Synthesis and applications of thieno[3,4-c]pyrrole-4,6-dione based linear to star-burst novel D–A conjugated oligomers for organic photovoltaics

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Abstract

A series of well-defined donor–acceptor (D–A) conjugated oligomers incorporating thieno[3,4-c]pyrrole-4,6-dione (TPD) acceptor and two symmetrical thiophene units as donor π -bridge along the axes of triphenyl amine core have been synthesized and explored in bulk heterojunction (BHJ) solar cells. Under illumination with AM 1.5 white light (100 mW/cm²), the performance of BHJ photovoltaic devices with an active layer of an electron-donor oligomeric material (**TPATP1**, **TPATP2** or **TPATP3**) blended with an electron acceptor {[6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) at various weight ratios has been investigated. The photovoltaic device containing the donor **TPATP1** and the acceptor PC₇₁BM at a 1:3 weight ratio exhibited the best efficiency of 1.87% with an open circuit voltage (V_{oc}) of 0.86 V, short circuit current (J_{sc}) of 6.59 mA/cm², and a fill factor (FF) of 33%. These results demonstrate that irrespective of conjugation length, tuning of materials with efficient donor and acceptor materials can enhance the optical, electrochemical and eventually the power conversion efficiency (PCE) values of BHJ solar cells. Furthermore oligomers containing TPD acceptor in different structural form have different unique contribution towards photovoltaic properties.

Keywords Organic solar cell · Low bandgap · Small molecule solar cell · Star shape small molecule · Thieno[3,4-c]pyrrole-4,6-dione

1 Introduction

Organic photovoltaics have attracted remarkable interest as an alternate sustainable and renewable source of energy over the conventional silicon based solar cell, due to their low manufacturing costs, low environmental impact during manufacturing and mechanical flexibility which is compatible with foldable or rollable substrates [1–4]. Over a decade, π -conjugated D–A small molecules dragged significant attention of scientific community owing to its notable advantages including easier

purification, control in molecular weight distribution, and better batch-to-batch reproducibility. Furthermore, small molecule based organic photovoltaics has been made a tremendous progress accompanied by a rapid increase in energy conversion efficiencies [5–14].

Low-band-gap organic materials can potentially increase the light harvesting from solar spectrum due to its extended conjugation and panchromatic absorption. One approach of designing these materials is the use of alternating electron-rich (donor) and electron-poor (acceptor) units giving rise to a material with a low-energy absorption

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band that is generally ascribed to a charge transfer band. In addition the TPD moiety imparts high optical density while its electron affinity lowers frontier energy levels to complement those of PC_{61/71}BM. Concurrently, the differential architects of the oligomers from linear to starburst shape D–A extension along the axes of hole transporting triphenyl amine core with thiophene π -bridge contributes enhanced electron transfer and high hole mobility [15, 16]. The TPD–thiophene motif also provides broader absorption spectra so as to increase the light harvesting efficiency. Hence structural configuration having TPD acceptor was found as promising acceptor moiety and have tunable optical, electrochemical properties to be used in BHJ solar cells [17–20].

Herein we report the synthesis and characterization of a series of novel low band-gap D–A oligomeric semiconductors **TPATP1**, **TPATP2** and **TPATP3** (shown in Fig. 1) based on TPD acceptor which contain ethylhexyl substituent and two symmetric oligo thiophene donors along the triphenyl arms. The presence of TPD acceptor at different structural configuration i.e., from linear to star shape tuned the optical and electrochemical properties. BHJ photovoltaic devices were fabricated by using small molecules (**TPATP1**, **TPATP2** and **TPATP3**) as the donor and PC_{61/71}BM as the acceptor. The optimized photovoltaic devices revealed that the device containing blend of **TPATP1** and PC₇₁BM with 1:3 weight ratio, having spin 3000 rpm have the PCE of 1.87%, with $V_{oc} = 0.86$ V, $J_{sc} = 6.59$ mA/cm², and a $FF = 33\%$ under simulated AM 1.5 illumination (100 mW/cm²). Furthermore the device showed external quantum efficiency (EQE) of 32% at wavelength 460 nm and the photo response extended up to 700 nm.

2 Experimental

2.1 Materials

The various chemicals and solvents used were reagent grades and purchased from ACROS, Aldrich, Fluka, and TCI. Toluene, ether and tetrahydrofuran (THF) were distilled over Na/benzophenone. CHCl₃ was purified by refluxing over CaH₂ followed by distillation. The other solvents if not specified were deoxygenated through N₂ purging for 1 h prior to their use.

2.2 Measurements and characterization

¹H and ¹³C NMR spectra were recorded in Varian Unity 300 MHz spectrometer. HERAEUS CHN-OS RAPID elemental analyzer, Shimadzu was used for elemental analyses. Optical absorption studies are being carried out at 300 K using a dual beam UV–Vis spectrophotometer, Shimadzu

UV-1800 in dilute dichlorobenzene (DCB) solutions or in solid films that have been spin-coated onto glass substrate in same solution at a concentration of 10 mg/mL. BAS 100 electrochemical analyzer has been used to measure the cyclic voltammetry (CV) at room temperature using a standard three-electrode electrochemical cell. For CV measurement A solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in MeCN purged with nitrogen for 30 s, and a scanning rate of 100 mV/s has been taken. In each case, a carbon working electrode coated with a thin layer of the oligomer film, a platinum wire as the counter electrode, and a silver wire as the quasi-reference electrode were used, and Ag/AgCl (3 M NaCl) electrode was served as a reference electrode. The redox couple of ferrocene/ferrocenium ion (Fc/Fc⁺) was used as an external standard. The corresponding energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated using the values of $E_{ox/onset}$ and $E_{red/onset}$ determined from CV measurement. The solid films were drop-casted films at a similar thickness from DCB solutions (ca. 5 mg/mL) for all the potentials. The onset potentials were determined from the intersections of two tangents drawn at the rising currents and background currents of the CV measurements.

2.3 Fabrication of organic solar cells (OSCs)

The BHJ solar cell devices were fabricated by blending active layer of small molecules (**TPATP1**, **TPATP2** and **TPATP3**) with PC₆₁BM/PC₇₁BM in solid films, which were sandwiched between a transparent indium tin oxide (ITO) anode and Ca/Al as a cathode. Prior to fabrication ITO-coated glass substrates (1.5 × 1.5 cm²) were ultrasonically cleaned in detergent, deionized water, acetone, and isopropyl alcohol sequentially followed by UV ozone treatment of the substrates for 20 min. The ITO surface was then spin-coated with a layer of poly(ethylene dioxythiophene):polystyrenesulfonate (PEDOT:PSS) (thickness ca. 30 nm) followed by heat treatment for 1 h at 130 °C. The substrates were transferred to a N₂-filled glove-box and the active layer was deposited on top of the PEDOT:PSS layer through spin coating (ca. 2500 rpm, 60 s) of a small molecule (**TPATP1**, **TPATP2**, **TPATP3**) blended with a PCBM (PC₆₁BM or PC₇₁BM) at a ratio of 1:1, 1:2, or 1:3 (w/w); the thickness of the active layer was typically maintained ca. 80 nm. Initially, the blended solutions were prepared by dissolving both small molecules and PCBM in DCB solution (10 mg/1 mL), followed by continuous stirring for 12 h at 50 °C. Finally, a Ca layer (30 nm) and an Al layer (100 nm) were thermally evaporated sequentially through a shadow mask at a pressure of less than 6 × 10^{−6} torr. The active area of each device was kept 0.12 cm². All BHJ solar cell devices

were prepared and characterized under ambient conditions. The properties of solar cells were measured inside a glove box under simulated AM 1.5G irradiation (100 mW/cm^2) using a Xe lamp-based solar simulator (Thermal Oriol 1000 W). The EQE spectra were obtained under short-circuit conditions. The light source was a 450 W Xe lamp (Oriol Instrument, model 6266) equipped with a water-based IR filter (Oriol The light source was a 450 W Xe lamp (Oriol Instrument, Instrument, model 6123NS). The light output from the monochromator (Oriol Instrument, model 74100) was focused on the photovoltaic cell being tested.

2.4 Synthesis and structural characterization

As shown in Scheme 1 Compounds **1**, **3(a)**, **3(b)**, **3(c)**, **4(a)**, **4(b)**, and **4(c)**, were synthesized by known literature procedure [16, 17]. The controlled bromination in Compound **2** was carried through phase wise addition of NBS in chloroform [19, 20]. The oligomers **TPATP1**, **TPATP2**, **TPATP3** were synthesized through Suzuki coupling reactions between **4(a)** & **2**, **4(b)** & **2** and **4(c)** & **2** respectively. The detailed synthetic procedures of some are as follows.

1-(5-bromothiophen-2-yl)-5-(2-ethylhexyl)-3-(thiophen-2-yl)-5H-thieno[3,4-c]pyrrole-4,6-dione

Fig. 1 Molecular structures of **TPATP1** **TPATP2** and **TPATP3**

Scheme 1 Synthetic procedures for **TPATP1**, **TPATP2** and **TPATP3**

(2): *N*-Bromosuccinimide (NBS, 2.07 g, 11.65 mmol) was added in portions to a solution of **1** (5 g, 11.65 mmol) in CHCl_3 (100 mL) in a two-neck flask at 5 °C. The mixture was warmed to room temperature and stirred overnight. CH_2Cl_2 was added and then the solution was washed with brine. The organic phase was dried with anhydrous MgSO_4 and the solvent evaporated under reduced pressure. The crude product was purified chromatographically (SiO_2 , hexane/EtOAc, 1:1) to yield a red solid (3.61 g, 61%). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.02 (d, $J=3.6$ Hz, 1H), 7.66 (d, 4.2 Hz, 1H), 7.45 (d, $J=5.1$ Hz, 1H), 7.14–7.12 (m, 2H), 3.55 (d, 7.2 Hz, 2H), 1.85–1.81 (m, 1H), 1.36–1.31 (m, 8H), 0.94–0.86 (m, 6H).

2.4.1 TPATP1

Mixture of compound **4a** (0.36 g, 1.00 mmol), compound **2** (0.5 g, 1 mmol), and 2 M K_2CO_3 (359 mg, 2.6 mmol) were dissolved in 30 ml of toluene and ethanol (3:1) and degassed for 10 min, and then $\text{Pd}(\text{PPh}_3)_4$ (45 mg, 0.04 mmol) was added. The resulting mixture refluxed for 36 h. The solvent was removed in rotary evaporator and the product was extracted with dichloromethane with water wash followed by a little brine. The organic phase was dried with anhydrous MgSO_4 , and the solvent was removed under vacuum. Subsequently, the crude compound was purified by column chromatography (silica) using dichloromethane as an eluent and washed with methanol and hexane to yield black color solid (0.45 g, 68%). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 7.93 (d, $J=1.8$ Hz, 2H), 7.40 (d, $J=8.4$ Hz, 2H), 7.34 (d, $J=3.9$ Hz, 1H), 7.23–6.96 (m, 14H), 3.47 (d, $J=7.2$ Hz, 2H), 1.8 (m, 1H), 1.30–1.17 (m, 8H), 0.87–0.80 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 163.1, 148.4, 148.0, 147.4, 141.8, 136.9, 136.1, 132.7, 131.5, 130.8, 130.0, 129.6, 128.7, 128.6, 128, 127.1, 127.0, 125.0, 123.7, 123.5, 123.2, 122.9, 120.4, 42.7, 38.4, 31.8, 30.8, 29.9, 28.8, 24.1, 23.2, 22.8, 14.3, 10.7. MS (FAB): m/z [M^+] 671; calcd m/z [M^+] 672.19. Anal. Calcd for $\text{C}_{40}\text{H}_{36}\text{N}_2\text{O}_2\text{S}_3$: C, 71.39; H, 5.39; N, 4.16 Found: C, 71.89; H, 5.69; N, 4.20.

2.4.2 TPATP2

Followed the same procedure as that of **TPATP1**, by taking a mixture of compound **4b** (0.50 g, 1.00 mmol), compound **2** (1.05 g, 2.00 mmol), 2 M K_2CO_3 (359 mg, 2.6 mmol) and then $\text{Pd}(\text{PPh}_3)_4$ (45 mg, 0.04 mmol) in toluene and ethanol (3:1) solution to yield black color solid (0.44 g, 65%). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.02 (d, $J=2.7$ Hz, 4H), 7.52 (d, $J=8.7$ Hz, 4H), 7.43–7.41 (m, 2H), 7.25–7.23 (m, 4H), 7.13–7.09 (m, 9H), 3.56 (d, $J=7.5$ Hz, 4H), 1.8 (m, 2H), 1.34–1.25 (m, 16H), 0.94–0.87 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3): δ 163.2, 147.7, 146.9, 136.8, 136.2, 132.7, 131.5, 131.0, 130.0, 129.8, 128.7, 128.6, 128.1, 127.2, 125.5, 124.4,

124.1, 123.8, 122.9, 120.4, 42.7, 38.4, 30.8, 28.8, 24.1, 23.2, 14.3, 10.7. MS (FAB): m/z [M^+] 1100; calcd m/z [M^+] 1099.27. Anal. Calcd for $\text{C}_{62}\text{H}_{57}\text{N}_3\text{O}_4\text{S}_6$: C, 67.66; H, 5.22; N, 3.82 Found: C, 68.18; H, 5.69; N, 3.68.

2.4.3 TPATP3

Followed the same procedure as that of **TPATP1**, by taking a Mixture of compound **4c** (0.62 g, 1.00 mmol), compound **2** (1.6 g, 3.2 mmol), and 2 M K_2CO_3 (415 mg, 3.0 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (45 mg, 0.04 mmol) in toluene and ethanol (3:1) solution to yield black color solid (1.00 g, 67%). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.02–8.00 (m, 6H), 7.57–7.54 (m, 4H), 7.43–7.41 (m, 3H), 7.43–7.41 (m, 2H), 7.26–7.16 (m, 6H), 7.11–7.10 (m, 8H), 3.56 (d, $J=6.9$ Hz, 6H), 2.17 (m, 3H), 1.35–1.24 (m, 24H), 0.95–0.87 (m, 18H). ^{13}C NMR (75 MHz, CDCl_3): δ 163.1, 147.3, 146.9, 138.2, 136.5, 136.2, 132.7, 131.4, 131.3, 130.1, 128.7, 128.6, 128.2, 127.2, 124.4, 123.9, 42.7, 38.4, 30.8, 28.8, 24.1, 23.2, 14.3, 10.7. MS (FAB): m/z [M^+] 1526; calcd m/z [M^+] 1526.34. Anal. Calcd for $\text{C}_{84}\text{H}_{78}\text{N}_4\text{O}_6\text{S}_9$: C, 66.02; H, 5.14; N, 3.67 Found: C, 66.32; H, 5.56; N, 3.57.

2.5 Optical properties

Optical properties were investigated by measuring the absorption spectra of the D– π –A molecules (**TPATP1**, **TPATP2** and **TPATP3**) in DCB solutions (Fig. 2a) as well as in the solid films (Fig. 2b) and the relevant data are listed in Table 1. In solution, **TPATP1** exhibited absorption maxima at, 445 nm, **TPATP2** at 460 nm and **TPATP3** at 471 nm. In addition all the molecules extended their absorption spectra up to 550 nm which is attributed to the intramolecular charge transfer (ICT) transitions between their donor cores and the acceptor propellants [21]. Furthermore the spectra of the solid films, the absorption maxima and the absorption onset of all the small molecules (**TPATP1**, **TPATP2** and **TPATP3**) were bathochromically shifted significantly relative to those in solutions. These bathochromic shifts in solid films were attributed to the intermolecular interactions in the solid films. The absorption maxima in both solutions and solid films were increased from **TPATP1** to **TPATP3** chronologically which were ascribed to the increase in conjugations with increase in D–A arms from **TPATP1** to **TPATP3**. However in due course the increase in D–A arms decreased the net solubility of the molecule and consequently reflected as poor photocurrent densities in the photovoltaic devices [22].

2.6 Electrochemical properties

The electronic structures of D– π –A small molecules **TPATP1**, **TPATP2** and **TPATP3** including the HOMO

Fig. 2 UV-Vis spectra of **TPATP1**, **TPATP2** and **TPATP3** in (a) dilute dichlorobenzene solutions and (b) solid films

and LUMO levels were investigated by the cyclic voltammetry (CV) measurements in solid films with Ag/AgCl as a reference electrode, calibrated by ferrocene ($E_{1/2}(\text{ferrocene}) = 0.45$ mV vs. Ag/AgCl). The HOMO and LUMO levels were calculated by the onset oxidation and reduction potentials from the reference energy level of ferrocene (4.8 eV below the vacuum level) according to the following equation: [23] $E_{\text{HOMO/LUMO}} = [-(E_{\text{onset}} - 0.45) - 4.8]$ eV and the results are summarized in Fig. 3 and Table 2.

The HOMO/LUMO found for **TPATP1**, **TPATP2** and **TPATP3** were $-5.19/-3.34$, $-5.20/-3.35$, $-5.27/-3.50$ respectively. Thus the bandgap were 1.85, 1.85 and 1.70 eV for **TPATP1**, **TPATP2** and **TPATP3** correspondingly and the data were steady with the no of acceptor branches in the star-shaped molecules. In addition, the band gaps found were in the desirable range to be utilized in the organic photovoltaic applications [24]. The similar Homo energy levels can be ascribed as the identical core and repeating arms of the molecules. Furthermore the LUMO energy levels of small molecules **TPATP1**, **TPATP2** and **TPATP3** (-3.34 , -3.35 and -3.50) are positioned 0.3 eV above the LUMO level of PC₆₁BM/PC₇₁BM acceptor which ensures energetically favorable levels for electron transfer [25].

2.7 Photovoltaic properties

To demonstrate the potential application of the D-A conjugated small molecules (**TPATP1**, **TPATP2** and **TPATP3**) in organic photovoltaics, BHJ organic photovoltaic devices have been fabricated with the configuration ITO/PEDOT:PSS (30 nm)/**TPATP1**, **TPATP2** or **TPATP3**:PC₆₁BM/PC₇₁BM blend (ca. 80 nm)/Ca (30 nm)/Al (100 nm). The active layers of the devices were spin coated (3000 rpm) from 1,2-dichlorobenzene solutions containing a small molecules and PC₆₁BM/PC₇₁BM at 1:3 (w/w). Owing to its broader absorption and higher absorption coefficients in the region from 440 to 530 the small molecules (**TPATP1**, **TPATP2** or **TPATP3**) were blended with PC₇₁BM at 1:3 (w/w). Later the best performing active layer (**TPATP1**) was blended with PC₇₁BM using various weight ratios (1:1, 1:2, 1:3, and 1:4) which could complement the small molecule absorption valley better than PC₆₁BM [26]. All the devices were tested under simulated air mass coefficient AM 1.5 G illumination (100 mW cm^{-2}) and the data are summarized in Tables 3 and 4. The photovoltaic device containing the donor **TPATP1** and the acceptor PC₆₁BM (1:3 weight ratio) exhibited the best power conversion efficiency among the three small molecules with PCE of 0.89% open circuit voltage of 0.76 V, a short circuit current density of 3.47 mA cm^{-2} , and a fill factor of 34.7%. It has been demonstrated that the V_{oc} value in BHJ solar cells is linearly dependent on the difference between the HOMO

Table 1 Optical properties of **TPATP1**, **TPATP2** and **TPATP3**

Small molecule	$\lambda_{\text{abs, sol}}$ (nm) ^a	$\lambda_{\text{abs, film}}$ (nm) ^b	$\lambda_{\text{onset, film}}$ (nm)	$E_{\text{g}}^{\text{opt, film}}$ (eV) ^c
TPATP1	445	475	591	2.09
TPATP2	460	487	604	2.05
TPATP3	471	498	607	2.04

^aIn dilute dichlorobenzene solutions. ^bSpin coated from dichlorobenzene solutions. ^cThe optical bandgaps were obtained from the equation $E_{\text{g}}^{\text{opt, film}} = 1240/\lambda_{\text{onset, film}}$

Fig. 3 Cyclic voltammograms of **TPATP1**, **TPATP2** and **TPATP3** films (drop cast) on platinum electrode measured in 0.1 M ((TBA)PF₆) acetonitrile solutions at a scan rate of 100 mV/s

level of p-type oligomer and the LUMO level of an n-type PCBM [27]. However, as shown in Fig. 4 and Table 3 the V_{oc} value of the cell device based on **TPATP1**, **TPATP2** and **TPATP3** (HOMO energy level: -5.19 , -5.20 , -5.27) were 0.76 V, 0.47 V, 0.50 V respectively. In fact, this discrepancy in results indicated that V_{oc} is correlated not only to the difference between the HOMO of the donor and the LUMO of the acceptor but also the electronic properties of the donor, acceptor, and the D/A interface, charge recombination, degree of phase-separation between the components in the blend, the photo induced dipole formed at the interface due to the charge transfer, and the surface morphology of the active layers of small molecule:PCBM [28]. All these factors must be taken into account, which can alter expected V_{oc} value significantly. The increasing D–A arms in triphenyl core restricted the net J_{sc} which may be attributed to its decreasing solubility decreased the compatibility with PC₆₁BM molecules in the films cast from the DCB solutions. Altogether the increase in D–A arms in triphenyl core (**TPATP2** and **TPATP3**) decreased both the power conversion efficiency contributing

Table 3 Photovoltaic properties of bulkheterojunction solar cell devices with a configuration of ITO/PEDOT:PSS/smallmolecule:PC_{61/71}BM (1:3)/Ca/Al

Small molecule	V_{oc} (V)	J_{sc} (mA)	FF (%)	PCE (%)
TPATP1 /PC ₆₁ BM	0.76	3.47	33.7	0.89
TPATP2 /PC ₆₁ BM	0.47	2.37	30.5	0.34
TPATP3 /PC ₆₁ BM	0.5	1.76	37.4	0.329
TPATP1 /PC ₇₁ BM	0.86	6.59	33	1.87
TPATP2 /PC ₇₁ BM	0.70	6.05	34.2	1.45
TPATP3 /PC ₇₁ BM	0.66	5.10	32.1	1.08

Measured under AM 1.5 irradiation, 100 mW/cm²

Table 4 Photovoltaic properties of bulkheterojunction solar cell devices with a configuration of ITO/PEDOT:PSS/**TPATP1**:PC₇₁BM/Ca/Al

Small molecule:PC ₇₁ BM	V_{oc} (V)	J_{sc} (mA)	FF (%)	PCE (%)
1:1	0.22	2.75	30.2	0.182
1:2	0.78	5.44	34.6	1.46
1:3	0.86	6.59	33	1.87

Measured under AM 1.5 irradiation, 100 mW/cm²

parameters (V_{oc} and J_{sc}) so as to decrease the PCE value (**TPATP2**: PCE = 0.34% and **TPATP3**: PCE = 0.32%) eventually (Table 3). In order to get the advantage of high absorption coefficient of PC₇₁BM than PC₆₁BM in absorption spectra, BHJ photovoltaic devices were made with small molecules (**TPATP1**, **TPATP2** and **TPATP3**) as donor and PC₇₁BM acceptor in the same ratio. As expected, the PCE values of all the small molecules increased significantly compare to the earlier PC₆₁BM blended active layer. This is likely due to an increase in light harvesting by the acceptor materials. As shown in Fig. 4b and Table 3, though there is increase in absorption with increase in number of D–A propellants in triphenyl core but the lowest D–A propellant (**TPATP1**) has the highest PCE values (PCE = 1.87%), followed by **TPATP2** and **TPATP3** with PCE value of 1.45% and 1.08% respectively. The constraints in PCE values for the star-burst small molecules (**TPATP2** and **TPATP3**) are due to the decrease in solubility with increase in star-burst

Table 2 Electrochemical properties of **TPATP1**, **TPATP2** and **TPATP3**

Small molecules	$E_{ox,onset}$ (V) ^a	$E_{red,onset}$ (V) ^a	E_{HOMO} (eV) ^b	E_{LUMO} (eV) ^b	E_g^{cv} (eV)
TPATP1	0.86	−1.01	−5.19	−3.34	1.85
TPATP2	0.85	−1.00	−5.20	−3.35	1.85
TPATP3	0.92	−0.85	−5.27	−3.50	1.77

^aOnset oxidation and reduction potentials measured by cyclic voltammetry in solid films. ^b $E_{HOMO}/E_{LUMO} = [-(E_{onset} - 0.45) - 4.8]$ eV, where 0.45 V is the value for ferrocene versus Ag/Ag⁺ and 4.8 eV is the energy level of ferrocene below the vacuum

Fig. 4 Current-voltage (J - V) curves of bulkheterojunction solar cells containing blends of (a) **TPATP1**, **TPATP2** and **TPATP3**/ PC_{61}BM (b) **TPATP1**, **TPATP2** and **TPATP3**/ PC_{71}BM in 1:3 weight ratios under the illumination of AM 1.5G, 100 mW/cm^2

conjugations. In addition there was formation of pinholes in the device by shrinking of the materials film which is attributed to the decrease in the solution density. The lower value of FF (30–35%), which restricted the overall PCE values, could be due to increase in series resistance. As the blending ratio between the organic molecule and PC_{71}BM in active layer affects the device performance, we studied solar cell devices incorporating blending ratios ranging from 1:1 to 1:3 (**TPATP1**: PC_{71}BM) and the data are enlisted in Table 4. As shown in Fig. 5 and Table 4, with the increase in the amount of **TPATP1**: PC_{71}BM ratio from 1:1 to 1:2 and then to 1:3 in the active layer increased the J_{sc} from 2.75 to 5.44 and then to 6.59 respectively which is attributed to the phenomenon of sufficient number of electron and hole percolation pathways that were formed to allow more efficient charge separation [29].

Fig. 5 Current-voltage (J - V) curves of Bulkheterojunction solar cells containing blends of **TPATP1**/ PC_{71}BM in different weight ratios under the illumination of AM 1.5G, 100 mW/cm^2

The photovoltaic properties of **TPATP1**: PC_{71}BM in different ratios further analyzed by the surface morphologies. As shown in the AFM picture (Fig. 6), the **TPATP1**: PC_{71}BM with 1:3 ratios has the smoother surface with surface roughness 0.34 nm as that of 1:1 and 1:2 ratios with surface roughness 0.52 nm and 0.59 nm respectively. The higher roughness consequences a large-scale phase separation which decreases the diffusional escapes probability for mobile charge carriers, and hence increases recombination [30]. Thus the favorable morphology of the device containing **TPATP1**: PC_{71}BM based device resulted the best PCE value of 1.87% with V_{OC} of 0.86 V, J_{sc} of 6.59 mA and FF of 33%. In fact owing to the low and unequal proportion of hole and electron mobilities, the quality of the small molecule BHJ solar cells are comparably poor. Figure 7 presents the EQE spectra of the devices (**TPATP1**, **TPATP2**, **TPATP3**/ PC_{71}BM) in 1:3 weight ratios. The small molecule **TPATP1** got the maximum EQE of 32% where as **TPATP2**, **TPATP3** have EQE around 28% in between 400 to 700 nm and showed a great consistency with their PCE values.

3 Conclusion

We designed three well-defined linear to starburst, TPD based D- π -A conjugated small molecules and the optical, electrochemical and photovoltaic properties have been studied. The photovoltaic device containing the donor **TPATP1** and the acceptor PC_{71}BM at a 1:3 weight ratio exhibited the best open circuit voltage of 0.86 V, J_{sc} of 6.59 mA and FF of 33% with a power conversion efficiency of 1.87%. Furthermore the EQE spectra of the

Fig. 6 AFM images of **TPATP1/PC₇₁BM** in different weight ratios **a** 1:1 (w/w), **b** 1:2 (w/w), **c** 1:3 (w/w)

Fig. 7 External quantum efficiency (EQE) of bulk heterojunction solar cells containing blends of small molecules (**TPATP1**, **TPATP2**, **TPATP3**)/**PC₇₁BM** in 1:3 weight ratios

best device (**TPATP-1/PC₇₁BM** in 1:3 weight ratios) got a maximum EQE of 32%. Though the PCE values decreased with increase in D–A arms in starburst small molecules, however the optical and electrochemical results provides a great approach to engineer starburst molecules to increase the solubility and thus to increase the solar cell efficiencies eventually.

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Compliance with ethical standards

Conflict of interest Authors declare no conflict of interest for any part of the work reported in this article.

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