Synthesis and Photovoltaic Properties of New D-A Copolymers Based on 5,6-Bis(2-Ethylhexyl)Naphtha[2,1-b:3,4-b']Dithiophene-2,9-Diyi] Donor and Fluorine Substituted 6,7-Bis(9,9-Didodecyl-9H-Fluoren-2-yl)[1,2,5]Thiadiazolo[3,4-g]Quinoxaline Acceptor Units

Mukhamed L. Keshtov, Igor O. Konstantinov, Sergei A. Kuklin, Alexei R. Khokhlov, Natalia V. Nekrasova, Zhi-Yuan Xie, Emmanuel N. Koukaras, Ganesh D. Sharma

1Institute of Organoelement Compounds of the Russian Academy of Sciences, Vavilova St., 28, Moscow 119991, Russian Federation
2Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, LeninskyProspect, 31, Moscow 119071, Russian Federation
3State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China
4Nanotechnology and Advanced Materials Laboratory, Department of Chemical Engineering, University of Patras, Patras, Western Greece 26500, Greece
5Molecular Engineering Laboratory, Department of Physics, University of Patras, Patras, Western Greece 26500, Greece
6Department of Physics, The LNM Institute for Information Technology, Jaipur, Rajasthan, India

Correspondence to: M. L. Keshtov (E-mail: keshtov@ineos.ac.ru) or G. D. Sharma (E-mail: gdsharma273@gmail.com and gdsharma@lnmiit.ac.in)

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ABSTRACT: Two low band gap D-A copolymers 5,6-bis(2-ethylhexyl)naphtha[2,1-b:3,4-b']dithiophene-2,9-diyl] donor and without (P1) and with (P2) fluorine substituted 6,7-bis(9,9-didodecyl-9H-fluoren-2-yl)[1,2,5]thiadiazolo[3,4-g]quinoxaline were synthesized and their optical and electrochemical properties were investigated. These copolymers were employed as donor along with PC71BM as acceptor for the fabrication of solution processed bulk heterojunction polymer solar cells. After the optimization of the active layer, that is, different donor-to-acceptor weight ratios and concentration of DIO solvent additive, the resultant polymer solar cells showed overall PCE of 5.44% and 8.14% for P1 and P2, respectively, with low voltage loss of 0.40 eV. The higher value of power conversion efficiency of P2 based polymer solar cells as compared to P1 counterparts, may be related to the deeper highest occupied molecular orbital energy level of P2, higher hole mobility, balanced charge transport, suppressed bimolecular recombination and small \( p-p \) stacking distance and higher crystallinity of P2:PC71BM active layer. Although the dipole moment of P2 is slightly lower than P1, the enhanced values of power conversion efficiency of P2 may be related to improve stacking. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. 2018, 00, 000–000

KEYWORDS: D-A copolymers; low band gap; low energy loss; polymer solar cells; power conversion efficiency

INTRODUCTION Polymer solar cells (PSCs) have attracted lot of attention for their use in solar energy conversion into electrical energy due to their low cost of fabrication, light weight, flexibility, and large area production. Most of the efficient PSCs employ a bulk heterojunction (BHJ) active layer that consists of a conjugated polymer as donor material and fullerene or non-fullerene acceptor. The power conversion efficiency of PSCs based on BHJ active layers have recently reached up to 11% for fullerene acceptor and in the range of 12–13% for non-fullerene acceptors, following optimization of the active layers and interface engineering. The donor polymer in the active layer plays an important role in determining the \( J_{sc} \) of the resultant devices. Therefore, progress in PSCs is largely dependent on the design of new copolymers with variable electron-donating (D) and electron-accepting (A) units. By selecting appropriate D and A units, chemists can fine tune the optical absorption, energy levels, carrier mobility, and other inherent properties of the D–A copolymers. The overall PCE of PSCs is strongly dependent on the light harvesting ability of the BHJ active layer.
employed in the device. To improve the light harvesting ability of the active layer, it is essential to utilize the BHJ active layer consisting of donor and acceptor that can absorb photons in the wavelength region from 300 to 1100 nm. Therefore, it is necessary to design the new organic semiconducting materials (either donor or acceptor) that are capable of absorbing solar light up to 1100 nm or beyond. To design such materials, a combination of strong acceptor and weak donor is generally used in D–A systems. Among the various strong acceptor units, thiadiazoloquinoxalines (TQxs) possess outstanding electron affinity and variable chemical structures, thereby becoming a class of important building blocks for polymer semiconductors that absorb light in the above mentioned wavelength region. In addition to the acceptor, the donor in the D–A structured materials is also important to control the energy levels and enhance the intermolecular interactions. Heteroaromatic rings are mostly used for this purpose. Naphthodiophene (NDT) is an example of heteroaromatic ring, consists of two thiophene units fused together at the end of a naphthalene unit to yield an extended π-conjugation system and a highly planar NDT backbone. Most of the D–A copolymers based on NDT showed moderate PCE in between 2% and 5% due to the limited absorption profile up to only 650 nm.

In continuation to our work using the TQx as acceptor unit for the design of low band gap D–A copolymers, herein we report the synthesis of two ultra-low band gap copolymers denoted as P1 and P2 using a NDT donor unit and TQx (with and without fluorinated side chains). Recently fluorinated Qx-based polymers have been employed as donor and found the impressive PCE about 10% for resulting PSCs using non-fullerene acceptors. The presence of fluorne atoms in the side chain (fluorene) of TDQx in P2 to P1 leads to more deep-positioned HOMO energy levels without significant influence on the LUMO energy levels and allows achieving higher Voc values in PSCs. Low bandgap width values are needed for improving of the morphology of the active layer by adjusting donor-to-acceptor weight ratios and subjected to solvent vapor treatment of the active layer, the PCE values for PSCs based on P1 and P2 were 5.44% and 8.14%, respectively. It was found that Jsc, Voc, and FF values of corresponding PSCs improve with the introduction of F atoms in the side chain of TQx. The results show that introduction of F atoms on the side chain of TDQx in the copolymers is a promising strategy for overall improvement of performance of PSCs-based TDQx polymeric materials. Moreover, these PSCs showed very low voltage losses of 0.40 eV, which is the most important result of this investigation.

**EXPERIMENTAL SECTION**

**Synthesis of Copolymers**

All the chemicals and reagents were obtained from Sigma-Aldrich. Toluene was freshly dried over sodium and benzophenone prior to use. Monomers 4,9-dibromo-6,7-bis(9,9-didodecyl-9H-fluoren-2-yl) [1,2,5]thiadiazolo[3,4-g]quinoxaline (M1), 4,9-dibromo-6,7-bis(9,9-didodecyl-5,7-difluoro-9H-fluoren-2-yl) [1,2,5] thia diazolo[3,4-g]quin oxa line (M2), and 5,6-bis (2-ethylhexyl)naphtha[2,1-b:3,4-b']dithiophene-2,9-diyli (M3) were synthesized according to the previously reported procedures.  

**Copolymer P1.** Monomer M1 (0.6738 g, 0.5 mmol) and monomer M3 (0.3952 g, 0.5 mmol) were added into a 25 mL flask equipped with a condenser under argon atmosphere. Toluene (16 mL) was added, the mixture was degassed for 30 min followed by addition of Pd(Ph3P)4 (0.027 g, 0.040 mmol) in dry box. Solution was heated at 110 °C for 48 h. Then after cooling to room temperature copolymer solution was poured into vigorously stirred in methanol. The obtained polymer was purified by Soxlet extraction using methanol, hexane to remove oligomer and small molecular part, and finally extracted with chloroform. The chloroform solution was then concentrated and precipitated in methanol. Dark colored solid was collected and dried under vacuum for 20 h. P1 (yield: 0.66 g, 80%). 1H NMR (400 MHz,CDCl3): δ 10.50–7.30 (br,18H), 3.12 (br, 4H), 0.25–2.50 (br, 130 H). Anal. Calcd for C112H152N4S3, %: C, 81.50; H, 9.28; N, 3.39; S,5.83. Found, %: C, 81.02; H, 9.08; N, 3.11; S, 5.38.

**Copolymer P2** was prepared by similar way using M2 and M3 (yield: 0.71 g, 83%). 1H NMR(400 MHz,CDCl3) δ:10.50–6.50(br,14H), 3.03 (br, 4H), 0.25-2.25(br,130H). 19F NMR (CDCl3) δ: −109.88 (s), 115.03 (s). Anal. Calcd for C112H152F4N4S3, %: C,78.09; H, 8.66; N,3.35; F, 4.41, S, 5.58. Found, %: C, 77.44; H, 8.46; N, 3.25; F, 3.89, S, 5.25.

**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 overnight. A solution of polyethylene dioxy-thiophene: polystyrenesulfonate (PEDOT:PSS, Clevios Al 4083) was spin coated onto the cleaned ITO substrates at 3500 rpm for 2 min and then was annealed at 120 °C for 10 min in air environment. The mixture of electron donor P1 or P2 and electron acceptor PC71BM in different weight ratios were dissolved in chloroform solution (concentration is 14 mg/mL). The blend solutions were spin coated on top of the PEDOT:PSS film for 30 s at 1500 rpm and dried for 3 h under ambient conditions. For solvent additive (SA), 3 vol % of DIO was mixed into the host CF solvent. The thickness of the active layers is about 95 nm. 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 30 s. By means of thermal evaporation and under a pressure of 10^-5 Torr, the cathode aluminum (Al) (90 nm) was deposited 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 and electron-only devices (ITO/PEDOT:PSS/P1 or P2:PC71BM/Au) to measure the hole and electron mobility. 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/cm$^2$) 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.

RESULTS AND DISCUSSION

Synthesis and Characterization Copolymers

The copolymers were obtained through Stille-coupling polymerization using Pd(Ph$_3$P)$_4$ as catalysts in good yields as shown in Scheme 1 and the detailed synthetic processes are described in experimental section. Crude copolymers were purified by extracting with methanol, hexane, and chloroform, respectively. The chloroform solution was concentrated and the product reprecipitated into methanol several times to give the resulting copolymers. The structures of the copolymers were confirmed by $^1$H NMR, $^{19}$F NMR spectroscopy (as shown in Supporting Information, Figs. S1 and S2) and elemental analysis. The number-average molecular weight ($M_n$) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using chloroform as the eluent and polystyrene as the internal standard. The $M_n$ of P1 and P2 are 15,500 and 17,700 with a polydispersity of 2.00 and 2.10, respectively. These indicate that the introduction of fluorine atoms has no significant influence on the molecular weight of the copolymers. Both the copolymers are well soluble in chloroform, chlorobenzene, and o-dichlorobenzene (Table 1).

The thermal properties of the copolymers were investigated using thermal gravimetric analysis (TGA) (as shown in Supporting Information, Fig. S3) and were carried out under nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$. The copolymers showed good thermal stability with onset decomposition temperature (5% weight) is 390 °C and 356 °C, respectively for P1 and P2. The high thermal stability of these copolymers ensured their applications in organic electronic devices.

Optical and Electrochemical Properties

Absorption spectra of both copolymers in dilute ($1 \times 10^{-4}$ M) chloroform solution and in thin films are shown in Figure 1 and their absorption properties are listed in Table 2. Both the copolymers demonstrate similar absorption profiles and have two main characteristic absorption bands. The absorption band around 350–600 nm can be attribute to the $\pi-\pi^*$ transition, whereas the absorption band in the range of 600–1250 nm corresponds to intramolecular charge transfer (ICT) inside the polymeric chain, between electron donor and electron acceptor units. This is a characteristic of the most of D–A copolymers. The absorption of the fluorinated copolymer P2 is slightly blue shifted as compared to P1. Similar blue shifts were observed previously for other fluorinated copolymers and were attributed to steric hindrance effects appearing due to the incorporation of fluorine atoms. Moreover, the electron density on F substitution weakens the $\pi$-conjugation in the backbone due to its strong

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**TABLE 1 Molecular Weights and Thermal Properties of Copolymers P1 and P2**

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Yield (%)</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
<th>$T_d$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>80</td>
<td>15,500</td>
<td>31,000</td>
<td>2.00</td>
<td>390</td>
</tr>
<tr>
<td>P2</td>
<td>83</td>
<td>17,700</td>
<td>37,200</td>
<td>2.10</td>
<td>356</td>
</tr>
</tbody>
</table>

$^a$ Determined by GPC in chloroform with polystyrene standards.

$^b$ Decomposition temperature, determined by TGA in nitrogen based on 5% weight loss.
electro-negativity and results in a blue shift of the absorption band. The absorption band that corresponds to the ICT in thin film of both copolymers is significantly red shifted to the longer wavelength region as compared to their spectra in solution and can be explained by packing effects which lead to planarization of polymer backbones. The optical bandgap values ($E_{\text{opt}}^g$) of polymers P1 and P2 were calculated to be 1.04 and 1.10 eV, respectively. The absorption spectra of P2 thin film showed a shoulder in the longer wavelength region which is not observed in the absorption spectrum of P1. This may be due to the greater rigidity of P2 backbone which enhances its light harvesting ability, consequently rendering it more efficient in harvesting photons and generating photocurrent than P1.\(^{15}\)

Cyclic voltammetry (CV) was employed to examine the electrochemical properties and determine HOMO and LUMO energy levels of these copolymers. The measured cyclic voltammograms are illustrated in Figure 2 and the results are summarized in Table 2. The energy levels of the HOMO and LUMO of the polymers were calculated according to the equations:

$$E_{\text{HOMO}} = -q(E_{\text{onset}}^\text{ox} + 4.40)$$

$$E_{\text{LUMO}} = -(E_{\text{onset}}^\text{red} + 4.40)$$

Where $E_{\text{onset}}^\text{ox}$ and $E_{\text{onset}}^\text{red}$ are the onset oxidation and reduction potentials, respectively. The LUMO energy levels of P1 and P2 are −3.72 and −3.74 eV, respectively. Thus, one can find that the LUMO energy level was not affected by the introduction of fluorine atoms. The LUMO energy values for both copolymers are ca. 0.3 eV higher than that for the fullerene PC\(_{71}\)BM acceptor (−4.1 eV)\(^ {16}\) providing fast electron transfer from the polymeric donor to fullerene acceptor in polymer solar cells. The HOMO energy level value of P1 was estimated to be −5.18 eV. After the introduction of fluorine atoms into each FL fragment, the HOMO energy of polymer P2 was lowered to −5.29 eV. The deeper HOMO of P2 may be due to the electron withdrawing effect of fluorine atoms (strong electron negativity) and beneficial for the high $V_{\text{oc}}$ of the corresponding PSCs without sacrificing the $J_{\text{sc}}$. The electrochemical bandgap values of copolymers P1 and P2 were calculated from the difference of HOMO and LUMO energy levels and are of 1.46 and 1.55 eV, respectively. The values of $E_{\text{ec}}^g$ of the copolymers are larger than their optical bandgap values. This discrepancy between the optical ($E_{\text{opt}}^g$) and electrochemical ($E_{\text{ec}}^g$) bandgap values can be explained by the exciton binding energy in the copolymers and/or the

\[E_{\text{opt}}^g = 1240/\lambda_{\text{onset}}^\text{film} .\]

**FIGURE 1** Normalized optical absorption spectra of P1 and P2 is dilute chloroform solution and thin film cast from chloroform. [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 2** Optical and Electrochemical Properties of Copolymers P1 and P2

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$\lambda_{\text{max}}^{\text{soln}}$ (nm)</th>
<th>$\lambda_{\text{max}}^{\text{film}}$ (nm)</th>
<th>$E_{\theta}^{\text{opt}}$ (eV)</th>
<th>$E_{\text{HOMO}}^{\text{ec}}$ (eV)</th>
<th>$E_{\text{LUMO}}^{\text{ec}}$ (eV)</th>
<th>$E_{\text{g}}^{\text{ec}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>425 (c = 6.3 $\times$ 10$^4$ M$^{-1}$ cm$^{-1}$), 898 (c = 4.1 $\times$ 10$^4$ M$^{-1}$ cm$^{-1}$)</td>
<td>437, 970</td>
<td>1.04</td>
<td>−5.18</td>
<td>−3.72</td>
<td>1.46</td>
</tr>
<tr>
<td>P2</td>
<td>419 (c = 6.3 $\times$ 10$^4$ M$^{-1}$ cm$^{-1}$), 874 (c = 5.3 $\times$ 10$^4$ M$^{-1}$ cm$^{-1}$)</td>
<td>437, 972</td>
<td>1.10</td>
<td>−5.29</td>
<td>−3.74</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Calculated from the absorption band onset of thin film, $E_{\theta}^{\text{opt}} = 1240/\lambda_{\text{onset}}^{\text{film}}$. 

\[E_{\text{HOMO}}^{\text{ec}} = -q(E_{\text{onset}}^\text{ox} + 4.40)\]

\[E_{\text{LUMO}}^{\text{ec}} = -(E_{\text{onset}}^\text{red} + 4.40)\]
interfacial barriers for charge injection. The results agree well with the reports that the incorporation of fluorine is effective to control the HOMO and LUMO energy levels.

X-Ray Diffraction Measurements
To get the information about the effect of fluorination on the crystalline properties of copolymers in thin film form, the X-ray diffraction patterns were measured (Fig. 3). Both copolymers showed two strong diffraction peaks in (100) and (010) planes, which corresponds to the lamellar stacking and π–π stacking, respectively. The (100) diffraction peak of P1 and P2 located at 2θ = 4.87° and 5.06°, respectively, which corresponds to the lamellar d-space of 2.21 nm and 2.03 nm, respectively. The (010) diffraction peaks are observed at 2θ = 22.78° and 23.04° for P1 and P2, correspond to the π–π stacking distance of 0.42 and 0.39 nm, respectively. It is to be noted here that the lamellar stacking distance and π–π stacking distance was decreased with the fluorination of side chains of TQx. The decrease in lamellar distance may be due to strong H–F interaction. Moreover, the (100) diffraction peak for P2 is stronger than P1 also gave an evidence of its higher crystallinity than that of P1 counterpart. The smaller lamellar distance and more compact π–π stacking are beneficial charge transport in PSCs. Therefore, higher molecular aggregation in P2:PC71BM blend could be expected to induce the higher charge carrier mobility than P1:PC71BM counterpart and is favorable for the improved values of Jsc, FF and PCE of the resultant PSCs as will be discussed in the later part of this article.

Theoretical Calculations
We have studied the P1 and P2 structures theoretically employing density functional theory (DFT) and time-dependent density functional theory (TD-DFT). The computations account for solvent effects with chloroform (CF) as solvent. We have performed the ground state and excited state computation using the B3LYP and M06 functionals. In place of the alkyl groups, we have introduced ethyl groups to reduce the computational cost for both structures. The initial structural optimizations were performed using the Turbomole package. The results reported are all from computations performed using the Gaussian package. Technical details on the computational methods and methodology used are provided in the Supporting Information.

The main bodies of the P1 and P2 structures are highly planar and consist of a NDT moiety linked to a thiadiazoloquinoxaline (TQx). Attached to the TQx moiety are two fluorene groups in the case of P1 and two difluoro-fluorene groups in the case of P2. The fluorene (based) groups are not coplanar to the main structure and form dihedrals angles of in the range of 36°–44° with the main body (that depends on the functional and the presence of solvent). In Table 3, we provide the computed frontier orbitals’ energy levels, the optical gaps, the main contributions to the first excitation, and the wavelength of the first excitation as well as of the excitations with the largest oscillator strengths.

The fluorination of the fluorene groups does have no significant effect on the frontier orbital energies or localization. We find that the HOMO and the LUMO levels, as well as the computed HOMO–LUMO (HL) gaps unchanged. The addition of electron withdrawing fluorene atoms is known to lower the HOMO and LUMO energies and widen the band gap. In our case this is not noted as the fluorination is not on the backbone groups of the structures. The ultraviolet/visual absorbance profiles also are almost the same for the fluorinated and non-fluorinated structures. Improvement in the photovoltaic performance of the actual device can be attributed (a) to more efficient stacking between the fluorinated polymers, and (b) to differences in the electric dipole...
moment. The former, that is, the PCE rise with increasing fluorination of end-capped groups, has also been identified in the work of Deng et al.\textsuperscript{25} on small molecules, and results from the denser and more ordered $\pi-\pi$ stacking for the fluorinated species. For the latter, several studies in the literature\textsuperscript{23–27} strongly indicate a correlation between the oscillator strengths, the main contributions to the first excited state, and the dipole moment (D), $\mu$.

Specifically, HOMO and LUMO energies (eV), HOMO–LUMO gap (eV), $\lambda_{1\text{ac}max}$ (nm), oscillator strengths, the main contributions to the first excited state, and the dipole moment (D), $\mu$.

TABLE 3 Calculated Properties of P1 and P2

<table>
<thead>
<tr>
<th></th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>HL (eV)</th>
<th>OG (eV)</th>
<th>$\lambda_{1\text{ac}max}$ (nm)</th>
<th>$F$</th>
<th>Main Contributions</th>
<th>$\mu$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>$-4.66$</td>
<td>$-3.64$</td>
<td>$1.02$</td>
<td>$1.37$</td>
<td>$906$</td>
<td>$0.25$</td>
<td>H–L(94%)</td>
<td>$2.21$</td>
</tr>
<tr>
<td></td>
<td>$-4.80^a$</td>
<td>$-3.77^a$</td>
<td>$1.04^a$</td>
<td>$1.33^a$</td>
<td>$933^a$</td>
<td>$0.32^a$</td>
<td>H–L(94%)</td>
<td>$2.78^a$</td>
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<tr>
<td>B3LYP</td>
<td>$-5.22$</td>
<td>$-3.22$</td>
<td>$2.00$</td>
<td>$1.73$</td>
<td>$718/537/365/339/309$</td>
<td>$0.30$</td>
<td>H–L(99%)</td>
<td>$1.74$</td>
</tr>
<tr>
<td></td>
<td>$-5.36^a$</td>
<td>$-3.33^a$</td>
<td>$2.03^a$</td>
<td>$1.70^a$</td>
<td>$729/554/357/342/313^a$</td>
<td>$0.37^a$</td>
<td>H–L(99%)</td>
<td>$2.07^a$</td>
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<tr>
<td>M06</td>
<td>$-5.50$</td>
<td>$-3.16$</td>
<td>$2.34$</td>
<td>$1.81$</td>
<td>$687/502/327/301$</td>
<td>$0.30$</td>
<td>H–L(99%)</td>
<td>$1.78$</td>
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<tr>
<td></td>
<td>$-5.66^a$</td>
<td>$-3.28^a$</td>
<td>$2.38^a$</td>
<td>$1.79^a$</td>
<td>$694/516/330/303^a$</td>
<td>$0.36^a$</td>
<td>H–L(99%)</td>
<td>$2.04^a$</td>
</tr>
<tr>
<td>P2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>$-4.72$</td>
<td>$-3.70$</td>
<td>$1.02$</td>
<td>$1.36$</td>
<td>$909$</td>
<td>$0.25$</td>
<td>H–L(94%)</td>
<td>$2.42$</td>
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<tr>
<td></td>
<td>$-4.83^a$</td>
<td>$-3.79^a$</td>
<td>$1.03^a$</td>
<td>$1.32^a$</td>
<td>$936^a$</td>
<td>$0.32^a$</td>
<td>H–L(94%)</td>
<td>$2.80^a$</td>
</tr>
<tr>
<td>B3LYP</td>
<td>$-5.30$</td>
<td>$-3.30$</td>
<td>$1.99$</td>
<td>$1.72$</td>
<td>$720/530/366/337/307$</td>
<td>$0.30$</td>
<td>H–L(99%)</td>
<td>$2.60$</td>
</tr>
<tr>
<td></td>
<td>$-5.39^a$</td>
<td>$-3.36^a$</td>
<td>$2.03^a$</td>
<td>$1.70^a$</td>
<td>$731/546/358/340/310^a$</td>
<td>$0.36^a$</td>
<td>H–L(99%)</td>
<td>$2.98^a$</td>
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<tr>
<td>M06</td>
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<td>$-3.24$</td>
<td>$2.33$</td>
<td>$1.80$</td>
<td>$689/495/385/327$</td>
<td>$0.30$</td>
<td>H–L(99%)</td>
<td>$2.27$</td>
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<tr>
<td></td>
<td>$-5.69^a$</td>
<td>$-3.31^a$</td>
<td>$2.38^a$</td>
<td>$1.79^a$</td>
<td>$694/510/331/300^a$</td>
<td>$0.37^a$</td>
<td>H–L(99%)</td>
<td>$2.54^a$</td>
</tr>
</tbody>
</table>

The energy gaps calculated using the hybrid B3LYP functional is underestimated compared to value using the meta-hybrid M06 functional. For the HOMO–LUMO (HL) gap the values computed using B3LYP are lower by ~0.35 eV and for the optical gaps by <0.1 eV. The computed UV/Visual absorbance spectra the P1 and P2 structures calculated at the TD-DFT/M06 level of theory is given in Figure 5 and with B3LYP in the Supporting Information Figure S4, both accounting for solvent effects for chloroform and in gas phase. The spectra computed using the two functionals are in excellent agreement on the form and range. The spectra of P1 and P2 exhibit three peaks that are centered about 333, 510, and 693 nm. The small wavelength peak has two side

TABLE 4 Dipole Moments of the P1 and P2 Structures

<table>
<thead>
<tr>
<th>Copolymers</th>
<th>$\mu_g$ (D)</th>
<th>$\mu_e$ (D)</th>
<th>$\Delta\mu_{ge}$ (D)</th>
<th>$\mu_{eg}$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>2.04</td>
<td>6.81</td>
<td>4.77</td>
<td>7.28</td>
</tr>
<tr>
<td>P2</td>
<td>2.54</td>
<td>5.31</td>
<td>2.77</td>
<td>7.36</td>
</tr>
</tbody>
</table>

$\mu_g$, ground state dipole moment; $\mu_e$, excited state dipole moment; $\Delta\mu_{ge}$ change between the ground state and excited state dipole moments.
peaks that are more pronounced for P2, located about 302 and 380 nm.

PHOTOVOLTAIC PROPERTIES

PSCs were fabricated using these copolymers as donor and PC71BM as the acceptor in a conventional ITO/poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS)/copolymers: PC71BM/PFN/Al device structure. PSCs based on P1 and P2 with different weight ratios of copolymers and PC71BM (1:0.5, 1:1, 1:1.5, 1:2, and 1:2.5) in blend have been fabricated and tested to optimize the device fabrication conditions (as complied in Supporting Information, Table S3a,b) and found weight ratio of 1:2 for both the copolymer showed best photovoltaic response. After that we have used blend ratio of 1:2 (copolymer: PC71BM) with 1, 8-diiodooctane (DIO) (3 vol %) as a processing additive to optimize the morphology of the active layer. The inclusion of DIO was found to increase $J_{sc}$, FF, and PCE for the PSCs based on both copolymers and related to the morphological changes in the active layers. The current–voltage ($J$–$V$) characteristics under illumination and incident photon to current conversion efficiency (IPCE) spectra of the PSCs based on optimized P1:PC71BM and P2:PC71BM active layers are shown in Figure 6 and corresponding photovoltaic parameters are summarized in Table 5.

As shown in Figure 6(a), P1 based PSC exhibits overall PCE of 5.44% with $J_{sc}$ of 14.17 mA/cm², $V_{oc}$ of 0.61 V, and FF of 0.63. When incorporation of fluorine atom in the side chain of TQx, the P2 based PSC showed a simultaneous improved $V_{oc}$ of 0.70 V, $J_{sc}$ of 16.15 mA/cm², and FF of 0.72, resulting high value of PCE of 8.14%. The improved photovoltaic
parameters of PSC based on P2 can be attributed to synergistic effect of its deeper HOMO energy level (related to $V_{oc}$), higher absorption coefficient and higher charge carrier mobility (related to $J_{sc}$ and FF). The improvement in the $J_{sc}$ has been also confirmed from the IPCE spectra of the PSCs. As shown in Figure 6(b), both the PSCs based on P1 and P2 exhibited a spectral response in the wavelength region of 350–1200 nm, which agrees well with the optical absorption spectra of corresponding copolymer films. The maximum IPCE value for the P2-based PSC is about 58% at 964 nm, which is higher than that for P1 counterpart (IPCE 554% at 994 nm). The $J_{sc}$ values estimated from the integration of IPCE spectra of PSCs based on P1 and P2 are about 14.06 and 16.02 mA/cm², respectively, and agree with those obtained from the $J-V$ characteristics under illumination.

To understand the higher PCE of PSCs based on P2 then P1, the hole mobility ($\mu_h$) and electron mobility ($\mu_e$) in the blend films were estimated from the dark $J-V$ characteristics of hole and electron only devices (Fig. 7) and fitting them with space charge limited current model. The $\mu_h/\mu_e$ values for P1:PC71BM and P2:PC71BM blend were calculated to be 9.96 x 10⁻⁵/2.18 x 10⁻⁴ cm²/Vs and 1.68 x 10⁻⁴/2.31 x 10⁻⁴ cm²/Vs, respectively. The ratio between $\mu_e$ and $\mu_h$ for P1:PC71BM and P2:PC71BM blend are 2.18 and 1.37, respectively. These results clearly indicate that substitution of F atom into the side chain of TQx acceptor not only increases the both electron and hole mobilities but also keeps more balance of electron and hole transport in the active layer and may also be contributed to the higher FF value.

### TABLE 5 Photovoltaic Parameters of PSCs Based on P1:PC71BM and P2:PC71BM Copolymers

<table>
<thead>
<tr>
<th>Copolymers</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω cm²)</th>
<th>$R_{sh}$ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 (as cast)</td>
<td>10.16 (10.09)⁺</td>
<td>0.65</td>
<td>0.48</td>
<td>3.17 (3.08)⁺</td>
<td>38.73</td>
<td>796</td>
</tr>
<tr>
<td>P2 (as cast)</td>
<td>11.98 (11.89)⁺</td>
<td>0.73</td>
<td>0.53</td>
<td>4.63 (4.52)⁺</td>
<td>31.67</td>
<td>857</td>
</tr>
<tr>
<td>P1 (SA)</td>
<td>14.17 (14.06)⁺</td>
<td>0.61</td>
<td>0.63</td>
<td>5.44 (5.34)⁺</td>
<td>23.12</td>
<td>934</td>
</tr>
<tr>
<td>P2 (SA)</td>
<td>16.15 (16.02)⁺</td>
<td>0.70</td>
<td>0.72</td>
<td>8.14 (8.03)⁺</td>
<td>16.23</td>
<td>996</td>
</tr>
</tbody>
</table>

⁺ Average of 8 devices.

b Estimated form the IPCE spectra.
To get more information about the effect of fluorine atom substitution in the copolymer on the exciton dissociation efficiency, we have plotted the photocurrent density ($J_{ph}$) as a function of effective voltage ($V_{eff}$) in log–log plot and shown in Figure 8. The $J_{ph}$ is defined as $J_L - J_D$, where $J_L$ and $J_D$ are the current densities under illumination and in the dark, and $V_{eff}$ is defined as $V_0 - V$, where $V_0$ is the voltage at which $J_{ph} = 0$, and $V$ is the applied voltage. It can be seen from Figure 6 that the $J_{ph}$ increases linearly with the increase in $V_{eff}$ in the low-voltage region and saturates at high value of $V_{eff}$. In the case of P2, the $J_{ph}$ saturates at $V_{eff} = 0.7$ V, whereas for P1, this value is 1.2 V and beyond that $J_{ph}$ is independent of $V_{eff}$. This indicates that most of the excitons generated after the absorption of light by the active layer are dissociated into free charge carriers and effectively extracted by the corresponding electrodes. Under the short circuit conditions, the exciton dissociation probability ($P_{diss} = J_{ph}/J_{ph sat}$) for PSCs based on P1 and P2 was calculated to be 0.89 and 0.94, respectively. The higher value of $P_{diss}$ for P2 implied that more efficient charge collection in P2-based PSCs.

To get information about the charge recombination in the PSCs, we have measured the current-voltage characteristics under different illumination intensities and plotted the variation of $J_{sc}$ and $V_{oc}$ with illumination intensity ($P_{in}$) and shown in Figure 9(a,b). The variation of $J_{sc}$ with $P_{in}$ can be related as $J_{sc} \propto P_{in}^s$ where slope $s$ represents the degree of recombination in the devices. The value of $s$ for P2-based device is 0.96 which is higher than that for P1-based counterpart (0.91), suggesting a reduced bimolecular recombination in P2-based devices. As shown in Figure 7(h), the slope

![FIGURE 9 Variation of (a) $J_{sc}$ and (b) $V_{oc}$ with illumination intensity ($P_{in}$) for the PSCs based on optimized P1:PC$_{71}$BM and P2:PC$_{71}$BM active layers. [Color figure can be viewed at wileyonlinelibrary.com]](image)

![FIGURE 10 TEM images of optimized P1:PC$_{71}$BM and P2:PC$_{71}$BM thin films. Scale bar is 200 nm.](image)
for the variation of $V_{oc}$ with $P_{m}$ for P2-based device is about 1.25 kT/q which is smaller than that for P1-based device (1.41 kT/q) indicating reduced trap-assisted recombination in P2-based devices.

To get information about the nanoscale morphology and phase separation in the solvent additive cast blend films, we have recorded the transmission electron microscopy (TEM) image and shown in Figure 10. As can be seen from TEM images, the lengths of the fibrils in the blends are different. These fibrils correspond to highly crystalline features of copolymers, as confirmed from XRD measurements. The phase separation and bi-continuous interpenetrating networks have been enhanced for P2:PC$_{71}$BM active layer as compared to P1:PC$_{71}$BM, which is beneficial for the charge transport in active layer toward the electrode. The TEM images of P2:PC$_{71}$BM blend showed more distinct phase separated domains with more interpenetrating network than P1:PC$_{71}$BM counterpart. The optimized nanoscale morphology is desirable in the blend thin film promote exciton diffusion, exciton dissociation, and charge transport, and thereby lead to enhanced $J_{sc}$ and FF with suppressed charge recombination.\textsuperscript{32}

As shown in Table 5, the $R_g$ value of the SA-treated devices is lower as compared to as cast counterpart, also confirms the increase in the values of $J_{sc}$ and FF, due to the efficient charge extraction.

CONCLUSIONS

In brief, we have synthesized two new D–A-type copolymers using nonfluorinated (P1) and fluorinated (P2) TQx electron acceptor units and same NDT electron donor unit and investigated their optical and electrochemical properties. Both P1 and P2 exhibit ultra-low optical band gaps of 1.04 and 1.10 eV, respectively, and have HOMO and LUMO energy levels matched with the energy level of PC$_{71}$BM for efficient photo-induced charge transfer and used as donor for the fabrication of bulk heterojunction polymer solar cells. The optimized PSCs based on P2 showed higher PCE of 8.14% with energy loss of 0.40 eV than that of P2 based counterpart (5.44% with energy loss of 0.43 eV) is due the improved values of $J_{sc}$ $V_{oc}$ and FF. Compared to P1, P2 exhibits a higher absorption coefficient, deeper HOMO energy level, higher crystallinity, and shorter $\pi-\pi$ stacking distance translating to higher $J_{sc}$ and FF and deeper HOMO energy level of P2 resulted in high value of $V_{oc}$. The value of 8.14% is the highest value of PCE for PSCs using ultra-low band gap D–A copolymers. Therefore, substitution of fluorine atom in the TQx acceptor can be used to prepare ultra-low band gap D–A copolymers with higher absorption coefficients and can be utilized for tandem and ternary organic solar cells with higher PCE.

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