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The Improved Efficiency of Polymer Solar Cells by Fluorine Atoms at Ortho-Position of Alkxoyphenyl Group in Benzodithiophene (BDT) Units

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In this article, two novel donor polymers containing fluorine atoms at *ortho*-position of alkxoyphenyl group in benzodithiophene (BDT) units are constructed. Compared with the reference polymer(P1) without fluorine atom, the polymers with fluorine atoms (P2 and P3) show their great different electrochemical properties, optical properties, morphology and hole mobility. Most significant change is their photovoltaic performances. The devices formed by P2 and P3 show much higher power conversion efficiency (PCE), 5.44% and 6.12%, respectively. The reasons should be that the incorporation of fluorine atom at *ortho*-position of alkoxyphenyl side chains increases the oxidation potential, decreases the highest occupied molecular orbit (HOMO) level of donor polymers, and thus increases the open circuit voltage (Voc) in device. Moreover, the linear hexyl side chain of P3 causes much higher PCE because it generates better molecular aggregation and hole transport in device.

Keywords: new donor materials, fluorine atom incorporation, increase oxidation potential, better molecular aggregation, polymer solar cell.

1. INTRODUCTION

Bulk-heterojunction polymer solar cells (BHJ-PSCs) have gained great developments over past decades for their virtues including flexibility, light weight, low-cost[1-3]. Through developing new

low band-gap donor materials and applying advanced fabrication technologies, the power conversion efficiency (PCE) surpass 12%, which is more and more approaching the efficiency that commercialization needed[4-11].

It has been well known that donor-acceptor (D-A) copolymer strategy is one of the most efficient design approaches to gain high photovoltaic performance donor polymer materials, because of its distinctive features of tunning the energy levels, optical band gaps, and the charge carrier mobility by optimizing the chemical structure of D and A moieties[1, 2, 12-14]. Benzodithiophene (BDT) as one of the most efficient electron-rich building block to synthesis high-performance D-A structure copolymers possesses a rigid and planar structure, because of its structure of fusing benzene with two thiophene moieties [1, 2, 14, 15]. Different substitutions on the central benzene of BDT can be applied to tune the electrical properties, optical band gap, and molecular aggregations etc. compared with alkyl chain substitutions, the conjugated group substitutions of the aromatic structure will enhance the π - π stacking and the photovoltaic performances[16-18]. As has been well known, the introduction of fluorine atom on the BDT structure can decrease the highest occupied molecular orbit (HOMO) level of the polymer, thus improve the open circuit voltage (Voc) the device[1, 2]'[19]. Moreover, the incorporation of the fluorine atom also changes the surface energy of photo-active layer through C-F...H and F...S atom interactions[19]'[20]. 4,7-Dithien-2-yl-2,1,3-benzothiadiazole (DTBT) is one of the most popular electron-deficient moieties for constructing efficient D-A structure donor materials[21]. After the chemical modification of DTBT by fluorine substitution, pyridine replacement and heteroatom bridging, the constructed D-A polymers obtained PCEs up to 7.2% [20, 22]. Apart from the selecting of D and A building blocks, appropriate alkyl side chains play important roles in determining photovoltaic performance of donor materials in PSCs[23, 24], because the alkyl side chains greatly influence not only the solubility of polymers but also the chemical conformations, molecular weights, molecular aggregations.



Figure 1. The chemical structures of P1, P2 and P3.

In this work, we construct new D-A donor materials with ortho-position fluorinated BDTP unit and DTBT unit. Compared with un-fluorinated donor polymer Poly(4-(5-(4,8-bis(4-((2hexyldecyl)oxy)phenyl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-4-(2-ethylhexyl)thiophen-2-yl)-7-(4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole) (P1), the ortho-position fluorinated Poly(4-(5-(4,8-bis(2-fluoro-4-((2-hexyldecyl)oxy)phenyl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-4-(2-ethylhexyl)thiophen-2-yl)-7-(4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole) (P2)show enhanced photovoltaic performances. Furthermore, the polymer structure are further optimized by replacing branched 2-ethyl-hexyl side chain of P2 with the linear hexyl side chain Poly(4-(5-(4,8-bis(2-fluoro-4-((2-hexyldecyl)oxy)phenyl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-4-hexylthiophen-2-yl)-7-(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole) (P3), thus lead to improved aggregation ability, which benefits the transport of hole carrier in donor materials. Therefore, devices based on P3 exhibits high PCE up to 6.12%.

2. EXPERIMENTAL

2.1. Synthesis



Scheme 1. Synthetic routes of the monomers and polymers.

spectra of compounds can be found in Supporting Information.

The synthesis routes for the monomers and the polymers are shown in Scheme 1. The ofluorine substituted alkoxyphenyl or alkoxyphenyl groups were chemical bounded to BDT unit via the nucleophilic and reduction reaction to afford compound 2 and 4, respectively[25]. Then, o-FBDTP monomer was obtained from bromated BDT unit (compound 3) by lithiation using n-butyl lithium and then reacted with trimethyltin chloride[26]. C8DTBT and C6DTBT of electron deficient monomers were synthesized by Stille coupling reaction between 4,7-dibromo-2,1,3-benzothiadiazole and 2tributylstannyl-4-alkyl-thiophene, followed by the bromination reaction[20, 27], respectively. Lastly, P1, P2 and P3 polymers were synthesized via Stille cross-coupling polycondensation with Pd₂(dba)₃ catalyst and tri(o-tolyl)phosphine ligand[28]. All the polymers dissolved well in common organic

solvents (chloroform, chlorobenzene, and 1,2-dichlorobenzene). All the ¹H NMR and ¹³C NMR

2.2. Characterization

¹H NMR and ¹³C NMR spectra were obtained by a Bruker DRX-600 spectrometer. The ultraviolet-visible (UV-Vis) spectra were taken by a Varian Cary 50. The electrochemical behaviors of polymers were characterized by cyclic voltammograms (CV). The CV measurements were performed in the solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in acetonitrile. A three-electrode cell including a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl as reference electrodes was utilized. The scanning rate was 100 mV/s. The polymer solid films were coated on glassy carbon electrode by dipping the polymer solutions onto the electrode. The potential of ferrocene/ferrocenium (Fc/Fc⁺) was measured to be 0.40 V under the same conditions. It was assumed that the Fc/Fc+ has an absolute energy level of -4.8 eV to vacuum[16]. Atomic force microscopy (AFM) measurements were performed on an Agilent 5400 scanning probe microscope.

2.3. Fabrication of photovoltaic devices

Photovoltaic devices with the structure of ITO/PEDOT:PSS/Polymers:PC₇₁BM /Ca /Al were fabricated on the substrates of ITO coated glass. The ITO coated glasses were cleaned by ultrasonic cleaning for 20 min with detergent, ultra pure water, acetone, and isopropyl alcohol, step by step, and then treated with oxygen plasma for 6 min. The substrates were spin-coated with PEDOT:PSS solution at 4000 rpm, and dried at 160 °C for 30 min in air[29]. The copolymers and PC₇₁BM were dissolved in *o*-dichlorobenzene in different weight ratios, and stirred overnight in glove box. The blend of the copolymer and PC₇₁BM was spin coated on PEDOT:PSS to form active layers. A concentration of the polymer blending solution was 10 mg/mL. Besides, 1,8-diiodooctane (DIO) was utilized as additive to further improve the photovoltaic performances of the polymers, and additive ratios were optimized according the photovoltaic performances. Subsequently 10 nm Ca and 100 nm Al were respectively thermal evaporated on top of the active layer as cathode in a vacuum of 5×10^{-4} Pa. The device area was fixed to 0.1 cm² by a shadow mask when evaporating the cathode. Photovoltaic performance was characterized under the illumination of AM 1.5G (100 mW cm⁻²), and the I-V curves were recorded by

the Keithley 2400 source meter. The external quantum efficiencies (EQE) of solar cells were measured using a certified Newport incident photon conversion efficiency (IPCE) measurement system[30]. In order to check the optical properties of P1, P2 and P3 polymers, the absorption of solid films and solvents were measured. P1, P2 and P3 films were prepared by spin coating from P1, P2 and P3 chlorobenzene solutions, and the light absorptions of P1, P2 and P3 in chlorobenzene solutions were also measured.

3. RESULTS AND DISCUSSION

3.1 Electrochemical properties and optical Properties

The electrochemical properties of the polymer are important for the exctions dissociation and electrons transportation in PSCs. The cyclic voltammetry (CV) measurement combined with absorption band gaps can be utilized to evaluate the highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO)[31]. Figure 1 shows the CV curves of the polymers, and all of them exhibited irreversible oxidative potential. As well known, the polymer HOMO energy levels can be obtained from the onset oxidation potentials based on the equation: HOMO = $-[(E_{\text{oxonset}} - E_{\text{foc}}) + E_{\text{ref}}]$ (eV), where the E_{foc} is the potential of the ferrocene/ferrocenium ion (Foc/Foc⁺) couple as the external standards, and the E_{ref} is the reference energy level of ferrocence which is 4.8 eV below the vacuum level. As summarized in Table 1, the HOMO energy levels of P1, P2 and P3 calculated from CV methods are -5.24 eV, -5.40 eV and -5.32 eV, respectively. The HOMO level of P2 and P3 are lower than that of P1, which can be ascribed to the incorporation of fluorine atom on the orthoposition of phenyl unit on BDT.



Figure 2. CV curves of P1, P2 and P3 polymers, and the reference CV curve of Ferrocene.

Hence, with deeper HOMO levels, higher Voc of the P1 and P2 constructed devices would be expected, because Voc is related to the difference values of donor HOMO energy level and acceptor LUMO energy level. The optical band gaps of the polymers are calculated according the absorption

edges. Hence, the LUMO energy levels can be obtained by the HOMO energy levels and the corresponding optical band gaps[16]. As shown in Table 1, the LUMO energy levels of P1, P2 and P3 are -3.54 eV, -3.64 eV and -3.61 eV, respectively. All of the LUMO energy levels are larger than the LUMO energy level of $PC_{71}BM$ (-3.90 eV), which will provide effective energy gaps for excitons dissociation with $PC_{71}BM$.

Polymer	Solution		Film		E_{g}^{opt}	HOMO	LUMO
	λ_{max} [nm]	$\lambda_{shoulder}$	λ_{max} [nm]	λ_{edge} [nm]	$[eV]^a$	$[eV]^b$	$[eV]^{c}$
		[nm]					
P1	560	644	605	728	1.70	-5.24	-3.54
P2	555	N/A	587	705	1.76	-5.40	-3.64
P3	554	N/A	607	725	1.71	-5.32	-3.61

Table 1. Optical	l and electrochemical	parameters of P1	, P2 and P3.
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^a Optical band gaps were calculated from the onset of film absorption curves. ^b The HOMO energy levels were obtained by CV measurements. ^c The LUMO level of the polymers can be calculated by the optical band gap and the CV calculated HOMO energy levels.

The normalized light absorptions of P1, P2 and P3 in chlorobenzene solutions and solid film states were measured, as the results illustrated in Figure 2. The absorption peak, shoulder peaks and the absorption edges were also summarized in Table 1. The absorption maximum peaks of the polymers in chlorobenzene solutions are 560 nm, 555 nm and 554 nm for P1, P2 and P3, respectively, and the absorption peaks are ascribed to the intra-molecular charge transfer (ICT)[26]. The shoulder peak only can be observed in P1 solution, which indicates that the aggregation of P1 is much greater than that of P2 and P3. There are various red-shifts observed compared with the light absorption in solutions and in films. The red-shifts are ascribed to the aggregation of the molecular. The absorption curves P2 and P3 solutions are very similar, whereas, P3 film exhibits a broader light absorption compared with that of P2 film, which indicates that the aggregation ability of P3 is greater than that of P2. Compare the chemical structure of P2 and P3, the only difference is the linear hexyl side chain or branched 2-ethylhexyl side chain substituted on the thiophene unit. The branched 2-ethyl-hexyl side chain of P2 must provide a greater steric hindrance than that of P3 with linear hexyl side chain, therefore, the grater steric hindrance effects broke the molecular aggregation [14, 24]. As mentioned above, the molecular aggregation of P1 is much greater than P2, which caused by the incorporation of fluorine atoms on the ortho-position of the phenol substituent of BDT. As has been detailed illustrated in our previous article, the inclusion of fluorine atoms could enlarge the dihedral angle between the conjugate side chains and backbone of the polymer[17]. In addition, the inclusion of the fluorine atoms on the orthoposition could reduce the electron density of the conjugated backbone, which would weaken the π orbital overlap between BDT and DTBT moiety[20]. Hence, fluorine on the ortho-position of phenol can significantly affect the aggregation of polymer.



Figure 3. Normalized UV-Vis absorption spectra of donor materials in solid film and in chlorobenzene solution at room temperature.

3.2 Photovoltaic performances of P1, P2 and P3

	Polymer:PC71BM	DIO vol%	Voc (V)	$Jsc (mA cm^{-2})$	FF (%)	PCE (%)
	Mass ratio					
P1	1:0.5		0.86	11.74	47.65	4.82
	1:1	NO	0.87	11.43	52.08	5.18
	1:1.5		0.87	11.17	50.31	4.86
		1%	0.79	6.8	53.67	2.88
	1:1	2%	0.78	8.69	47.79	3.25
		3%	0.77	7.5	46.96	2.7
P2	1:1.5		1.05	9.14	38.34	3.66
	1:2	NO	1.03	9.63	38.06	3.79
	1:2.5		1.03	8.98	39.26	3.63
		3%	0.88	9.98	48.22	4.22
	1:2	4%	0.89	11.30	54.12	5.44
		5%	0.9	9.74	52.43	4.61
P3	1:1		0.91	10.35	38.03	3.58
	1:1.5	NO	0.9	10.09	49.49	4.5
	1:2		0.89	10.47	42.98	4.01
		1%	0.79	10.09	55.32	4.43
	1:1.5	2%	0.80	13.19	58.08	6.12
		3%	0.81	11.72	61.23	5.83

Table 2. Photovoltaic parameters of P1, P2 and P3 constructed devices with different donor/acceptor ratios and different DIO additive percents.



Figure 4. J-V curves of devices for P1, P2 and P3 polymers with different DIO ratios.

To investigate the photovoltaic performances of the polymers, normal structure devices were fabricated as: ITO/PEDOT:PSS/Polymer:PC71BM/Ca/Al, and the measurements were taken under the illumination of AM 1.5 G at 100mA/cm^2 . The weight ratios of the polymers to PC₇₁BM were optimized according the performances of the corresponding devices. The detail photovoltaic parameters of the devices with different donor-acceptor ratios were summarized in Table 2. As results, the optimal D/A mass ratios for P1, P2 and P3 are 1:1, 1:2 and 1:1.5, respectively. With the optimized ratio of 1:1, the P1 devices can obtain a PCE of 5.18%, with Voc of 0.87 V, short current density (Jsc) of 11.43 mAcm⁻², and fill factor (FF) of 52.08%. The enhanced PCE for device with optimized ratio is mainly caused by the large value of FF. For P2 devices, the photovoltaic performance of devices changes slightly with different D/A ratios, and with the best ratio, the PCE reaches 3.79%, with a high Voc of 1.03 V, a Jsc of 9.63 mAcm⁻², and a FF of 38.06%. The Voc of P2 devices is 0.16 V higher than that of P1 devices, which is caused by the deeper HOMO energy level of P2 polymer[20]. The optimized ratio of P3 device is 1:1.5, and its PCE is 4.5%, with of 0.90 V, a Jsc of 10.09 mAcm⁻², and a FF of 49.49%. In order to further optimize the morphology of the polymer/PC₇₁BM blends to get the interpenetrating network structure with a ideal domain size (~ 20 nm). DIO is added to as the additive. The additive ratios are optimized, and the detail photovoltaic parameters of the devices with DIO are also summarized in Table 2. As results, the incorporation of DIO in the P1/PC₇₁BM blend system would decrease the performance of the device, which indicated that without DIO, the pure P1/PC₇₁BM blend can acquire a relatively ideal donor or acceptor domain size, and the incorporation of the DIO would destroy the ideal structure. On the contrary, with 4 vol% DIO addition, the photovoltaic performances of the P2 devices are improved to 5.44%, with enhanced Jsc and FF are 11.30 mAcm⁻² and 54.12%, respectively. As for P3/PC71BM blend system with 2% DIO, the photovoltaic performances of the devices can be improved to 6.12%, with enhanced Jsc of 13.19 mAcm⁻² and

enhanced FF of 58.08%. As has been illustrated above, the best device performances can be ascribed to the dual effect of F atom incorporation and the linear hexyl side chain effect.

The EQE measurements were utilized to verify the photovoltaic performances of the devices. The devices with best photovoltaic performances for three polymers were taken to measure the EQE spectra, as the results shown in Figure 4. The EQE curves of P3 device shows a maximum photoresponse in the wavelength range from 300 nm-750 nm, which is in consistence with the results of Jsc. As shown in Figure 5, the P2 device shows a much narrow photo-response compared with that of P1 and P3 devices, which is caused by the narrow light absorption of P2 film[32].



Figure 5. EQE curves of best devices with P1, P2 and P3 as donor materials.



Figure 6. AFM images of the (a) P1/PC₇₁BM, (b) P1/PC₇₁BM with 2% DIO, (c) P2/PC₇₁BM, (d) P2/PC₇₁BM with 4% DIO, (e) P3/PC₇₁BM, (f) P3/PC₇₁BM with 2% DIO. The RMS values of each films were marked in the images.

The morphologies of the active blend films of polymers and $PC_{71}BM$ were characterized by tapping mode atomic force microscopy (AFM). The neat polymer/ $PC_{71}BM$ with optimized mass ratios and the films prepared with optimized DIO addition were taken to the AFM measurements. As the results shown in Figure 5 a and b, the $P1/PC_{71}BM$ neat film shows a much smooth layer compared with that of $P1/PC_{71}BM$ film fabricated with 2% DIO, as the surface root mean square (RMS) are 2.5 nm and 7.2 nm, respectively. The increased RMS indicates much enhanced polymer and $PC_{71}BM$ aggregations, and leads to overlarge domain sizes, which are bad to the excitons separation[18, 33]. For $P2/PC_{71}BM$ system, the incorporation of 4% DIO decrease the RMS value from 3.1 nm to 2.1 nm, this result can be ascribed to that the incorporation of 4% DIO would destroy the molecular aggregation in the solution. Whereas, for $P3/PC_{71}BM$ system, the incorporation of 2% DIO increase the RMS values from 1.2 nm to 3.0 nm, which is caused by the increased aggregation. And the relatively large aggregation may cause the enhancement of photovoltaic performances after adding 2% DIO.

3.3 Hole mobility measurements

To investigate the hole mobility in the donor materials of the devices, devices that only transport holes were fabricated, as the structure was: ITO/PDEOT:PSS/donor polymer:PC₇₁BM/Au. The hole mobility of devices are characterized based on the model of space charge limited current (SCLC), according to the equation of $J_{SCLC}=(9/8) \epsilon_0 \epsilon_r \mu_h ((V^2)/(L^3))[34]$, where μ_h is the hole mobility, J_{SCLC} is current density, ϵ_0 and ϵ_r stand for the permittivity of free spaces and the relative dielectric constant of transport medium, respectively, V is the internal potential of the devices, and L is the thickness of the active layer. Besides, the mass ratios of donor-acceptor materials and the DIO additive percent are same with that of preparing best devices for each polymer. After calculation, the hole mobilities of P1, P2 and P3 constructed devices are $3.76 \times 10^{-5} \text{ cm}^2/(\text{V S})$, $8.70 \times 10^{-5} \text{ cm}^2/(\text{V S})$ and $1.07 \times 10^{-5} \text{ cm}^2/(\text{V S})$, respectively. Higher hole mobility promises high Jsc and high FF of the P3 constructed devices[5].



Figure 7. SCLC curves of hole transport only devices for P1, P2 and P3 polymers.

4. CONCLUSIONS

In this work, two novel donor polymers containing fluorine atoms at *ortho*-position of alkxoyphenyl group in BDT units are constructed. By systematically characterization, it can be found that the electrochemical properties, optical properties, morphology and hole mobility showed great differences for three polymers, which leads to significantly different photovoltaic performances. For instance, P3 device with 2% DIO as additive shows a best PCE of 6.12%, which is much higher than that of P1 devices and P2 devices. One of the reasons for the enhancement is the incorporation of fluorine atom on the *ortho*-position of alkoxyphenyl side chains, which decreases the HOMO level, thus increases the Voc value. Another reason is that, the linear hexyl side chain of P3 promises better molecular aggregation than that of P2 with branched 2-ethyl-hexyl side chain, which is good for the transport of holes in donor materials. Hence, fluorine atom on the *ortho*-position of alkoxyphenyl side chains on BDT unit is an effective electron-donor building block for efficient donor materials, besides, selecting appropriate alkyl side chains on the D-A conjugated polymers is very important. These two conclusions are quoteworthy in future designing high photovoltaic performances donor polymers.



SUPPORTING INFORMATION:

Figure S1. ¹HNMR spectrum of compound 1.



wn20151120cb;1HNMR;CDC13





Figure S6. ¹³CNMR spectrum of compound BDTP.





Figure S10. ¹HNMR spectrum of P2.



Figure S11. ¹HNMR spectrum of P3.

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