (BHJ) active layer are the promising candidates to convert the solar energy into electrical energy, due to their low cost, light weight, large scale production from the solution processing and mechanical flexibility which impart the green energy technology at low cost [1]. In a BHJ PSC whose active layer consists a blend of donor (conjugated polymers and small molecules) and acceptor (fullerene derivatives and non-fullerene small molecules) phases. The nanoscale morphology of the blended active layer provides important pathways for charge generations, carrier transports, and collections at electrodes, which significantly influence the photovoltaic performance [2]. Through continuous improvement in the optical and electrochemical properties of organic materials and device structures, power conversion efficiencies (PCEs) of PSCs has been achieved more than 11% at lab scale level and 7% at module level, respectively, after the constant improvement in the optical and electrochemical properties of organic materials and device structure [3]. The PCE of the PSCs is highly influenced by the light harvesting ability of the electron donating component in the BHJ active layer. Therefore, efficient harvesting of solar energy requires the development of new polymers with high absorption coefficient and extended absorption spectra in order to enable photocurrent generation from longer wavelength region of solar spectrum. This in turn will require low energy bandgap polymers that absorb at near infrared (NIR) wavelengths. While the magnitude of the energy gap has great importance in the design of these materials, it is also important to tailor the energy difference between the HOMO of the polymer donor and the LUMO of the fullerene acceptor in the BHJ active layer. The development of low band gap conjugated copolymers with donor-acceptor (D-A) alternating structure have...
concerned great deal of attention because their electronic properties can be easily tuned by proper combination of D and A units [4]. Moreover, the energy level control of the D-A type polymers facilitates the intramolecular charge transfer (ICT) transition, which results in reduced band gaps and thus the absorption ranges can be extended to longer wavelengths [5]. In general, thiophene, thiophene, benzodithiophene, cyclopentadithiophene, dithienosilole and dithienopyrrole are commonly used as strong electron donating units; benzothiadiazole, isodindigo, diketylpyrrolopyrrole and naphthalene diimide are used as strong electron withdrawing units with weak quinoid characteristics; and ester/carbonyl-substituted thieno [3,4-b]thiophene, thieno [3,4-b]pyrazine (TP) and quinoxaline (Qx) are weak electron withdrawing unit with strong quinoid characteristics.

Thiadiazolequinoxaline (TDQ) is a promising building block for the synthesis of ultra low bandgap D-A copolymers due to its strong electron withdrawing properties due to four amino groups in TDQ units. Bis(trimethylsil)-4,5- bis(undecyl)benzo [2,1-b; 3,4-b'] dithiophene monomer is an electron donor monomer for the copolymerization because of its beneficial properties, such as high and balanced charge carrier mobility with high absorption capability in NIR region of solar spectrum [5]. It is reported that the fluorination on the polymer backbone has shown immense advantages such as (i) lowering the HOMO energy level of conjugated polymer thereby increasing the $V_{oc}$ of the resulting PSCs [7], (ii) increasing the dipole moment between the ground state and excited state of the polymer which can suppress the charge recombination, resulting the improvement in the $J_{sc}$ and FF [8], and (iii) enhancing the inter/intramolecular interaction of the polymers, leading to high charge carrier mobility [9]. Therefore, fluorination on the polymer backbone has become one of the strategies in tailoring the molecular structure to achieve the high performance PSCs [5d,10]. Moreover, the incorporation of different numbers of fluorine atoms would definitely change the structural symmetry of the repeat units, leading to the regioregular polymer structure, which is crucial for photovoltaic properties [11].

Recently we have reported an electron accepting TDQx based monomer by introducing fluorene and thiazole units into the TDQx block to increase the electron accepting strength of TDQx and the resultant copolymer showed optical bandgap of 1.24 eV [12]. The PSCs based on this copolymer as donor showed overall PCE of 5.80% [12]. In continuation to our research work we have introduced two fluorine atoms in each fluorene sub unit of TDQx acceptor along with BT donor, in the copolymer denoted as P(ffFITDQx-BT) in order to lower the HOMO energy level to get high $V_{oc}$. After the optimization of donor to acceptor (PC71BM) weight ratios and concentration of DIO additive, we have achieved overall PCE of 7.27% which is significantly higher than that of the device based on non-fluorinated counterpart polymer. The increase in PCE has been attributed to the increase hole mobility and balanced charge transport. Moreover, we have adopted o-chlorobenzaldehyde (CBA) as solvent additive for spin coating of active layer and found the resulted PSC showed overall PCE of 8.10%, related to simultaneous increase in $J_{sc}$ and FF. The improvement in PCE may be attributed to the more favourable nanoscale morphology of the active layer, resulting an increase in the hole mobility and charge collection efficiency.

2. Experimental

2.1. Synthesis of copolymer

The monomers M1 [13] and M2 [14] were synthesized as reported in literature. Monomers M1 (0.7098 g, 0.5 mmol), M2 (0.4122, 0.5 mmol) and Pd(PPh3)4 (0.027 g, 0.023 mmol) were dissolved in 15 ml of dry toluene. Reaction mixture was heated at 110 °C for 48 h in argon atmosphere. After cooling the product was precipitated with methanol (200 ml) and filtered. The raw P(ffFITDQx-BT) copolymer was dissolved in small volume of chloroform and precipitated with methanol again and then it was additionally purified by means of sequential extractions with methanol, hexane and chloroform. Chloroform fraction was concentrated and precipitated with methanol. The copolymer P(ffFITDQx-BT) was filtered and dried in vacuum and the yield is 73%.

2.2. Device fabrication and characterization

Indium tin oxide (ITO) coated glass substrates were cleaned in ultrasonicated bath containing detergent, deionized water acetone and iso-propanol sequentially and then dried in vacuum oven at 40 °C for overnight. A solution of polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS, Clevios A14083) was spin coated onto the cleaned ITO substrates at 3500 rpm for 30 min and then it was annealed at 120 °C for 10 min in air environment. The mixture of donor electron acceptor P(ffFITDQx-BT) and electron acceptor PC71BM in different weight ratios were dissolved in chloroform solution (concentration is 16 mg/mL). The blend solutions were spin coated on top of the PEDOT:PSS film for 30 s at 1500 rpm and at ambient conditions and dried for 2 h. For solvent additive (SA), 3% of DIO was mixed into the host CB solvent. A methanol solution of PFN with a concentration of 1.5 mg/mL was then spin-coated on top of the active layer at 3000 rpm for 30s. By means of thermal evaporation and under a pressure of 10−5 Torr, the cathode aluminium (Al) (90 nm) was placed on top of the active layer. The active area is about 16 mm2 which is defined as the vertical overlap of ITO and Al electrodes. We have fabricated hole-only devices (ITO/PEDOT:PSS/P(ffFITDQx-BT):PC71BM/Au) and electron only (ITO/Au/P(ffFITDQx-BT):PC71BM/AI) to measure the hole and electron mobility respectively. A Keithley Source Meter was used to measure the current-voltage (J-V) characteristics of the solar cells in ambient conditions and under AM1.5 G (100 mW/cm²) provided by a solar simulator. The incident photon-to-current efficiency (IPCE) of the devices was measured by illuminating the devices through the light source and a monochromator and the resulting current was measured using a Keithley electrometer under short-circuit conditions.

3. Results and discussion

Synthetic route for the preparation of copolymer P(ffFITDQx-BT) was presented on Scheme 1. Initially, we had synthesized aromatic dibromide M1 [13] and aromatic bistannyl derivatives M2 [14] as reported in literature. Interaction of equimolar amounts of fluorinated aromatic dibromide M1 and aromatic distannlated monomer M2 in refluxing toluene for 48 h in the presence of Pd(PPh3)4 under Stille reaction conditions gives copolymer P(ffFITDQx-BT). Reaction was conducted in homogeneous conditions and allowed to obtain the polymers with reasonable high yields and moderate molecular weights; it allowed preparing sufficiently durable polymeric films for photovoltaic investigation. The copolymer was purified by double precipitation of their chloroform solution with methanol and sequential extraction of solids with methanol, hexane and chloroform using Soxhlett apparatus. Chloroform fractions were concentrated and precipitated with methanol. Solid precipitate was filtered and dried in vacuum at 80 °C for 24 h. Yield of P(ffFITDQx-BT) was about 73% and exhibits good solubility in chlorinated solvents such as chloroform, chlorobenzene or o-dichlorobenzene. Composition and chemical structure of the P(ffFITDQx-BT) was confirmed by 1H
NMR and 19F NMR spectroscopy (as shown in Figs. S1a and S2b, supplementary information). Molecular weights of the copolymer were elucidated with gel-permeation chromatography (GPC) with polystyrene as standard. Number-averaged ($M_n$), weight-averaged ($M_w$) molecular weights and polydispersity ($M_w/M_n$) of P(ffFlTDQx-BT) were estimated to be 7790 kDa, 17600 kDa and 2.26, respectively.

Thermal properties of polymer play an important role in BHJ polymer solar cells (PSCs). Thermal properties of the P(ffFlTDQx-BT) was studied using thermogravimetric analysis (TGA) Fig. S2 (see the supplementary information) and 5% weight loss temperature of P(ffFlTDQx-BT) is about 369$^\circ$ C. Differential scanning calorimetry (DSC) plot shows no glass transition temperature for copolymer indicates that the P(ffFlTDQx-BT) is quite stable and suitable for photovoltaic and other optoelectronic devices.

3.1. Optical and electrochemical properties

Optical properties of copolymer P(ffFlTDQx-BT) were investigated by means of UV spectroscopy in dilute solution and thin film and shown in Fig. 1. P(ffFlTDQx-BT) showed a broad absorption profile in the range of covering from 350 nm to 1000 nm, featuring two absorption bands 350–600 nm (centered at 400 nm) and 600–1000 nm (centered at 832 nm). The absorption band in shorter wavelength region is assigned to the localized $\pi-\pi$ transitions, while the lower energy absorption band corresponds to the intramolecular charge transfer (ICT) between the donor and acceptor segments present in the copolymer backbone. The absorption spectra of the P(ffFlTDQx-BT) in thin film exhibited broader ICT absorption band and red-shifted by 102 nm compared to that in solution which is probably caused by intermolecular interactions in solid state, aggregation of macromolecules, more structured and improved packing of polymeric molecules of P(ffFlTDQx-BT) in solid state. Optical bandgap ($E_g^{on}$) of P(ffFlTDQx-BT) was estimated from the absorption onset in the absorption spectra in film and is 1.29 eV. The broad range of absorption (350–1000 nm) and narrow bandgap of P(ffFlTDQx-BT) favor its application as electron donors in PSCs for efficient light harvesting.

Electrochemical properties of copolymer was studied by means of cyclic voltammetry; and typical voltammograms are presented in Fig. S3 (see the supplementary information). Onsets of oxidation ($E_{ox}^{on}$) and reduction ($E_{red}^{on}$) potentials of P(ffFlTDQx-BT) were determined from the cyclic voltammograms and are of 1.06 and −0.53, respectively. Energy values of HOMO and LUMO levels and electrochemical bandgap values ($E_g^{ec}$) of the copolymer P(ffFlTDQx-BT) were estimated by following equations:

\[ \text{LUMO} = -e(E_{red}^{on} + 4.4) \text{ (eV)} \]
\[ \text{HOMO} = -e(E_{ox}^{on} - 4.4) \text{ (eV)} \]
\[ E_g^{ec} = e(E_{ox}^{on} - E_{red}^{on}) \text{ (eV)} \]

The HOMO and LUMO energy values, estimated from the onsets of oxidation and reduction potentials, are of −5.46 eV and −3.87 eV, respectively and electrochemical bandgap is about 1.59 eV. The HOMO energy level of the P(ffFlTDQx-BT) is deeper than that for the non-fluorinated counterpart copolymer [12] which is in accordance with previous reports [15]. However, the LUMO energy level is slightly lowered from −3.84 eV to −3.87 eV. The electrochemical bandgap is higher than that of optical bandgap may be resulted from exciton binding energy of the polymer [16] and the fact that electron and hole remain electro-statically bound to each other in the excited state.

3.2. Photovoltaic properties

The copolymer P(ffFlTDQx-BT) as donor was tested along with PC\textsubscript{71}BM as acceptor, in BHJ PSCs with standard architecture glass/ITO/PEDOT:PSS/P(ffFlTDQx-BT):PC\textsubscript{71}BM/PFN/Al. The weight ratio between P(ffFlTDQx-BT) and PC\textsubscript{71}BM was optimized between 1:0.5 to 1:2.5 using chlorobenzene (CB) as processing and found that weight ratio is 1:2 showed the best photovoltaic performance. The current–voltage (J-V) characteristics under illumination (AM1.5, 100 mW/cm\textsuperscript{2}) shown in Fig. 2a. We found that the device based on active layer processed with CB showed PCE of 3.92% with J\textsubscript{sc}, V\textsubscript{oc} and FF values of 9.56 mA/cm\textsuperscript{2}, 0.86 V and 0.54, respectively, which is low may be arises from the non-optimal blend morphology of the
active layer processed with CB. In order to optimize the morphology of the active layer a high boiling point additive, 1,8 \text{diiodooctane (DIO) was incorporation in the CB host solvent in}

different volume concentration. The J-V characteristics of the device based on the P(\text{ffITDQx-BT}):\text{PC}_{71}\text{BM (1:2) processed with 3v% DIO/CB shown Fig. 2a and photovoltaic parameters are compiled in Table 1. The device showed overall PCE of 7.27% (J_{sc} of 15.08 mA/cm\(^2\), V_{oc} of 0.73 V and FF of 0.67), which is higher than that of the device based on non-fluorinated D-A polymer (5.80%) under identical conditions [12].

The increase in the PCE for the device based on the active layer processed with DIO additive is mainly attributed to the enhancement in J_{sc} and FF at low voltages and gradually saturates at high value of V_{eff}, where J_{ph} is field independent. On the other hand, device processed with CB, also show a linear relationship at low voltages and exhibits field dependence. The estimated values hole mobility for non-fluorinated [12] and fluorinated copolymers, respectively. Therefore, fluorine addition leads to shorter stacking distance, and favourable crystalline orientation as confirmed by the X-ray diffraction.

In order to get information about the exciton generation, exciton dissociation and photocurrent generation in the devices processed CB and DIO/CB cast active layers, the photocurrent density (J_{ph}) (J_{ph} = J_{L}-J_{D}, where J_{L} and J_{D} are the current densities under illumination and in dark, respectively) is plotted as a function of effective voltage (V_{ef}) (V_{ef} = V_{o}-V_{app}, where V_{o} is the voltage when J_{L} = J_{D} and V_{app} is applied voltage) for the devices [18] and shown in Fig. 5. OE/PC_{71}BM (1:2) processed with 3v% DIO/CB shown Fig. 2a and photovoltaic parameters are compiled in Table 1. The device showed overall PCE of 7.27% (J_{sc} of 15.08 mA/cm\(^2\), V_{oc} of 0.73 V and FF of 0.67), which is higher than that of the device based on non-fluorinated D-A polymer (5.80%) under identical conditions [12]. The device showed overall PCE of 7.27% (J_{sc} of 15.08 mA/cm\(^2\), V_{oc} of 0.73 V and FF of 0.67), which is higher than that of the device based on non-fluorinated D-A polymer (5.80%) under identical conditions [12].
device is not sufficient for the extraction of free charge carrier that may results in the continuous increase in the $J_{ph}$. Moreover, the device based on the active layer processed with CB only, displayed square root dependence in the intermediate effective voltage region, indicating that the charge carrier transport causes the bimolecular recombination leading to the low FF [18]. The maximum exciton generation rate, $G_{\text{max}}$ of the devices was estimated using expression, $J_{\text{phsat}} = qG_{\text{max}}L$, where $q$ is the electronic charge and $L$ is the thickness of the active layer. The calculated values of $G_{\text{max}}$ for CB cast and DIO/CB cast based devices are $8.6 \times 10^{27} \text{m}^3\text{s}^{-1}$ and $1.27 \times 10^{28} \text{m}^3\text{s}^{-1}$, respectively. In general, $G_{\text{max}}$ is quantifies to the maximum number of photon absorbed and related to the light harvesting efficiency of the active layer [19]. Since the $J_{\text{phsat}}$ depends on $G_{\text{max}}$, the increased value of $J_{sc}$ is directly associated with the corresponding increase of $G_{\text{max}}$ for DIO/CB based active layer device, that clearly indicates a higher photon absorption from the DIO/CB active layers as confirmed from the

**Table 1**

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(FFITDQx-BT):PC71BM (CB)</td>
<td>9.56</td>
<td>0.76</td>
<td>0.54</td>
<td>3.92 (3.81)$^a$</td>
</tr>
<tr>
<td>P(FFITDQx-BT):PC71BM (DIO/CB)</td>
<td>15.08</td>
<td>0.72</td>
<td>0.67</td>
<td>7.27 (7.14)$^a$</td>
</tr>
<tr>
<td>P(FFITDQx-BT):PC71BM (CBA/CB)</td>
<td>15.62</td>
<td>0.74</td>
<td>0.70</td>
<td>8.10 (8.02)$^a$</td>
</tr>
</tbody>
</table>

$^a$ Average of ten devices.

Fig. 2. (a) Current—voltage characteristics under illumination and (b) IPCE spectra of the PSCs based on optimized P(FFITDQx-BT):PC71BM active layers cast in different conditions.
corresponding absorption spectra (Fig. 3) in which the values absorption coefficient correspond to ICT band of P(FFITDQx-BT) in active layer processed with DIO/CB are higher than for the CB processed counterpart. The charge collection efficiency ($P_c$) was estimated using $P_c = J_{sc}/J_{phsat}$ at short circuit conditions and the values of $P_c$ are 0.78 and 0.87 for the devices based on CB and DIO/CE cast active layers, respectively. Therefore, processing the active layer using DIO/CB offers significant improvement in overall PCE of PSC compared to the as cast counterpart device, in terms of charge collection and exciton generation rate.

Fig. 3. Normalized absorption spectra of P(FFITDQx-BT):PC$_{71}$BM (1:2) thin films processed with CB and DIO/CB.

Fig. 4. Current–voltage characteristics of hole only devices based on P(FFITDQx-BT):PC$_{71}$BM from CB, DIO/CB and CBA/CB.
The nanoscale morphology of the active layer should have a bi-
continuous network of donor and acceptor phases presenting the
best compromise between two contradictory requirements: (i) the
D-or A-rich regions should be small enough to increase the D/A
interfacial area in the active layer so that all excitons should reach
D-A interfaces before quenched by radiative or non-radiative pro-
cesses, and (ii) they should large enough to avoid charge recom-
bination after the exciton dissociation into free charge carrier. In
order to get information about the morphology of the active layer,
we have examined the morphology of the active layer by trans-
mission electron microscopy (TEM) and the images are shown in
Fig. 6. The bright regions of the TEM images are correspond to
polymer phase whereas dark regions assigned to PC_71BM phase. As
shown in figure that the blended P(FFITDQx-BT):PC_71BM cast from
CB showed the bigger domains and leading to decrease the D/A
interfacial area in the active layer which hamper the exciton
dissociation rate, associated with the low J_{sc} value in the device.
However, the domain sizes in morphology of the active layer process-
ed with DIO/CB were reduced, resulting in a favourable for
exciton dissociation and even also for efficient charge transport in
different phases toward the respective electrodes, thereby
enhanced values of J_{sc} and FF for resulted device.

The XRD patterns of the pure non-fluorinated copolymer and
P(FFITDQx-BT) in pure and blended films are recorded and shown in
Fig. 7a. The diffraction pattern indicates that nonfluorinated
copolymer film showed a diffraction peak located at 28 = 5.23°, cor-
responding to the orientation of (100) with d-spacing of
11.13 nm. Moreover, the diffraction peak corresponding to π–π
stacking is located at 28 = 22.16°, which gives the stacking distance
0.45 nm. The blended of nonfluorinated copolymer with PC_71BM
showed similar diffraction peaks as observed in pristine film. The
crystal coherence length (CCL) in nonfluorinated blended film
processed with CB and DIO/CB are about 11.06 nm and 11.68 nm,
respectively, indicating the DIO additive increases the crystallinity
of the nonfluorinated copolymer. The P(FFITDQx-BT) copolymer
showed a different microstructure in comparison to P(FTIDQx-BT).

As can be seen from the XRD pattern in pristine film, intensity of
diffraction pattern for the π–π stacking, which is located at
28 = 23.24° is higher, corresponds to a distance of 0.38 nm and
(100) diffraction peak is located at 28 = 5.06° with d-spacing of
12.45 nm. Therefore the polymer chain is more packed in
P(FFITDQx-BT) than the nonfluorinated counterpart, owing to the
fluorination effect. The π–π stacking peak of P(FFITDQx-BT) in
blended film processed from CB remains at same position at
pristine film (Fig. 7b). In a blended film processed CB, the crystal size
corresponds to (100) and π–π stacking crystal size are about 15.6 nm and 2.4 nm, respectively and these values are
about 16.1 nm and 2.56 nm, respectively, when DIO solvent additive
is used. These values are quite different for the nonfluorinated
copolymer counterpart. Therefore, fluorine atom addition leads to
more favoured polymer chain orientation and contracted π–π
stacking, may be resulted from the increased inter-chain interaction,
which is beneficial for the J_{sc} and FF [20], which is the partly
one of the reasons for the higher PCE for P(FFITDQx-BT) based PSCs
as compared to nonfluorinated copolymer counterpart. Addition-
ally, P(FFITDQx-BT):PC_71BM blended film processed with DIO/CB
promote the chain crystallization and π–π stacking in blended film
(as shown in Fig. 7b). Such improved crystalline quality in combi-
nation with phase separation (as shown in TEM images) at finer
scale resulted improved PCE of PSC processed with DIO/CB solvent.

We have determined the energy loss (E_{loss}) using the expression,
E_{loss} = E_g – qV_{oc}, for the devices with optimized active layers based
on fluorinated and non-fluorinated copolymers and are 0.57 eV and
0.66 eV, respectively. The E_{loss} for the P(FFITDQx-BT);PC_71BM
active layer is lower than the threshold value of 0.6 eV. In our case,
the LUMO offset (ΔE_{LL}) between P(FFITDQx-BT) and PC_71BM is
about 0.21 eV, which is lower than that threshold value of 0.3, for
efficient exciton dissociation. Recently, Janssen et al. [21] and other
researchers [22] have reported that PSCs for which E_{loss}<0.6 eV and
ΔE_{LL} ~0.2 eV. Recently, PSC based on a D-A copolymer as donor
showed overall PCE of about ~9.0% with ΔE_{LL} ~0.1 eV [22].

Although, the PCE of the PSC based on the P(FFITDQx-
BT):PC71BM active layer processed with DIO/CB has improved to 7.27%. In general, DIO is a good solvent for fullerene derivatives and non-solvent for most of the copolymer donors. DIO exhibits high boiling point of 332 °C and much higher than that for 132 °C for CB. When, the active layer processed with DIO/CB, during the film formation, the host solvent is quickly removed and the donor phase establishes earlier than acceptor phase because DIO still remains in the neighbour of fullerene domains. Therefore, in order to remove the DIO additional processing such as vacuum drying and inert solvent washing is required to form a better nano-phase morphology [23] and these additional treatment of active layer increases the overall cost of PSC and not favourable for roll-to-roll processing of BHJ active layer. Recently Chen et al. have employed a o-chlorobenzaldehyde (CBA) as new solvent additive for morphology optimization of PTB7:PC71BM active layer and achieved PCE more than 9.11% [24], which is higher than that for DIO processed counterpart PSCs. Inspired by this work, we have CBA as solvent additive to explore the possibility to further improve the PCE of our device. We have varied the concentration of CBA in host CB solution and found that 4v% exhibit the highest PCE. The current—voltage characteristics under illumination and IPCE spectra of the optimized device is shown in Fig. 2a and b, respectively. With 4 v% of CBA, Jsc and FF were improved up to 15.62 mA/cm² and 0.70, respectively, giving overall PCE of 8.10%. The values of IPCE for the device processed with CBA/CB are higher for all wavelengths than the DIO/CB processed counterpart also confirm the higher value of Jsc. The Jsc value estimated from the integration of IPCE spectra is about 15.53 mA/cm². CBA exhibits lower boiling
point of 132 °C. The calculated boiling point difference in CBA/CB is about 80 °C is lower than that of DIO/CB system (200 °C). The increase in PCE may be the fast removal of additive from the active layer due to the lower boiling point of CBA relative to DIO, may lead to the better nanoscale morphology as observed in TEM image (Fig. 6) of the active layer for efficient exciton dissociation and charge transport. Moreover, the hole mobility in the active layer processed with CBA/CB system is about 1.16 \times 10^{-4} \text{cm}^2/\text{V} \cdot \text{s} (as shown in Fig. 4) which is higher than that for DIO/CB processed active layer, leading to better balanced charge transport, resulting higher Jsc, FF and overall PCE. The charge collection efficiency (Pc) estimated the variation of Jph with Voc as shown in Fig. 5, is about 0.90, which is higher than that for device processed with DIO/CB solvent. The increase in Pc also indicates that the recombination processes have been suppressed. Moreover, as shown in Figure that the Jph undergo to the saturation at lower Voc, indicating that low internal electric field is needed to extract the free charge carriers.

4. Conclusion

In summary, we have synthesized a fluorinated D-A copolymer, denoted P(fifITDQx-BT) consisting of fifITDQx as strong electron acceptor and BT as electron donor, exhibit low bandgap of 1.26 eV and deeper HOMO energy level of −5.46 eV. We have used this copolymer as donor along PC71BM as acceptor for the fabrication of solution processed BHJ PSCs. PSC based on the optimized P(fifITDQx-BT):PC71BM active layer (weight ratio 1:2 and solvent CBA/CB) showed higher Jsc and FF resulting in an overall PCE of 7.27% (Jsc of 15.08 mA/cm², Voc of 0.72 and FF of 0.67) which is higher than that for nonfluorinated copolymer (5.80%) under same experimental conditions. The higher PCE of the fluorinated copolymer relative to the nonfluorinated counterpart has been attributed to the deeper HOMO energy level (high Voc) and higher hole mobility (balanced charge transport) and higher charge collection efficiency. Moreover, when the active layer is processed with CBA solvent additive, the PCE further improved up to 8.10%, related to the fast removal solvent additive during the film formation, leading to the more favourable nanoscale morphology for better charge transport. To our best of our knowledge, PCE of 8.10% is also the highest for the PSCs with low bandgap of below 1.30 eV with low energy loss of 0.57 eV, which indicates that this copolymer could be excellent candidate for the PSC employing ternary active layer and tandem device.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2017.01.032.

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