New D-A1–D-A2-Type Regular Terpolymers Containing Benzothiadiazole and Benzothiophene Acceptor Units for Photovoltaic Application

Mukhamed L. Keshtov,*† Alexei R. Khokhlov,* Serge A. Kuklin,† Fang-Chung Chen,‡ Emmanuel N. Koukaras,§∥ and Ganesh D. Sharma*⊥

1Institute of Organoelement Compounds of the Russian Academy of Sciences, Vavilova St., 28, 119991 Moscow, Russian Federation
2Department of Photonics, National Chiao Tung University, Hsinchu, Taiwan 300, Taiwan, ROC
3Nanotechnology and Advanced Materials Laboratory, Department of Chemical Engineering, University of Patras, Patras 26500 GR, Greece
4Molecular Engineering Laboratory, Department of Physics, University of Patras, Patras 26500 GR, Greece
†Department of Physics, The LNM Institute for Information Technology, Jamdoli, Jaipur, India

ABSTRACT: Two novel regular terpolymers that are of D-A1–D-A2 type and contain benzothiadiazole and 2,5-dibromo-8-dodecanoylbenzene[1,2-b:3,4-b′:5,6-d′]trithiophene (P1) or 2,8-dibromo-5-dodecanoylbenzene[1,2-b:3,4-b′:5,6-d′]trithiophene (P2) acceptor units with the same thiophene donor were synthesized through Stille coupling, and their optical and electrochemical properties were investigated. The highest occupied molecular orbital (HOMO) and lowest unoccupied (LUMO) molecular orbital energy levels of these terpolymers indicate that there is sufficient LUMO offset with PCBM for efficient exciton dissociation, and their deeper HOMO levels ensure the high open-circuit voltage for the resultant bulk heterojunction solar cells. Measurements on the solar cell devices also confirm that compared to those based on P2 the devices based on P1 possess a higher short-circuit photocurrent (Jsc) as well as a higher fill factor (FF), which is attributed to the lower bandgap and higher hole mobility for P1, whereas the Voc is higher for the devices that are based on P2, which may be a result of P2 having a lower HOMO energy level than P1. The optimized polymer solar cells fabricated using P1:PC71BM (DIO/CF) and P2:PC71BM (CF/DIO) for the active layers showed a PCE of 7.19% and 6.34%, respectively. Atomic force microscopy (AFM) images of P1:PC71BM blend films show that they exhibit more suitable morphology with favorable interpenetrating networks, which favors high Jsc and FF. Moreover, P1 exhibits a more crystalline nature than P2 that also favors the charge transport. This may be a result of better molecular packing, more distinct phase separation of the blended films, as well as a reduction of charge recombination.

KEYWORDS: D-A1–D-A2 terpolymer, bulk heterojunction, polymer solar cells, solvent additive, power conversion efficiency

INTRODUCTION

Due to the depletion of traditional energy sources, there is worldwide increasing demand for renewable energy sources. Among those, considerable attention has been given to polymer solar cells (PSCs) that specifically have an active layer with a bulk heterojunction (BHJ) morphology since they offer certain highly desired advantages; namely, their prospects for low cost, low weight, and flexible large-area device manufacturing.1–7 During the past few years, the efficiency of BHJ PSCs has significantly increased to more than 10% due to efficient conjugated polymers development, morphology control, and device engineering.8–10 Recently, Zhao et al. reported PCE values of 11.7% for single-layer BHJ polymer solar cells processed using solvent additive.11 However, despite significant progress made in energy conversion efficiency (PCE), PSC performance is still inferior to inorganic analogues. To improve PSC efficiency and further commercialization, we still need improved conjugated copolymer development.

For the PSC devices to achieve high PCEs, polymers should have a deep HOMO energy level to increase open-circuit voltage (Voc), a narrow bandgap to enhance absorption to achieve higher short-circuit current (Jsc), as well as high hole mobility for better charge transport. Design tactics that are commonly used for appropriate donor materials that have absorption characteristics matched with a broad part of the solar spectrum, as well as suitably aligned energy levels to allow efficient electron transfer to the acceptor, have been the donor–acceptor (D–A) structure.12–18 In these materials,
transitions associated with intramolecular charge transfer (ICT) broaden the absorption spectrum and narrow the HOMO–LUMO bandgap. Although D–A copolymers showed excellent optical and electrochemical properties, many of them need further optimization. Therefore, to augment the photovoltaic characteristics of D–A copolymers, π-bridges, terpolymers, and regioregular structures were developed to optimize the backbone of the polymers. It is interesting and promising to design copolymers with three or more building blocks. Terpolymers with three units in the backbones of conjugated polymers are good examples to further utilize the properties of varied donors/acceptors. Taking advantage of the complementary absorption properties of two different components, a full visible-light absorption can be achieved. The terpolymers have been designed in random as well as regioregular configurations. D–A terpolymers based on two acceptor blocks located randomly in the main chain usually show only moderate photovoltaic characteristics that may result from structural defects present internally in the materials. Nevertheless, some polymers based on two acceptor units and with regioregular configurations showed high efficiency in PSC devices. Regioregular alternating structure of donor/acceptor units not only facilitates intramolecular charge transfer but also favors intermolecular chain ordering and increases charge carriers mobility. Furthermore, unlike random polymers, regular triple copolymers are typically obtained from regularly bonded construction blocks. Therefore, ordered structures can achieve higher carrier mobility, which leads to increased PSC efficiency. Recently, Lee and co-workers synthesized the regioregular PBDTT–C–T terpolymers which exhibit a red shift absorption spectrum, higher degree of crystallinity, and higher hole mobility than its random counterpart and when used as a donor for BHJ PSC showed high PCE of 7.79%. Hou and co-workers synthesized a new regioregular terpolymer PBDT-TSI which achieved a record PCE of 10.2%. These results demonstrated that regioregular terpolymers are an emerging feasible and facile method used to tune the backbone of photovoltaic copolymers.

Benzo[1,2-b:4,5-b’]dithiophene (BDT) has been the most used donor unit for highly efficient photovoltaic devices with fullerene derivatives. The rigid and planar conjugated structure of BDT makes it attractive for achieving highly tunable energy levels and optical bandgap as well as high hole mobilities. Inspired by the BDT structure, the design of the benzo[1,2-b:4,5-b’]thiophene (BTT) has a central benzene to which three thiophenes are fused that leads to a more extended (larger size) aromatic block and with a higher electronic density. Due to its attributes that hold promise for efficient charge transport and effective π-stacking, such as having an extended π-conjugation along with high coplanarity, BTT has given rise

Figure 1. 1H NMR spectra of (a) P1 and (b) P2.
to a class of structural units that are used in the design of organic semiconducting materials.\textsuperscript{27–30} Benzothiadiazole (BT) is a well-known electron-accepting unit that has been employed to construct high performance photovoltaic organic materials.\textsuperscript{31,32}

BT is a weaker acceptor compared to BT but offers a route to improved solubility through an easily applied alkyl substituent functionalization. When BT and BT acceptor units are introduced into the same polymer chain, it is possible to configure the D–A interaction, and what is important, number and distribution of alkyl side chains can be easily configured to control polymer chain planarity and interchain π–π interaction, along with its morphology and solubility. To extend the polymers’ absorption range and to achieve high PSC performance, two new terpolymers, that we denote here as P1 and P2 and that are of type D-A1–D-A2, were synthesized using BT (A1) and BT (2,5-dibromo-8-dodecanoylbenzo[1,2-b:3,4-b′:5,6-d′]trithiophene (P1) and 2,8-dibromo-5-dodecanoylbenzeno[1,2-b:3,4-b′:5,6-d′]trithiophene (P2) (A2) as acceptor building blocks, linked by thiophene donor π linkers, by Stille coupling. We have investigated their electrochemical and optical properties. Indeed, BT is an electron donor unit, but we have used its acyl derivative monomers for the design of copolymers. It is well-known that the carbonyl group is an acceptor, and we suggest that carbonyl-containing fragments of monomers are an electron-deficient unit; therefore P1 and P2 correspond to the D-A1–D-A2 structure. Employing two different acceptor fragments with different electron-withdrawing properties is a well-known approach to broaden the absorption spectrum as well as shift in the longer-wavelength region, which leads to improving the light absorption. Using PC\textsubscript{71}BM for the electron acceptor we were able to extend the polymers’ absorption range and to achieve high PSC performance. Two new terpolymers, that we denote here as P1 and P2, were synthesized according to the methods reported. Details of instrumentation have already been described in our earlier communication.\textsuperscript{33,34}

### EXPERIMENTAL DETAILS

Reagent grade chemicals and reagents were used throughout, without further purification, as purchased from the companies Across and Aldrich. Before usage, tetrahydrofuran and toluene were freshly distilled. 4,7-(bis(5-trimethylstannyl)thiophene-2-yl)benzo[c][1,2,5]thiadiazole (M1),\textsuperscript{35,36} 2,5-dibromo-8-dodecanoylbenzo[1,2-b:3,4-b′:5,6-d′]trithiophene (M2), and 2,8-dibromo-5-dodecanoylbenzeno[1,2-b:3,4-b′:5,6-d′]trithiophene (M3)\textsuperscript{35} were synthesized according to the methods reported.

#### Synthesis of Terpolymer P1

Stille coupling was used for the polymerization. Monomers M1 (0.3130 g, 0.5 mmol) and M2 (0.2932 g, 0.5 mmol) were dissolved in 15 mL of toluene in a 50 mL flask, and the solution was flushed with argon for 15 min with argon. In that solution Pd (PPh\textsubscript{4}) was added in a quantity of 27 mg and was flushed with argon for 20 min. The reaction mixture was heated for 48 h in reflux, cooled to room temperature, and added dropwise to methanol (400 mL). After being collected the precipitate was purified by Soxhlet extraction sequence in methanol, hexane, and chloroform. The chloroform fraction was concentrated and added dropwise into methanol. The precipitates were collected and dried under vacuum overnight to get polymer P1 as a black solid (0.319 g, yield 85\%).\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) (Figure 1a): δ (ppm) 1.58–0.64 (br, 21H, CH\textsubscript{3},CH\textsubscript{2}). Elem. Anal. for (C\textsubscript{33}H\textsubscript{12},N,S,\text{O})\textsubscript{1}: Calc. C, 63.03; H, 4.45; N, 3.87; S, 26.57. Found: C, 62.82; H, 4.29; N, 3.49; S, 26.17.

#### Synthesis of Terpolymer P2

For the synthesis of terpolymer P2 the same procedure was followed as for P1 using M3 in the place of M2. Starting materials for the polymerization were monomers M1 (0.3130 g, 0.5 mmol) and M3 (0.2932 g, 0.5 mmol). At the end P2 was obtained as a black solid (0.29 g, yield 80\%).\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) (Figure 1b): δ (ppm) 1.69–0.69 (br, 21H, CH\textsubscript{3},CH\textsubscript{2}). Signals of aromatic moieties may overlap with the signal arising from chloroform. In the range of 3.5 ppm the spectra of both polymers show a weak signal of methylene groups with low intensity. Elem. Anal. for (C\textsubscript{33}H\textsubscript{13},N,S,\text{O})\textsubscript{1}: Calc. C, 63.03; H, 4.45; N, 3.87; S, 26.57. Found: C, 62.77; H, 4.27; N, 3.56; S, 26.24.

#### Device Fabrication and Characterization

Ultrasound baths were used for the cleaning procedure of the glass substrates that were coated with indium tin oxide (ITO), which contained detergent, deionized water, acetone, and ethanol sequentially. Nitrogen gas was used to dry the cleaned ITO substrate and after that exposed for 10 min to UV-ozone. A solution of polyethyleneoxy-thiophene:poly-
tyrosilane (PEDOT-PSS, Clevis AI4083) was spin coated onto the cleaned ITO substrates at 3500 rpm for 30 min and then was annealed at 120 °C for 10 min in air environment. Using various weight ratios, the electron donors P1 or P2 and electron acceptor PC71BM were dissolved in chloroform solution (concentration is 20 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. By means of thermal evaporation and under a pressure of 10⁻⁵ Torr, the cathode aluminum (90 nm) was placed on top of the active layer. The active area is about 10 mm² which is defined as the vertical overlap of ITO and Al electrodes. Following a procedure similar to that for the PSCs, we fabricated hole-only devices layered as ITO/PEDOT:PSS/P1 or P2:PC71BM/Au. A Keithley Source Meter was used to measure the current–voltage characteristics of the solar cells in ambient conditions and under AM1.5 G (100 mW/cm²) provided by a solar simulator.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

The chemical structures and synthetic routes of P1 and P2 are shown in Scheme 1. 4,7-(Bis[(5-trimethylstanny l)thiophene-2-yl]benzo[c][1,2,5]thiadiazole (M1), 2,5-dibromo-8-dodecanoylbenzo[1,2-b:3,4-b‴:5,6-d‴] thiophene (M2), and 2,8-dibromo-5-dodecanoylbenzene[1,2-b:3,4-b‴:5,6-d‴]thiophene (M3) were synthesized according to the methods reported. Stille-coupling polymerization of M2 or M3 and M1 was achieved catalyzed with Pd(Ph3P)4 affording respective crude copolymers as dark solids. To dispose of low-molecular-weight oligomers and residual catalytic metal the purification of these copolymers was performed by sequential Soxhlet extraction with chloroform, hexane, and chloroform; chloroform extracts were found to be good for chlorinated solvents such as chloroform, oligomers and residual catalytic metal the purification of these copolymers as dark solids. To dispose of low-molecular-weight oligomers and residual catalytic metal the purification of these copolymers was performed by sequential Soxhlet extraction with chloroform, hexane, and chloroform; chloroform extracts were found to be good for chlorinated solvents such as chloroform, oligomers and residual catalytic metal the purification of these copolymers as dark solids. To dispose of low-molecular-weight oligomers and residual catalytic metal the purification of these copolymers was performed by sequential Soxhlet extraction with chloroform, hexane, and chloroform; chloroform extracts were found to be good for chlorinated solvents such as chloroform, oligomers and residual catalytic metal the purification of these copolymers as dark solids. To dispose of low-molecular-weight oligomers and residual catalytic metal the purification of these copolymers as dark solids. To dispose of low-molecular-weight oligomers and residual catalytic metal the purification of these copolymers as dark solids. To dispose of low-molecular-weight oligomers and residual catalytic metal the purification of these copolymers as dark solids. To dispose of low-molecular-weight oligomers and residual catalytic metal the purification of these copolymers as dark solids.

The solubility of the copolymers was examined and was found to be good for chlorinated solvents such as chloroform, chlorobenzene, and o-dichlorobenzene. However, for organic solvents such as tetrahydrofuran, toluene, hexane, and alcohols, the solubility was found to be poor. 1H NMR spectroscopy and elemental analysis were used to characterize the new polymers. Gel permeation chromatography (CHCl₃, eluent, polystyrene calibration) was used to determine the molecular weights and polydispersity index (PDI) of the copolymers. The number-average molecular weights ($M_n$), the weight-average molecular weights ($M_w$), and polydispersity indexes (PDI) are 15.6, 30.4 kDa, and 1.95 for P1 and 14.7, 43.8 kDa, and 2.98 for P2, respectively.

### Thermal Properties

Thermogravimetric analysis (TGA) was performed to establish the thermal properties of the copolymers. The TGA results for P1 and P2 are tabulated in Table 1, and the corresponding curves are shown in Figure 2. Both P1 and P2 exhibit good thermal stability with a 5% weight-loss. Temperature ($T_{5\%}$) under N₂ is found at 343 and 358 °C, respectively, for P1 and P2. These $T_{5\%}$ values are suitable for the usage of P1 and P2 as the donor in active layers of BHJ PSCs.

### Optical and Electrochemical Properties

In Table 2 we have tabulated the wavelengths for maximum absorption, with the corresponding normalized ultraviolet/visual/near-infrared (UV/vis/NIR) absorption spectra shown in Figure 3 when diluted in chloroform, as well as in thin-film form. Both copolymers exhibit broad absorption spectra, in the range from 300 to 750 nm. As is common for D–A-type copolymers, two main absorption bands can be identified. At the short-wavelength region of the absorption spectra the band centered at 382 nm for both P1 and P2 originates from the π–π* transitions of the conjugated backbones. At the long-wavelength region the bands of P1 and P2 centered, respectively, at 544 nm (with a molar extinction coefficient of 7.4 × 10⁴ M⁻¹ cm⁻¹) and 532 nm (with a molar extinction coefficient of 5.56 × 10⁴ M⁻¹ cm⁻¹) may be attributed to strong intramolecular charge transfer (ICT) transitions between the donor and acceptor units. As expected for the thin films, a red shift is noted of up to 12−24 nm that indicates a higher degree of molecular ordering that results from π-stacking interactions. Monomers M2 and M3 employed for the designing of P1 and P2 are isomeric. So, the geometries of polymeric backbones of P1 and P2 may be different. It was reported that the curvature of the polymeric backbone can strongly affect the properties of polymers (molecular weight distribution, absorption spectra, and bandgap). In our case the curvature of the polymeric backbone of P1 (based on M2 monomer) must be less than in the case of P2. This means that in the solid state the π-stacking interaction is stronger for P1 than for P2. It leads to the larger red shift noted in the thin-film absorption spectrum compared to that in solution, for the case of the P1 copolymer. Finally, the absorption onset ($λ_{onset}$) of the thin-film spectra of P1 and P2 were measured at 776 and 748 nm, respectively. These values correspond to optical band gaps ($E_{g}$) of 1.60 and 1.66 eV, respectively.

In order to examine the electronic energy levels of the copolymer films, cyclic voltammetry (CV) experiments were performed, and the results are shown in Figure 4. The HOMO and LUMO energy levels were calculated from the onset potential of oxidation ($E_{onset}^{ox}$) and the onset potential of reduction ($E_{onset}^{red}$), respectively, that we have summarized in Table 3. The HOMO and LUMO energy levels of the polymers were calculated using the equations $E_{HOMO} = -q(E_{onset}^{red} + 4.4)$ eV and $E_{LUMO} = -q(E_{onset}^{red} + 4.4)$ eV, respectively. The

![Figure 2. TGA curves of polymers P1 and P2 at a heating rate of 10 °C min⁻¹.](image-url)
HOMO/LUMO energy levels found for P1 and P2 were $-5.47/-3.78$ eV and $-5.54/-3.78$ eV, respectively. Since the HOMO levels of these copolymers are low, it was anticipated that they would offer high $V_{oc}$ for the solar cells based on them, as the $V_{oc}$ of PSCs depends on the energy level difference between the electron donor’s HOMO and the electron acceptor’s LUMO. The electrochemical band gaps ($E_{g}^{el}$) of the films of the copolymers were calculated according to the equation $E_{g}^{el} = \text{HOMO} - \text{LUMO}$ and listed in Table 2. The $E_{g}^{el}$ is found to be 1.69 and 1.76 eV for P1 and P2, respectively. A noted discrepancy is that these values are larger than the observed optical gaps which may be the result of the existence of the energy barrier that manifests between the polymer film and electrode surface interface. Moreover, the LUMO offset between P1 or P2 and PC$_{71}$BM is higher than 0.3 eV which ensures the efficient exciton dissociation within the BHJ active layer that takes place specifically at the D−A interfaces.

Table 2. Optical and Electrochemical Properties of P1 and P2 in Solution and the Thin Films

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\lambda_{\text{max}}$ soln (nm)</th>
<th>$\lambda_{\text{em}}$ film (nm)</th>
<th>$\lambda_{\text{onset}}$ film (nm)</th>
<th>$E_{g}^{opt}$ (eV)</th>
<th>$E_{\text{HOMO}}^{el}$ (eV)</th>
<th>$E_{\text{LUMO}}^{el}$ (eV)</th>
<th>$E_{g}^{el}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>319, 544</td>
<td>400, 563</td>
<td>780</td>
<td>1.59</td>
<td>$-5.47$</td>
<td>$-3.78$</td>
<td>1.69</td>
</tr>
<tr>
<td>P2</td>
<td>381, 531</td>
<td>381, 544</td>
<td>752</td>
<td>1.65</td>
<td>$-5.54$</td>
<td>$-3.78$</td>
<td>1.76</td>
</tr>
</tbody>
</table>

*Calculated from the absorption band onset of the small molecule film, $E_{g}^{opt} = 1240/\lambda_{\text{onset}}$.

HOMO/LUMO energy levels found for P1 and P2 were $-5.47/-3.78$ eV and $-5.54/-3.78$ eV, respectively. Since the HOMO levels of these copolymers are low, it was anticipated that they would offer high $V_{oc}$ for the solar cells based on them, as the $V_{oc}$ of PSCs depends on the energy level difference between the electron donor’s HOMO and the electron acceptor’s LUMO. The electrochemical band gaps ($E_{g}^{el}$) of the films of the copolymers were calculated according to the equation $E_{g}^{el} = \text{HOMO} - \text{LUMO}$ and listed in Table 2. The $E_{g}^{el}$ is found to be 1.69 and 1.76 eV for P1 and P2, respectively. A noted discrepancy is that these values are larger than the observed optical gaps which may be the result of the existence of the energy barrier that manifests between the polymer film and electrode surface interface. Moreover, the LUMO offset between P1 or P2 and PC$_{71}$BM is higher than 0.3 eV which ensures the efficient exciton dissociation within the BHJ active layer that takes place specifically at the D−A interfaces.

**Theoretical Simulation.** The monomers of the P1 and P2 copolymers were also examined theoretically. To this end we employed density functional theory (DFT) and time-dependent density functional theory (TD-DFT). Technical details on the methods used are provided in our earlier reports. First of all, the geometry optimizations of the P1 and P2 structures are performed. In order to reduce the computational cost we have used ethyl groups in place of all of the alkyl groups. The dynamic stability of the optimized structures of the copolymers was examined through vibrational analysis, and no imaginary eigenfrequencies were found for the vibrational eigenmodes. This means that the structures are true local minima. The core of the structures is comprised of a benzothiadiazole (BT) moiety and two thiophene moieties for both structures, along with a 1-(benzo[1,2-b:3,4-b’:6,5-b’’]trithiophen-5-yl)dodecan-1-one (BTTRO) moiety for P1, and a 1-(benzo[1,2-b:3,4-b’:6,5-b’]trithiophen-2-yl)dodecan-1-one moiety for P2 is almost fully planar (not accounting for the alkyl groups), independent of if they were in the gas phase or in solvent. Dihedral angles between the moieties are in the range of $\sim 2^\circ$−$7^\circ$. The specific values depend on the functional that was used for the geometry optimization as well as on if a solvation model was introduced. An issue that we opted to examine was with respect to the presence of steric effects and
the influence they may have in determining relative conformations of adjacent repeat units. To this end the dimers were examined, and in both cases the planarity of the main conformations of adjacent repeat units. To this end the dimers, tetramers, and hexamers of the structures by far are from the BT moiety, at 71% and 73% for P1 and P2, respectively. The thiophene moieties also contribute to the LUMO of both P1 and P2, respectively. The highest contributions to the LUMO of both P1 and P2, and 32% for P1, and 28% for P2, respectively. The thiophene moieties also contribute to the LUMO, at 71% and 73% for P1 and P2, respectively. The thiophene moieties also contribute to the LUMO of both structures by far are from the BT moiety, at 71% and 73% for P1 and P2, respectively. The highest contributions to the LUMO of both structures by far are from the BT moiety, at 71% and 73% for P1 and P2, respectively. The thiophene moieties also contribute to the LUMO, at 21% in both cases.

The computed UV/visual absorption spectra of both monomer structures are shown in Figure 7. The computations were performed using the M06 functional and within the TD-DFT framework. The most notable differences in the calculated absorption spectra of P1 compared to P2 are the absorbance in a broader range in the small-wavelength region and the larger first-excitation wavelength. P2 offers strong absorption in the region of ~380 nm.

To estimate the dependence of the energy gaps on chain size we extended the calculations to include the dimers, tetramers, and hexamers of the P1 and P2 structures. In Figure 8 we show this dependence of both the optical and HOMO–LUMO gaps with chain size, n. As the chain size increases, quantum confinement effects relax which leads to smaller energy gaps.

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>Amax (nm)</th>
<th>f</th>
<th>main contributions</th>
<th>μ (D)</th>
</tr>
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<tbody>
<tr>
<td><strong>P1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>PBE</td>
<td>−4.70</td>
<td>−3.45</td>
<td>1.25</td>
<td>1.58</td>
<td>785</td>
<td>0.45</td>
<td>H→L (91%)</td>
<td>4.10</td>
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<td>1.55b</td>
<td>801b</td>
<td>0.64</td>
<td>H→L (94%)</td>
<td>5.19b</td>
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<td>1.99b</td>
<td>622b</td>
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<td>0.84</td>
<td>H→L (98%)</td>
<td>4.24</td>
</tr>
<tr>
<td></td>
<td>−5.61b</td>
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<td>2.74b</td>
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<td>1.04b</td>
<td>H→L (98%)</td>
<td>5.26b</td>
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<tr>
<td><strong>P2</strong></td>
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<tr>
<td>PBE</td>
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<td>1.27</td>
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<td>775</td>
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<td>785b</td>
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<td>H→L (94%)</td>
<td>6.02b</td>
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<td>H→L (99%)</td>
<td>6.28b</td>
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<tr>
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<td>−2.88b</td>
<td>2.73b</td>
<td>2.16b</td>
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<td>2.13b</td>
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<td>0.94b</td>
<td>H→L (98%)</td>
<td>6.17b</td>
</tr>
</tbody>
</table>

*aSpecifically, HOMO and LUMO energies (eV), HOMO–LUMO gap (eV), HL, optical gap (eV), OG, with corresponding oscillator strengths, f, the wavelengths of the first excitation and excitations with the largest oscillator strengths, the main contributions to the first excited state (with contributions larger than 4%), and the dipole moment (D). bValues when solvent effects are taken into account for chloroform.

Figure 5. Frontier orbitals of the (left) P1 and (right) P2 monomers. (top) LUMO and (bottom) HOMO (the isovalue used is 0.02).
The computations were performed using the M06 functional. Convergence is practically achieved at the tetramer which is due to the size of the monomer, which is significantly larger than model systems used to examine such effects. Extrapolation is performed by fitting to a function of the form $f(n) = a + b/n^c$, with $a$, $b$, and $c$ being the fitting parameters. Fitting values for the optical gap of P1 are $a = 1.657$, $b = 0.451$, and $c = 1.505$ and for the HL gap $a = 2.205$, $b = 0.536$, and $c = 1.484$. Fitting values for the optical gap of P2 are $a = 1.788$, $b = 0.339$, and $c = 1.648$ and for the HL gap are $a = 2.377$, $b = 0.393$, and $c = 1.453$. The asymptotic values of the optical and HOMO–LUMO gaps are 1.66 and 2.20 eV for P1 and 1.79 and 2.38 eV for P2, respectively. The oligomer structures exhibit a red shift of the optical gap due to relaxation of quantum confinement. The asymptotic values at the polymer limit of the optical and HOMO–LUMO gaps are 1.66 and 2.20 eV for P1 and 1.79 and 2.38 eV for P2, respectively.

**Photovoltaic Properties.** The photovoltaic properties of P1 and P2 were investigated with a device structure of ITO/PEDOT:PSS/P1 or P2:PC71BM/Al under illumination intensity of AM1.5 G at 100 mW/cm². The fabrication conditions such as weight ratio of polymer to PC71BM and amount of 1,8-diiodooctane (DIO) additive in host chloroform solution were optimized. The optimal weight ratio for both P1 and P2 is 1:2. The current–voltage characteristics under illumination and incident photon to current conversion efficiency (IPCE) of the devices based on optimized conditions are shown in Figure 9a.
Table 4. Photovoltaic Parameters of PSCs Using P1:PC_{71}BM and P2:PC_{71}BM Active Layers Processed with Different Conditions

<table>
<thead>
<tr>
<th>active layers</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1:PC_{71}BM (CF cast)</td>
<td>8.82</td>
<td>0.96</td>
<td>0.46</td>
<td>3.89 (3.83 ± 0.06)$^a$</td>
<td>8.74</td>
</tr>
<tr>
<td>P2:PC_{71}BM (CF cast)</td>
<td>7.53</td>
<td>1.04</td>
<td>0.43</td>
<td>3.37 (3.27 ± 0.10)$^a$</td>
<td>7.47</td>
</tr>
<tr>
<td>P1:PC_{71}BM (DIO/CF cast)</td>
<td>12.6</td>
<td>0.92</td>
<td>0.62</td>
<td>7.19 (7.10 ± 0.009)$^a$</td>
<td>12.53</td>
</tr>
<tr>
<td>P2:PC_{71}BM (DIO/CF cast)</td>
<td>11.64</td>
<td>0.96</td>
<td>0.57</td>
<td>6.34 (6.23 ± 0.11)$^a$</td>
<td>11.58</td>
</tr>
</tbody>
</table>

$^a$Average of 10 devices. $^b$Estimated from IPCE spectra.

0.96 $V_o$, a $J_{sc}$ of 8.82 mA/cm$^2$, and FF of 0.46, resulting in a PCE of 3.89%. At the same conditions, the P2:PC_{71}BM-based device showed a $V_{oc}$ of 1.04 V, $J_{sc}$ of 7.53 mA/cm$^2$, and FF of 0.43 resulting in a PCE of 3.37%. The higher value of $V_{oc}$ for P2 as compared to P1 resulted from the deeper HOMO level of P2. The value of $J_{sc}$ for P1 is higher than for P2 that may be attributed to the low optical bandgap and slightly broader absorption spectrum in thin film. From the IPCE spectra that we provide in Figure 9b, it can also be seen that the values of the P1:PC_{71}BM-based device are higher than for the P2:PC_{71}BM-based device, in the entire range of wavelength that also confirms the higher value of $J_{sc}$ for former than the latter device. Moreover, the molar extinction coefficient of P1 is higher than P2, which may also be a contributing factor for the higher $J_{sc}$ of the P1-based device compared to the P2-based device. The $J_{sc}$ value computed by integrating the IPCE spectra of the devices (Table 4) also confirms the higher value of PCE for the device based on P1:PC_{71}BM.

DIO has proven to be an efficient and universal additive that greatly facilitates the improvement of the active layer morphology of BHJ PSCs. After the optimization of the weight ratio, we used DIO as the additive to further optimize the morphology of the polymer/PC_{71}BM active layers with a volume fraction of 1, 2, 3, and 4%. After the optimization of the solvent additive concentration, we found that 3 vol % DIO at 1, 2, 3, or 4% showed the best photovoltaic properties for both polymers. After the optimization of the solvent additive concentration, we found that 3 vol % DIO showed higher and broader absorption characteristics of the PSCs is their mobilities. The hole mobility ($\mu_h$) in the active layers was measured via the dark $J$--$V$ characteristics of the hole-only device structure ITO/PEDOT:PSS/P1 or P2:PC_{71}BM/Au and by fitting these characteristics (Figure 10) with space charge limited current model based on Mott-Gurney equation: $J = 9\varepsilon_0\varepsilon_r\mu_h V^2/8d^3$, where $J$ is space charge limited current density; $\varepsilon_r$ is the vacuum permittivity ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m); $\varepsilon_r$ is the dielectric constant of the active layer; and $d$ is the thickness of the active layer. The values of $\mu_h$ for P1:PC_{71}BM (7.56 × 10^{-5} cm$^2$/V s) and 1.45 × 10^{-4} cm$^2$/V s) for CF cast and DIO/CF cast, respectively) are higher than for P2:PC_{71}BM (6.13 × 10^{-5} cm$^2$/V s and 1.08 × 10^{-5} cm$^2$/V s) for DIO/CF and CF cast, respectively). This rationalizes the higher value of $J_{sc}$ of P1-based devices than that of P2-based device. Moreover, we have also measured the electron mobility in the active layers using electron-only devices in the same manner as for hole-only devices. Notably, the electron mobility of P1 and P2 is nearly the same, i.e., 2.36 × 10^{-4} cm$^2$/V s, and also the electron mobility of the DIO/CF cast active layer is 2.48 × 10^{-4} cm$^2$/V s. A balanced electron and hole mobility is required for BHJ solar cells to be efficient. A value considered as optimal for the electron to hole mobility ratio is 1 to 2. Upon processing the active layer with DIO/CF, the hole mobility is enhanced and better matches the electron mobility, which signifies more balanced charge transport in the devices, and overall a higher FF was achieved for the P1:PC_{71}BM (CF/DIO) based device.

Another contributing factor for achieving the high performance of the PSCs is their mobilities. The hole mobility ($\mu_h$) in the active layers was measured via the dark $J$--$V$ characteristics of the hole-only device structure ITO/PEDOT:PSS/P1 or P2:PC_{71}BM/Au and by fitting these characteristics (Figure 10) with space charge limited current model based on Mott-Gurney equation: $J = 9\varepsilon_0\varepsilon_r\mu_h V^2/8d^3$, where $J$ is space charge limited current density; $\varepsilon_r$ is the vacuum permittivity ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m); $\varepsilon_r$ is the dielectric constant of the active layer; and $d$ is the thickness of the active layer. The values of $\mu_h$ for P1:PC_{71}BM (7.56 × 10^{-5} cm$^2$/V s) and 1.45 × 10^{-4} cm$^2$/V s) for CF cast and DIO/CF cast, respectively) are higher than for P2:PC_{71}BM (6.13 × 10^{-5} cm$^2$/V s and 1.08 × 10^{-5} cm$^2$/V s) for DIO/CF and CF cast, respectively). This rationalizes the higher value of $J_{sc}$ of P1-based devices than that of P2-based device. Moreover, we have also measured the electron mobility in the active layers using electron-only devices in the same manner as for hole-only devices. Notably, the electron mobility of P1 and P2 is nearly the same, i.e., 2.36 × 10^{-4} cm$^2$/V s, and also the electron mobility of the DIO/CF cast active layer is 2.48 × 10^{-4} cm$^2$/V s. A balanced electron and hole mobility is required for BHJ solar cells to be efficient. A value considered as optimal for the electron to hole mobility ratio is 1 to 2. Upon processing the active layer with DIO/CF, the hole mobility is enhanced and better matches the electron mobility, which signifies more balanced charge transport in the devices, and overall a higher FF was achieved for the P1:PC_{71}BM (CF/DIO) based device.

The surface morphology of the fabricated active layers, as well as the phase separation, were further characterized by means of atomic force microscopy (AFM), in order to investigate the relationship between active layer morphology and power conversion efficiencies. Using DIO as an additive
may slow down the crystallization process during spin coating that leads to an improvement in the intermolecular ordering and also to a well-developed phase separation. Figure 11 shows the AFM images of active layer thin films cast with and without DIO additive. In the case of P1:PCBM cast from CF solution, it showed coarse phase separation with PCBM domains having diameter of 80–85 nm, and root-mean-square (rms) value of surface roughness is about 2.56 nm. This domain size is larger than the exciton diffusion length and reduces the exciton dissociation efficiency, resulting in low J_{sc} and FF. However, after the use of 3 vol % of DIO as additive, the homogeneity of the blend film morphology increased with a rms value of 1.48 nm and a bicontinuous interpenetrating network formed by nanofibrils, which are beneficial for exciton dissociation and efficient charge transport, leading to an increase in J_{sc} and FF.

The X-ray diffraction (XRD) pattern was used to obtain molecular level structural information pertinent to molecular orientation and packing in the blended films. Figure 12 shows the XRD pattern of P1:PC_{71}BM and P2:PC_{71}BM blended films with and without DIO additives. Compared to P2-based blended films, the scattering peaks (100) and (010) of P1:PC_{71}BM blended films were stronger and sharper, which indicates higher molecular ordering in the P1:PC_{71}BM blended films. The coherence lengths of CF cast P1:PC_{71}BM and P2:PC_{71}BM calculated from the Scherrer equation \(^{58}\) are found to be 4.8 and 4.2 nm, respectively. This confirms the superior molecular packing in P1:PC_{71}BM as compared to P2:PC_{71}BM. When the P1:PC_{71}BM and P2:PC_{71}BM were processed with DIO additive, coherence length was increased to 5.1 and 4.65 nm, respectively. The improved order from more effective \(\pi\)-stacking may be favorable for charge transport and therefore overall to the PCE of PSCs.\(^{59}\)

To obtain more information on the exciton dissociation and photocurrent generation in the devices using P1 and P2 as donor and processed under different conditions, the photocurrent density (\(J_{ph}\)) is plotted with respect to the effective voltage (\(V_{\text{eff}}\)) for all the devices, as reported in the literature\(^{60,61}\) and shown in Figure 13. In the case of DIO additive processed active layer devices, \(J_{ph}\) increases linearly with \(V_{\text{eff}}\) at low voltages and gradually saturates at high voltages, where \(J_{ph}\) is field-independent. On the other hand, the devices with active layers that were not processed with DIO additive also show a linear relation of \(J_{ph}\) on \(V_{\text{eff}}\) at low voltages, but the \(J_{ph}\) does not fully saturate at high voltage of measurement. If the internal field does not suffice for the efficient extraction of free charge carriers then this may result in the so noted continuous increase in \(J_{ph}\). Moreover, the devices based on the active layers that were cast with CF displayed a square root dependence on the effective voltages in intermediate region. This is an indication that the charge carrier transport has a higher dependence on the electric field, which is consistent with a low FF.

The maximum exciton generation rate, \(G_{\text{max}}\) of the devices was calculated using the equation \(J_{\text{phat}} = qG_{\text{max}}L\), where \(q\) is the electronic charge and \(L\) is the thickness of the active layer (90 nm for all devices). This was done for devices fabricated both with and without DIO additive. The calculated \(G_{\text{max}}\) values for P1:PC_{71}BM (as cast), P1:PC_{71}BM(DIO/CF), P2:PC_{71}BM (as cast), and P2:PC_{71}BM (DIO/CF) are \(6.23 \times 10^{24}\) cm\(^{-3}\) s\(^{-1}\).
In summary, we have synthesized two D-A1-D-A2 regular terpolymers containing the benzothiazole and 2,5-dibromo-8-dodecanoylbenzene[1,2-b:3,4-b′:5,6-d′]trithiophene (P1) and 2,8-dibromo-5-dodecanoylbenzene[1,2-b:3,4-b′:5,6-d′]-trithiophene (P2) acceptor units with the same thiophene donor, and their optical and electrochemical properties were investigated. These terpolymers were used as electron donor components along with PC71BM as an electron acceptor for solution-processed BHJ PSCs. PSC based on the optimized P1:PC71BM active layer showed higher J_{sc} and FF resulting in an overall PCE of 7.19%, whereas the device based on P2:PC71BM showed higher V_{oc} (1.04 and 0.96 V for the devices processed with CF and DIO/CF, respectively) than P1 with PCE of 6.34% under the same conditions.

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: keshtov@ineos.ac.ru (M. L. Keshtov).*
*E-mail: gdsharma273@gmail.com (G. D. Sharma).*

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is supported by the Russian foundation for basic research (grant number 14-03-92003). This work was supported by the Division of Chemistry and Materials Sciences, Russian Academy of Sciences, under programs of basic research IV-5.3 (Creation and Study of Macromolecules and Macromolecular Structures of New Generations) and IV-5.2 (Creation of New Metal, Ceramic, Glass, Polymer, and Composite Materials). F.C. Chen thanks the support by the Ministry of Science and Technology of Taiwan (grant number: MOST 103-2923-E-009-001-MY3). GDS is thankful to the Director, The LMN Institute of Information Technology, Jaipur, for financial support to visit Moscow (Russia) to perform the research work.

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