New Benzodithiophene- and Benzooxadiazole/Benzothiadiazole-Based Donor–Acceptor π -Conjugated Polymers for Organic Photovoltaics

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ABSTRACT: A new set of push-pull type 2D-conjugated polymers (P1–P4) were designed and synthesized where A1, A2 (oxygen analogues) and A3, A4 (sulfur analogues) are electron deficient units used as co-monomers. On introduction of new repeating units into the polymer backbone, significant changes were observed in optoelectronic properties. Furthermore, the heteroatom exchange in new repeating units has also brought notable changes in photophysical properties, in particular P1 and P2 (oxygen analogues) showed bathochromic shift in UVvis absorption spectra and deeper HOMO energy levels than P3, P4 (sulfur analogues). Interestingly P1, P3 absorption spectra shows a vibronic shoulder (659, 652 nm) peak in lower

INTRODUCTION Development of new π -conjugated polymers and continuous device optimization could able to achieve high power conversion efficiency (PCE) in bulk heterojunction polymer solar cells (BHJ PSCs).¹ To further improve the PCE, a systematic design strategy is required, in particular by fine tuning of optoelectronic properties of conjugated polymers such as appropriate energy levels, reduced band gap, planar polymer backbone etc. Synthesis of an alternating donoracceptor (D-A) copolymer by connecting an electron rich (D) and an electron deficient (A) unit is the best strategic way to get desired properties for a conjugated polymer used in PSCs.² In this regard, several kinds of D and A units have been designed and synthesized for potential PSCs applications so far. However, the accessibility of effective electron deficient moieties has been limited for PSC application when compared to the immense development of donor blocks in D-A conjugated polymers. Therefore, it is equally essential to design and synthesis of new electron deficient units for efficient PSCs via fine tuning of optoelectronic properties to get high PCEs.³

energy region, and this might originated from non-covalent interactions between the electron rich and electron deficient units. In addition, the systematic investigation of these polymers with additive and solvent treatment, yielded in enhanced power conversion efficiency of 4.29% for P3-based devices in bulk heterojunction organic solar cells. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

KEYWORDS: conjugated polymers; electron deficient units; heteroatom; organic solar cells; power conversion efficiency; structure-property relations; UV-vis spectroscopy

The optoelectronic properties of the conjugated polymers were significantly influenced by insertion of conjugated heterocyclic units such as 1,3-di(2-bromothien-5-yl)-5-(2ethylhexyl)thieno[3,4-*c*]pyrrole-4,6-dione, benzothiadiazole (BT), and so forth.³ Thus, the choice of suitable (A) unit in D-A polymers can effect on optoelectronic properties of resulting polymers in many ways such as, it can reduce the polymer band gap, affect the lowest unoccupied molecular orbital (LUMO) energy level and it can also make polymer backbone more planar by locking via noncovalent interactions between heteroatoms of D and A units and these interactions can significantly affect the bulk properties of resulting conjugated polymers.⁴⁻⁸ In addition, it has been observed that variations in optoelectronic and photovoltaic properties of conjugated polymers by simple exchange of heteroatom either in electron rich or electron deficient units of D-A polymers, which could able to show its clear impact on the photovoltaic properties.9

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SCHEME 1 Synthetic route for monomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Among the few effective electron deficient units, BT has been widely investigated unit in many conjugated copolymers. However, various kinds of modifications have been made on BT, and able to get high PCEs.¹⁰ In this work, we have designed and synthesized new ethylenedialkoxy (EDA) substituted BT as electron deficient units (A1, A2, A3, A4) to improve the solubility without disrupting the other optoelectronic properties of resulting polymers as shown in Scheme 1 and 2. These new monomers A1, A2 (oxygen analogues), A3, A4 (sulfur analogues) were used in synthesis of D-A polymers P1-P4 with good solution processability. We found significant changes in optoelectronic, thermal, and photovoltaic properties of new polymers on doping the new electron deficient units as repeating units. In particular, P1, P3 show vibronic shoulder at 650-660 nm which was not observed in P2, P4. Additionally P1, P2 (oxygen analogues) show bathochromic shift in absorption spectra and also deep highest occupied molecular orbital (HOMO) levels compared to the P3, P4 (sulfur analogues), and effect was further sustained on PSCs and polymer field effect transistor (PFETs) characteristics.

EXPERIMENTAL

Materials and Instruments

All chemicals and reagents were purchased from Sigma-Aldrich Chemical Co., Alfa Aesar and used as received. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer in CDCl₃ using tetramethylsilane as the internal reference. The chemical shifts were reported in ppm relative to the singlet of CDCl₃ at 7.26 and 77 ppm

for the ¹H and ¹³C NMR, respectively. The UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer at room temperature. Thermal gravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851e, under nitrogen (N₂) atmosphere at heating rate of 10 °C min⁻¹. Number-average molecular weight (M_n) , weight average molecular weight (M_w) , and polydispersity index (PDI) were determined against polystyrene as standard by GPC using photoluminescence (PL) gel 5 μ m MLXED-C column on an Agilent 1100 series liquid chromatography system with tetrahydrofuran (THF) as an eluent. Cyclic voltammetry (CV) studies were carried out in a 0.1 M solution of tetrabutylammonium perchlorate in anhydrous acetonitrile at a scan rate of 100 mV s⁻¹ using CHI 600C potentiostat (CH Instruments). A three electrode cell with platinum electrode as the working electrode, Ag/AgCl as the reference electrode and a platinum (Pt) wire as the counter electrode were used.

PFETs Fabrication and Characterization

The charge characteristic properties of P1–P4 were examined by bottom contact geometry PFETs. Thin films were spin casted from a 5 mg mL⁻¹ P1–P4 in chloroform under a N₂ atmosphere onto *n*-octyltrichlorosilane, *n*-doped silicon wafer with a 300-nm thickness of SiO₂ dielectric layer. The PFETs were then annealed for 10 min at 140 °C in a glove box under N₂ atmosphere. The field effect mobility was calculated in the saturation regime using the equation ID_s = ($\mu WC_i/2L$)(V_G-V_T)², where I_{DS} is the drain-source current, μ is the field effect mobility, *W* is the channel width (120 µm), *L* is the channel length (12 µm), C_i is the capacitance per



SCHEME 2 Synthetic route for polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

unit area of the gate dielectric layer, and $V_{\rm G}$ is the gate voltage.

$$J = (9/8)\varepsilon_{\rm r}\varepsilon_0\mu (V^2/L^3)$$

where ε_r is the dielectric constant ($\varepsilon_r = 3$), ε_0 is permittivity of free space, *L* the thickness of the active layer, μ is the charge mobility, and *V* is the voltage drop across the device.

Fabrication and Characterization of the BHJ PSCs

The ITO substrates that have been used for fabrication were cleaned ultrasonically with detergent, water, acetone, and isopropyl alcohol. PEDOT:PSS (Clevios P, AI 4083) with 40 nm thick layer of was coated on the electrodes by spin coating a diluted soluiton of PEDOT:PSS with isopropyl alcohol with the dilution ratio being 1:2 and baked at 150 °C for 10 min in oven. Active layer of P1-P4:PC71BM was spin coated using a mixture of polymer:PC71BM was dissolved in chlorobenzene (CB) and further mixed with 1-3 vol % 1,8 diiodooctane (DIO) and then washed with methanol (MeOH). LiF (0.7 nm) and Al cathode (100 nm) were deposited deposited via evaporation on the active layer. The BHJ PSCs performances were measured under simulated AM 1.5G illumination (100 mW cm^{-2}). The irradiance of the sunlight simulating illumination was calibrated using a standard Si photodiode detector fitted with a KG5 filter. The J-V curves were measured using a Keithley 2400 source measurement unit. The space charge limited current (SCLC) mobilities μ were extracted using the standard trap free SCLC transport equation:

Synthesis of Monomers Synthesis of [6,7]-Dihydro-[1,4]-Dioxino-[2,3-F[2,1,3]-Benzooxadiazole (3)

Compound 2 (6.0 g, 26.5 mmol), sodium azide (8.6 g, 131.9 mmol), n-Bu₄NBr (1.7 g, 1.7 mmol) were added to anhydrous toluene (50 mL) reflux for 24 h. And then triphenyl phosphine (8.2 g, 10.5 mmol) was added very slowly to reaction mixture and continued heating for 24 h (total 48 h). Cool the reaction mixture to room temperature and evaporated the excess of toluene. Crude was purified by flash chromatography on short bed of silica gel with chloroform. The filtrate was concentrated and recrystallized from ethanol to get orange needle like structures of compound 3 (3.0 g, 63%).

¹H NMR (CDCl₃, 300 MH_Z): 7.47 (s, 2H), 4.75 (s, 4H); ¹³C NMR (CDCl₃, 75 MH_Z): δ (ppm) 149.73, 146.96, 97.74, 64.56. HRMS: Calculated for C₈H₆N₂O₃ 178.0378; found: 178.0378.



Synthesis of 4,9-Dibromo-6,7-Dihydro-[1,4] Dioxino [2',3':4,5] Benzo[1,2,-C][1,2,5]Oxadiazole (A1)

Compound 3 (1.8 g, 10.0 mmol) was dissolved in methylene chloride (100 mL), to this acetic acid (15 mL) bromine (1.6 mL, 30.0 mmol) were added. The resulting mixture was stirred for 3 days under dark, then the reaction mixture was poured into sodium hydroxide solution and aqueous phase was extracted with methylene chloride (2×100 mL) and dried over anhydrous MgSO₄. The crude was purified by column chromatography on silica with hexane: methylene chloride (6:4, v/v) to get light yellow powder compound A1 (2.2 g, 64%).

¹H NMR (CDCl₃, 300 MH_z): δ (ppm) 4.52 (s, 4H); ¹³C NMR (CDCl₃, 75 MH_z): δ (ppm); 146.95, 146.45, 90.63, 65.25. HRMS: Calculated for C₈H₄Br₂N₂O₃ 335.8589; found: 335.8591.

Synthesis of 4,9-Di(thiophene-2-yl)-6,7-dihydro-[1,4]dioxino[2,3,4,5]benzo[1,2-C][1,2,5]oxadiazole (5)

Compound A1 (1.0 g, 2.9 mmol), 2-tributyl stannyl thiophene (2.3 mL, 7.4 mmol), and Pd (PPh₃)₄ (0.3 g, 0.3 mmol) were added to anhydrous toluene (20 mL) and purged with N₂ for 20 min and then refluxed the mixture for overnight (12 h). Evaporate the excess of toluene and extracted with methylene chloride and dried over anhydrous MgSO₄. Crude was purified by column chromatography on silica with hexane: methylene chloride (8:2, v/v) to furnish orange solid A1 (70%).

¹H NMR (CDCl₃, 300 MH_z): δ (ppm) 8.44–8.46 (m, 2H), 7.47–7.50 (m, 2H), 7.20–7.24 (m, 2H), 4.64 (s, 4H); ¹³C NMR (CDCl₃, 75 MH_z): δ (ppm); 145.73, 143.55, 133.11, 130.57, 127.76, 105.55, 64.44, 28.48. HRMS: Calculated for C₁₆H₁₀N₂O₃S₂ 342.0133; found: 342.0136.

Synthesis of 4,9-Di(5-bromothiphen-2-Yl) – 6,7-Dihydro-[1,4]Dioxino[2',3':4,5] Benzo[1,2-C] [1,2,5]Oxadiazole (A2)

Compound 5 (0.6 g, 1.7 mmol) dissolved in THF (50 mL), NBS (0.6 g, 3.5 mmol) in THF (10 mL) was added drop wise to the mixture at 0 °C and then slowly warm to room temperature and stirred for 6 h and reaction mixture was poured into water (200 mL) extracted with chloroform and dried over anhydrous MgSO₄. Crude was purified by column chromatography on silica gel with hexane: methylene chloride (9:1, v/v) to furnish red solid (74%).

¹H NMR (CDCl₃, 300 MH_z): δ (ppm) 8.23–8.24 (m, 2H), 7.17–7.18 (m, 2H), 4.65 (s, 4H). HRMS: Calculated for C₁₆H₈Br₂N₂O₃S₂ 499.8343; found: 499.8323.

Synthesis of 4,9-Dibromo-6,7-Dihydro-[1,4] Dioxino [2',3':4,5] *Benzo[1,2,-C][1,2,5]Thiadiazole (A3)*

Compound 4 (1.0 g, 6.0 mmol) was dissolved in 50 mL of chloroform cool to 0 °C and then add $SOBr_2$ (3.2 mL, 42.0 mmol) then pyridine (2 mL) then heat the reaction mixture at 70 °C for overnight (12 h), crude was purified by column chromatography on silica with hexane: methylene chloride (8:2, v/v) to furnish yellow solid (38%).

¹H NMR (CDCl₃, 300 MH_z): δ (ppm) 4.54 (s, 4H); ¹³C NMR (CDCl₃, 75 MH_z): δ (ppm) 148.89, 147.16, 97.17, 65.16. HRMS: Calculated for C₈H₄Br₂N₂O₂S 351.8340; found: 351.8340.

Synthesis of 4,9-Di(thiophene-2-Yl)-6,7-Dihydro-[1,4]Dioxino[2,3,4,5]Benzo[1,2-C][1,2,5]Thiazole (6)

A3 (1.0 g, 2.8 mmol), 2-tributylstannyl thiophene (2.7 mL, 8.0 mmol), and Pd(PPh₃)₄ (0.3 g, 0.3 mmol) were dissolved in anhydrous toluene and purged with N₂ for 20 min then reflux overnight (12 h). Crude was purified by column chromatography on silica with hexane: methylene chloride (8:2, v/v) to furnish orange solid (80%).

¹H NMR (CDCl₃, 300 MH_z): δ (ppm) 8.45 (d, 2H), 7.51 (d, 2H), 7.22 (d, 2H), 4.61 (s, 4H). ¹³C NMR (CDCl₃, 75 MH_z): δ (ppm) 149.43, 143.76, 134.25, 130.45, 127.18, 110.82, 64.27, 29.67. HRMS: Calculated C₁₆H₁₀N₂O₂S₃ 357.9904; found: 357.9904.

Synthesis of 4,9-Di(5-bromothiphen-2-Yl)-6,7-Dihydro-

[1,4]Dioxino[2',3':4,5] Benzo[1,2-C] [1,2,5]Thiadiazole (A4) Synthesized same procedure as followed for A2 as red solid (86%). ¹H NMR (CDCl₃, 300 MH₂): δ (ppm) 8.33–8.35 (d, 2H), 7.17–7.18 (d, 2H), 4.62 (s, 4H). HRMS: Calculated for C₁₆H₈Br₂N₂O₂S₃ 516.8094; found: 515.8094.

General Polymerization Procedure

The general procedure for the synthesis of polymer P1 is as follows: To a microwave tube BDTT (0.3 g, 0.26 mmol), and A1 (0.089 g, 0.26 mmol), Pd₂ (dba)₃ (5.4 mg, 2 mol %), (*o*-tol)₃ P (16 mg, 16 mol %) were dissolved in anhydrous CB (3 mL). The reaction mixture was purged with N₂ for 15 min. Tube was heated in the reactor at 120 °C for 1 h for P1 and P3;120 °C for 10 min for P2 and P4.

After cooling to room temperature, the reaction mixture was poured into MeOH to obtain precipitate, the resulted precipitate was purified by soxhlet method using MeOH, hexane, acetone, and chloroform. The chloroform fraction was evaporated to get polymer. M_n and PDI of P1–P4 are listed in Supporting Information Table S1.

Poly[4,8-bis(2-hexyldecyl-2-thiophenyl)-benzo[1,2-b:4,5-b']-dithiophene-alt-4,9-dibromo-6,7-dihydro-[1,4] dioxino [2',3':4,5] benzo[1,2,-c][1,2,5]oxadiazole]] (P1, 60%). ¹H NMR (CDCl₃ 300 MH_z): δ (ppm) 8.8 (br, 2H), 7.92 (br, 4H), 4.24 (br, 4H), 3.01 (br, 4H), 1.32 (br, 50 H), (0.86, br 12H). Anal. Calcd for C₅₈H₇₈N₂O₃S₄: C, 71.12; H, 8.03; N, 2.86; found: C, 70.88; H, 7.89; N, 2.66.

Poly[4,8-bis(2-hexyldecyl-2-thiophenyl)-benzo[1,2-b:4,5-b']dithiophene-alt-4,9-di(5-bromothiphen-2-yl)-6,7-dihydro-[1,4] dioxino[2',3':4,5]benzo[1,2-c] [1,2,5]oxadiazole (P2, 73%). ¹H NMR (CDCl₃, 300 MH₂]: δ (ppm) 8.8 (br, 10H), 4.62 (br, 4H), 2.98 (br, 4H), 1.35 (br, 50H), 0.87 (br, 12H). Anal. Calcd for C₆₆H₈₂N₂O₃S₆: C, 69.31; H, 7.23; N, 2.45; found: C, 68.28, H, 7.18, N, 2.55.



FIGURE 1 UV-vis absorption spectra of (a) P1–P4 solution, (b) P1–P4 film, (c) P1, P3, P5, and P6 solution, (d) P1, P3, P5, and P6 film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Poly[4,8-bis(2-hexyldecyl-2-thiophenyl)-benzo[1,2-b:4,5-b']dithiophene-alt-4,9-dibromo-6,7-dihydro-[1,4] dioxino [2',3':4,5] benzo[1,2,-c][1,2,5]thiadiazole)] (P3, 73%). ¹H NMR (CDCl₃, 300 MH₂): δ (ppm) 9.6 (br, 2H), 8.9 (br, 4H), 4.43 (br, 4H), 3.00 (br, 4H), 1.33 (br, 50H), 0.88, (br, 12H). Anal. Calcd for C₅₈H₇₈N₂O₂S₅: C, 69.97; H, 7.90; N, 2.81; found: C, 68.88; H, 7.80, N, 2.72.

Poly[4,8-bis(2-hexyldecyl-2-thiophenyl)-benzo[1,2-b:4,5-b']dithiophene-alt-4,9-di(5-bromothiphen-2-yl)-6,7-dihydro-

[1,4]dioxino[2',3':4,5] benzo[1,2-c] [1,2,5]thiadiazole (P4, 64%). ¹H NMR (CDCl₃ 300 MH₂) δ (ppm) 8.76-8.07 (br, 10H), 4.56 (br, 4H), 2.92 (br, 4H), 1.30 (br, 50H), 0.86 (br, 12H). Anal. Calcd for C₆₆H₈₂N₂O₂S₇: C, 68.35; H, 7.13; N, 2.42; found: C, 68.23, H, 7.06, N, 2.34.

RESULTS AND DISCUSSION

Synthesis and Characterization

6, 7-Dinitro-2,3-dihydor[b][1, 4] dioxine was synthesized using previously published procedure,^{11,12} and then followed by ring closing with NaN₃ and triphenylphosphine resulted the compound 1 and then followed by bromination results electron deficient unit A1, which on coupling with 2-tributylstannyl thiophene and then brominating the second position of thiophene spacer results the electron deficient unit A2. All new electron deficient monomers were further

confirmed by ¹H NMR and ¹³C NMR and HRMS spectroscopy. The intermediates 1, 2, 4, A3, A4 were synthesized and confirmed according to literature.^{11,12}

Thermal Properties

The thermal stability of polymers was investigated via TGA at scanning rate of 10 °C min⁻¹. All the polymers possess good thermal stability to fabricate PSCs, which is revealed by its thermal decomposition temperatures of 387–391 °C as shown in Supporting Information Figure S1. It is worth to mention that new electron deficient units doped polymer have better thermal stability than alkoxy substituted BT containing polymers.¹³

Optical Properties

The UV-vis absorption spectra of P1–P4 in chloroform solution and film state are shown in Figure 1(a,b). P1–P4 shows $\pi - \pi^*$ transition and intramolecular charge transfer (ICT) bands, which are originated from the interactions between polymer backbone, and charge transfer between electron rich and deficient units respectively. The ICT bands of P1, P2 (oxygen analogues) are red shifted than P3, P4 (sulfur analogues) which could be attributed to the more electron negativity of oxygen than that of sulfur in their electron deficient repeating unit of backbone, which led to enhanced ICT resulting in more reduced optical band gaps for P1, P2





FIGURE 2 Temperature (a, b) and concentration (c, d) dependent UV-vis absorption spectra of P1 and P3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(1.66, 1.64 eV) than P3, P4 (1.68, 1.65 eV). The P1–P4 showed red shifted absorption spectra in film state relative that of solution state. Further P2, P4 showed reduced band gaps than P1, P3 due to the extended backbone conjugation with thiophene π -spacer. Interestingly P1, P3 shows additional shoulder peak at (659, 652 nm) in their absorption spectra which was not observed in P2, P4 and we assumed that the vibronic shoulder would be originated from non-covalent interactions between sulfur and oxygen atoms in benzodithiophene (BDT) and EDA bridge in electron rich and deficient units of P1, P3.¹⁴

To better understand this phenomenon, we have additionally synthesized polymers P5, P6 without EDA bridge. The absorption spectra of P5, P6 do not have any additional shoulder peaks in their absorption spectra as shown in Figure 1(c,d), whereas in P1, P3 solution and film state spectra show very strong shoulder peaks. This would partially explain the origin of vibronic shoulder in P1, P3 due to interactions between oxygen atom of EDA bridge and sulfur atom in BDT.

To further understand the reason for origin of vibronic shoulder, temperature dependent absorption spectra were measured for P1 and P3 in dilute CB as shown in Figure 2(a,b). The vibronic shoulder peak at 650–660 nm was very sharp and pronounced at room temperature, whereas on

gradual increase in temperature (25-100 °C) gradual dip in the intensity of shoulder peak was observed, which infer that both the polymers P1 and P3 have strong aggregation properties at room temperature which might be due to noncovalent interactions, and this aggregation is gradually reduced at higher temperature. Thus, the effective conjugation length will decrease because of more twisting or coplanarity of the repeating units at elevated temperatures. However, the P1, P3 polymers still have significant absorption shoulder at elevated temperature indicating the presence of polymer aggregates.^{15–17} Furthermore, we also measured the concentration dependent absorption spectra for P1 and P3, as shown in Figure 2(c,d). The intensity of shoulder peak increases when concentration of polymer (P1, P3) increases indicates that the existence of strong interactions between the sulfur atom of BDT unit and oxygen atom of EDA bridge.

Altogether from the above results it is clear that the origin of vibronic shoulder in P1 and P3 is due to the non-covalent interactions between the sulfur atoms of BDT and oxygen atoms in EDA bridge of new electron deficient units. Thus, the newly synthesized electron deficient units not only improve the solubility but also induce the non-covlent interactions between the electron rich and deficient units which will help in new avenues such as attaining additional

Polymer	Solution	Film	Film	E_{g}^{opt}	НОМО	LUMO
	λ _{max} (nm)a	λ_{\max} (nm)b	λ_{\max} (nm)c	(eV)d	(eV)	(eV)
P1	338, 592, 643	344, 605, 659	746	1.66	-5.40	-3.74
P2	358, 583	366, 597	756	1.64	-5.29	-3.64
P3	346, 582, 643	347, 603, 652	738	1.68	-5.36	-3.68
P4	358, 577	363, 597	751	1.65	-5.21	-3.56

TABLE 1 Optical and Electrochemical Properties of P1-P4

^{a,b}Absorption maxima from UV-vis absorption spectra in chloroform solution and film state.

^cThe onset of the film absorption edge.

planarity, reduced bandgap, and $\pi - \pi$ stacking and so forth, which might be beneficial for improving the hole mobility and photovoltaic properties.¹⁴

Electrochemical Properties

CV measurements were carried out to measure the HOMO and LUMO of the P1-P4. The corresponding cyclic voltammograms are shown in Supporting Information Figure S2 and the respective values are listed in Table 1. The calculated HOMO energy levels are -5.40, -5.29, -5.36, and -5.21 eV. The LUMO energy levels (-3.74, -3.64, -3.68, and -3.56 eV) were calculated from $E_{\rm g}^{\rm opt}$ and corresponding HOMO energy levels. The HOMO energy levels of P1 and P2 showed deeper HOMO levels than P3, P4 because of high electro negativity of oxygen in P1and P2. The HOMO energy levels of P1, P3 are deeper than P2, P4 as introduction of thiophene spacer in P2, P4 increases the electron rich part in backbone. Expectedly, all the donor polymers showed the LUMO value greater than 0.3 eV of LUMO level of PC71BM. The HOMO and LUMO levels of the new polymers clearly indicating their good air stability and efficient exciton dissociation at donor/ acceptor interfaces, respectively.

Computational Study

To gain deep insight into the optoelectronic properties of new electron deficient unit's doped new conjugated polymers (P1-P4), density functional theory (DFT) calculations were carried out using a suite of Gaussian 09 programs. Becke's three parameterized Lee-Yang-Parr exchange functional (B3LYP) and 6-31G* basis sets were used.¹⁸ The DFT calculated HOMOs and LUMOs are shown in Figure 3. The HOMOs and LUMOs of P1-P4 are -4.88, -4.83, -4.79, -4.75 eV and -2.23, -2.43, -2.17, -2.37 eV respectively which are well concurred with the experimental values. Interestingly the torsional angles between the electron rich and new electron deficient units (3.17, 7.51°) shows P1, P3 are highly planar compared to the P2, P4 (19.67, 21.65°). The above results also partially explaining that the possibility of enhanced non-covalent interactions between the sulfur atom of BDT and oxygen atom of EDA bridge in electron deficient units in P1, P3. Here, it is noteworthy to mention that our new electron deficient unit doped conjugated polymers are more planar than conventional alkoxy substituted dEstimated from the onset of the absorption in thin films ($E_g^{opt}=$ 1240/ $\lambda_{onset}).$

BT-based polymers (PBDT-TBT) with zig-zag polymer conformation due to high torsion angle of 56° .¹³

PFETs Characteristics

The charge transport properties of new electron deficient units containing polymers (P1-P4) were investigated by fabricated polymer thin film transistor devices. Here, PFETs were fabricated in bottom contact geometry device on a silicon wafer with channel lengths (12 μ m) and width (120 µm) under N2 atmosphere. All devices were fabricated with polymer thin films as active layer, which were annealed at 140 °C. The transfer characteristics of the devices were shown in Figure 4, and the corresponding data are summarized in Supporting Information Table S2. P1-P4 delivered prominent field effect hole mobilities, indicating that they possess typical p-type behavior. Among the four polymers P2 and P4 showed higher hole mobility than P1 and P3 owing to their extended conjugation in P2 and P4 via introduction of π -spacers. The mobilities of P1 and P3 are higher than that of P5 and P6 indicates enhanced planarity of P1 and P3 than P5, P6, this enhanced planarity of P1 and P3 which might be attained via non-covalent interactions of the heteroatoms of electron rich and electron deficient units.

Photovoltaic Properties

The photovoltaic performance of new electron deficient unit doped copolymers P1-P4 were used in making conventional BHJ PSC devices, with an architecture of ITO/PEDOT:PSS/ P1-P4:PC71BM/LiF/Al, and device performances were investigated under the illumination of AM 1.5G (100 mW cm⁻²). It is known that careful choice of suitable processing solvent and blend ratio are important to get nanoscale morphology for BHJ PSC photoactive layer to obtain best device performance. The solvent for solution processing and concentration of blend (polymer to $PC_{71}BM$) were optimized as CB and 1:2 and for P1 is (1:1.5). Initially the optimized blends of pristine devices of P1-P4 exhibited moderate PCEs with maximum of 2.08% for P2. The best photovoltaic parameters obtained for optimized blends of pristine devices are shown in Table 2, and Figure 5 shows the current density-voltage (J-V) curves for champion devices P1-P4. Among the four polymers, P1-, P2-based devices shown high open circuit voltages (V_{oc}) (0.87, 0.64 V) than P3, P4 (0.84, 0.56 V) because of deeper HOMO levels. Even though P1 and P3 possess higher $V_{\rm oc}$ values, the PCEs are moderate due to poor short-





FIGURE 3 DFT calculated HOMO and LUMO of P1–P4 repeating units. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

circuit current density (J_{sc}) and fill factor (FF), which can be explained from their poor nanoscale morphology.

Active layer morphology can be improved via various ways such as addition of high boiling additives, polar solvent treatment, thermal annealing. As an initial attempt to improve the photovoltaic properties of P1–P4-based devices, a small amount of external additive DIO was added to the active layers. On addition of DIO to the active layers, the photovoltaic properties of P1–P4-based devices were slightly improved. Among the four polymers, optimized P2-based BHJ PSCs showed maximum PCE of 2.43% after addition of 1% DIO to the active layer. This improved PCE could be attributed to the enhanced J_{sc} and FF. Rest of the polymers also showed little improvement in PCE after addition of DIO to the active layer, the corresponding *J–V* curves are shown in Figure 5(a,b).

To further optimize the photovoltaic properties of P1-P4based devices, we have used polar solvent treatment for active layers before deposition of Al electrode.^{19,20} Here, we used several polar solvents and found that MeOH is the best suited for our polymers and showed enhanced PCEs in Table 3. Even though the effect of solvent treatment on active layers was positive toward all the four polymers, interestingly P3-based devices showed significant improvement in photovoltaic properties on treatment with various polar solvents such as ethanol (EtOH), acetone, and MeOH. The PCEs of P3-based devices showed good improvement after solvent treatment with maximum PCEs of 3.49 (EtOH), 2.89 (acetone), 4.29% (MeOH), respectively, the corresponding J-V, external quantum efficiency (EQE) of P3-based PSCs are shown in Figure 6(a,b). This enhanced PCEs attributed to the improved J_{sc} and FF after solvent treatment. This improved Jsc and FF might originated from nanoscale morphology



FIGURE 4 Transfer characteristics of P1–P6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

attained after solvent treatment in P3-based active layers which was further studied with electrical impedance spectroscopy (EIS) and atomic force microscopy (AFM) studies (*vide infra*).^{19,20}

EQE curves of P1–P4-based devices without and with DIO are shown in Figure 5(c,d); all the devices showed photo response from 300 to 700 nm, and the EQE spectra of P1–P4 are similar to their absorption spectra's. Although all

Polymer	DIO (%)	Polymer:PC ₇₁ BM	Thickness (nm)	$J_{ m sc}~(m mA~cm^{-2})$	$V_{\rm oc}$ (V)	FF (%)	PCE (%)
P1	0	1:1.5	85–90	2.90	0.87	45.99	1.17
P2	0	1:2	75–80	5.77	0.67	53.61	2.08
P3	0	1:2	85–95	5.85	0.78	40.64	1.86
P4	0	1:2	80–85	6.09	0.56	38.13	1.30
P1	1	1:1.5	85–90	3.65	0.83	45.09	1.39
P2	1	1:2	75–80	6.76	0.64	55.76	2.43
P3	1	1:2	85–95	7.29	0.76	42.89	2.37
P4	1	1:2	80–85	6.94	0.52	42.47	1.53

TABLE 2 Photovoltaic Properties of Optimized BHJ PSCs of P1-P4 without and with DIO



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FIGURE 5 *J–V*, EQE characteristics of P1–P4-based PSCs without and with DIO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pristine devices showed a weak spectral response in visible region, after addition of additive to the active layers, little improvement of EQE response was observed in all the PSCs. Further improvement in spectral response was observed after polar solvent treatment to the active layers, especially for P3 up to 65–70% at 350–450 nm and 50% at 500–700 nm as shown in Figure 6(b), which was well correlated with its higher $J_{\rm sc}$. The integrated $J_{\rm sc}$ values were obtained from the integration of the EQE spectra are well concurred well with $J_{\rm sc}$ obtained from the J-V measurements.

Impedance Spectroscopy Studies

To understand this improved PCEs after solvent treatment, we probed EIS to the active layers of P3-based devices without and with various solvent treatment, and their corresponding Nyquist plots are shown in Figure 6(c). The impedance results well correlates with device data as reported in Table 4 for P3-based devices treated with solvents like MeOH, EtOH, and acetone. The Nyquist plot of P3based devices clearly depicts the significant reduction in bulk resistance of all the solvent treated devices, especially for MeOH, which can be inferred from the diameter of semicircle on the real axis (Re Z) of the EIS curve. Thus, among all the solvents the MeOH showed considerably reduced interfacial resistance for P3-based devices.

PL Quenching Studies

PL quenching studies [Fig. 6(d)] were performed to the active layer blends of P3 to understand the effect of solvent treatment, here we measured PL of P3: $PC_{71}BM$, P3: $PC_{71}BM$ (DIO), P3: $PC_{71}BM$ (DIO/MeOH). Emission intensity was decreased gradually for P3: $PC_{71}BM$ (DIO/MeOH) blends

TABLE 3 Photovoltaic Properties of BHJ PSCs of P1-P4 with MeOH Treatment

Polymer	Polymer: PC71BM	Thickness (nm)	J_{m} (mA cm ⁻²)	Vac (V)	FF (%)	PCE (%)
i orymor						1 02 (70)
P1	1:1.5	90	3.83	0.84	47.48	1.53
P2	1:2	95	7.24	0.64	57.80	2.69
P3	1:2	90	9.99	0.78	54.92	4.29
P4	1:2	85	7.90	0.53	42.95	1.81



FIGURE 6 *J*–*V*, EQE, Nyquist plots, and PL quenching of BHJ PSCs of P3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compared to the P3: $PC_{71}BM$ (DIO) and P3: $PC_{71}BM$ on addition of additive and solvent treatment emission intensity was decreased, and the emission intensity was further decreased when tested with P3: $PC_{71}BM$ (DIO), as well as solvent treated active layers. From this study, it is clear that addition of small amount of DIO and further solvent treatment improves the exciton dissociation at donor acceptor interface, which is well correlated with the improved PCEs of P3-based devices on addition of DIO and solvent treatment.

Hole Mobility

The hole mobility of the P1–P4:PC₇₁BM blend films measured via the SCLC method. The calculated SCLC hole mobility of P1–P4: PC₇₁BM are 1.31×10^{-5} , 1.17×10^{-4} , 9.83×10^{-5} , 3.22×10^{-5} cm² V⁻¹ s⁻¹. The obtained SCLC hole mobility characteristics are shown in Supporting Information Figure S4. The obtained SCLC mobilities are well correlated with the photovoltaic properties.

Morphology

Morphology of the active layers of P1-P4 was investigated via tapping mode AFM. To understand the differences in the pristine, additive and solvent treated active layer morphology of P1-P4:PC71BM-based blends were analyzed by AFM and the corresponding images are shown in Supporting Information Figure S3, as pristine active layers concerned P2:PC₇₁BM showed better morphology than rest of the blends which was well correlated with its maximum PCE for pristine blends. The poor photovoltaic parameters of pristine P1-based devices were due to unfavorable morphology occurred in the active layer due to improper mixing of polymer and PC71BM. Furthermor, the active layer morphologies were improved slightly with proper mixing of polymer and PC₇₁BM on addition of DIO, and this could the reason for slight improvement in the PCEs of P1--P4-based devices, whereas polar solvent treatment has shown very good effect on all the active layers, and attain smooth morphologies

TABLE 4 Optimized Photovoltaic Properties of BHJ PSCs of P3 with Various Solvent Treatments

Polymer	Polymer: PC ₇₁ BM	Solvent	$J_{\rm sc}~({\rm mA~cm^{-2}})$	V _{oc} (V)	FF (%)	PCE (%)
P3	1:2	MeOH	9.99	0.78	54.92	4.29
P3	1:2	EtOH	8.29	0.76	55.01	3.49
P3	1:2	Acetone	7.56	0.77	49.85	2.89



compared to pristine and additive-based active layers, especially P3-based active layer showed very good phase separation after MeOH treatment with reduced root mean square roughness, this favorable nanoscale morphology of P3-based devices would be the reason for improved J_{sc} and FF which results in maximum PCE of 4.29%.

CONCLUSIONS

In summary, we have synthesized new electron deficient units and were successfully used as repeating units in new polymers, all the new polymers showed good optoelectronic properties, in particular P1 and P3 showed strong vibronic shoulders due to non-covalent interactions between sulfur atom of BDT and oxygen in EDA bridge induces better planarity of polymer backbone by non-covalent locks, thus results enhanced PFET hole mobility for P1, P3 than P5, P6. We also found notable changes in photophysical properties on exchanging the heteroatom in new electron deficient unit and which are reflected on their optoelectronic and photovoltaic properties. Furthermore, P1-P4 were used in BHJ PSCs as donor materials and they delivered a maximum PCE of 4.29% for P3-based PSCs on MeOH treatment, which was further studied by EIS, the reduced interfacial resistance of MeOH treated active layers was well concurred with the enhanced FF and J_{sc} of the P3-based PSCs. Therefore, from the above observations, we believe that the new electron deficient unit doped polymers exhibit good optoelectronic properties and reasonable PCEs which demonstrate that new electron deficient units can be considered as potential candidates for the PSCs. Further improvement in PCE of PSCs via structural modification and device optimization is underway.

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