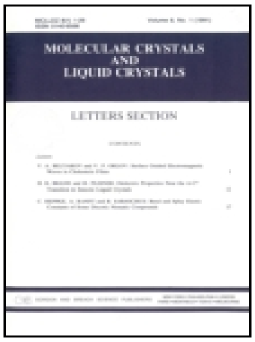

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Effect of fused thiazolothiazole on the photovoltaic performance of fluorene-thiazole-based conjugated polymers

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ABSTRACT

In this work, we utilized two fluorene-based polymers (**F8TBTT** and **F8TTZT**) as donor materials in organic photovoltaic cells (OPVs) and compared their performance to explain the effect of substituting fused thiazolothiazole for the bithiazole moiety. The OPV device based on **F8TTZT** showed a power conversion efficiency of 0.24%, which is three times higher than that of **F8TBTT** (0.07%) under the same conditions. The better performance can be explained by the increased planarity and enhanced intermolecular charge transport.

KEYWORDS

Organic photovoltaic cells; fluorene; thiazolothiazole; bithiazole

1. Introduction

Solar energy has received significant attention as one of the most important alternative energy systems. Although organic photovoltaic cells (OPVs) show relatively low efficiencies compared to silicon-based ones, they have advantages such as low-cost manufacturing and facile synthesis. Recently, power conversion efficiencies (PCEs) above 10% have been achieved with polymer-based OPVs.[1] The photovoltaic performance of donor–acceptor (D–A)type conjugated polymer donors has been increased by tuning the energy band gap (E_g) to achieve efficient absorption of the solar spectrum[2] and/or enhancing the charge transport in the films by strengthening intermolecular π–π interactions.[3] The introduction of fused aromatic systems such as thienothiophene and thiazolothiazole into the polymer backbone is one of the strategies for increasing charge mobility in the films. In our previous work, we introduced a fused ring compound, the thieno[3,2-b]thiophene group, into a fluorene-based alternating copolymer, and a higher degree of order could be obtained by introduction of groups with high degrees of planarity and rigidity.[4]

In this work, fluorene and thiazole moieties were chosen as electron-donating and electron-accepting units, respectively, for developing D–A-type copolymers. Fluorene groups are well-known electron-rich units of semiconducting polymers, in which alkyl chains can be easily introduced to the 9-position to achieve good solubility.[5] On the other hand, thiazole units containing an electron-withdrawing imine could behave as electron-deficient units in conjugated polymers.[6] Furthermore, the thiazolothiazole (TZ) moiety, which is the fused

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analogue of bithiazole (BT), was also copolymerized with fluorene to enhance intermolecular ordering and π-π stacking.

2. Experimental

2.1. *Materials*

Poly[(5,5′-bis(4-hexylthiophen-2-yl)-2,2′-bithiazole-5,5′-diyl)-*alt*-(9,9-dioctylfluorene-2,7-diyl)] (**F8TBTT**) and poly[(2,5-bis(4-hexylthiophen-2-yl)thiazolo[5,4-d]thiazole-5,5′-diyl)-*alt*-(9,9-dioctylfluorene-2,7-diyl)] (**F8TTZT**) were synthesized through the well-known palladium-catalyzed Suzuki polymerization reactions.[7] 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**F8**), 5,5′-bis(5-bromo-4-hexylthiophen-2-yl)-2,2′-bithiazole (**TBTT**), and 2,5-bis(5-bromo-4-hexylthiophen-2-yl)-thiazolo[5,4-*d*]thiazole (**TTZT**) were prepared according to the literature.[8,9]

2.2. *Measurements*

The weight-average (M_w) and number-average (M_n) molecular weights of polymers were measured by gel permeation chromatography. The UV-visible absorption spectra were obtained using a Shimadzu UV-visible spectrometer. The optical energy band gaps (E_g) were estimated from the absorption onset wavelengths of the UV-visible spectra of the films ($E_g = 1240/\lambda_{onset}$ (eV)). The photoluminescence (PL) spectra of the polymers were obtained using a Perkin Elmer spectrofluorometer. The electrochemical properties of the polymers were characterized by cyclic voltammetry (CV). The films were prepared by dip-coating the polymer solution onto Pt wire and the measurements were calibrated using the ferrocene value of −4.8 eV as the standard. The highest occupied molecular orbital (HOMO) energy levels of the polymers were determined according to the empirical relationship proposed by Leeuw et al.[10] ($I_p(\mathrm{HOMO}) = -(E_{onset} + 4.39)$ (eV), where E_{onset} is the onset potential of oxidation). The lowest unoccupied molecular orbital (LUMO) levels were calculated from the HOMO and optical E_g.

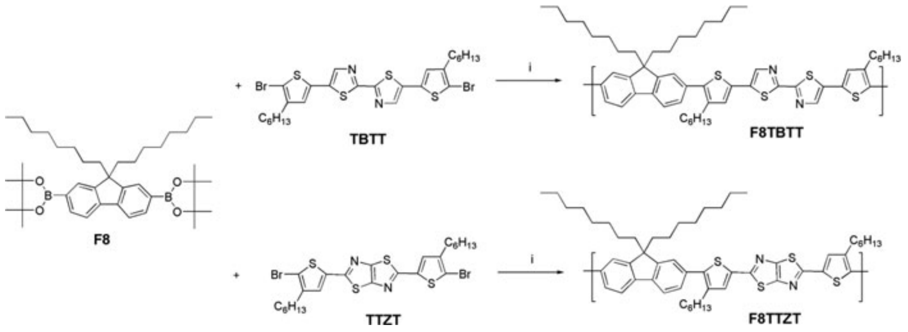
2.3. *Fabrication of OPV device*

The OPVs were fabricated with the configuration indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, 40 nm)/polymer:[6,6]-phenyl-C_{71} butyric acid methyl ester ($PC_{71}BM$, 1:3, 80 nm)/LiF (1 nm)/Al (100 nm). The PEDOT:PSS layer was spin-coated on the cleaned ITO-coated glass substrate (3000 rpm, 30 s) and annealed at 120 °C for 20 min. The active layer consisting of the donor (**F8TBTT** or **F8TTZT**) and acceptor ($PC_{71}BM$) was spin-coated from a chlorobenzene solution. The devices were completed by evaporating LiF and Al electrode. The area of the device was 4 mm^2. The current–voltage (J–V) characteristics were measured with a Keithley 2400 source-measure unit under white light AM 1.5 G illumination (100 mW/cm^2).

3. Results and discussion

3.1. *Synthesis and physical properties of the polymers*

Two fluorene-based conjugated polymers were synthesized for use as donor materials in OPVs. The synthetic schemes for **F8TBTT** and **F8TTZT** are shown in Scheme 1. The



Scheme 1. Synthetic routes for **F8TBTT** and **F8TTZT**: (i) Pd(PPh$_3$)$_4$, toluene, Na$_2$CO$_3$ (*aq.* 2 M), Aliquat®336, 95°C, N$_2$.

weight-average molecular weights (M_w) of **F8TBTT** and **F8TTZT** were 189,000 (polydispersity index (PDI) = 2.68) and 137,400 (PDI = 2.64), respectively. The synthesized polymers were sufficiently soluble in common organic solvent to be used for organic electronics owing to the dioctyl groups substituted in the 9-position of fluorenes. The optical properties of the polymers were studied by UV-visible and PL spectra. Figure 1 shows the UV-visible absorption and PL emission spectra of the polymers in chlorobenzene solution and films. In solution, **F8TBTT** and **F8TTZT** show similar UV-visible absorption spectra owing to their similar conjugation length. The absorption maxima (λ_{max}) of **F8TBTT** and **F8TTZT** were 451 and 452 nm, respectively. As films, the two copolymers exhibit slightly red-shifted and broader UV absorption compared to the corresponding solution state, which can be explained by the enhanced interchain π-π stacking of the films. The E_g values of the **F8TBTT** and **F8TTZT**, calculated using the λ_{onset} of the polymer films, were found to be 2.32 and 2.34 eV, respectively. The PL emission spectra of the polymer films show the same tendency of shifting to longer wavelength relative to that of the solution state. In addition, the PL spectra of **F8TTZT** are quenched upon addition of PC$_{71}$BM, indicating efficient charge transfer, as shown in Figure 2. The UV-visible absorption and PL emission maxima of the polymers are listed in Table 1, along with the E_g and molecular energy levels. The electrochemical properties of the two polymers were investigated using CV. The anodic scans showed that the onsets of oxidation for **F8TBTT** and **F8TTZT** occurred at 1.31 and 1.28 V (*vs.* SCE), respectively. The calculated HOMO levels of **F8TBTT** and **F8TTZT** are −5.70 and −5.67 eV, respectively. The estimated LUMO energy levels of **F8TBTT** and **F8TTZT** are −3.38 and −3.33 eV, respectively, using the HOMO levels and E_g of polymers.

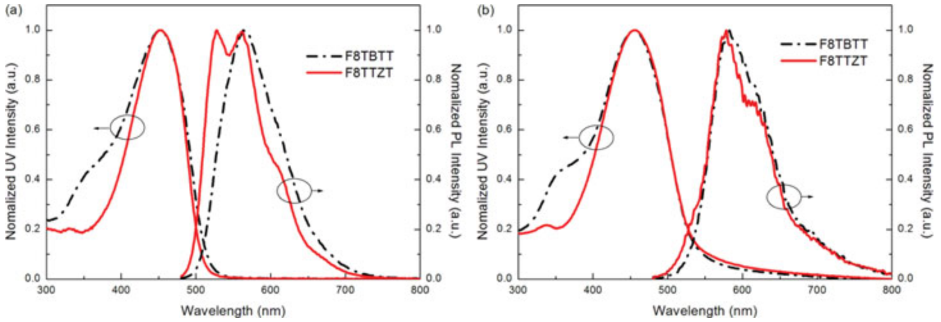


Figure 1. UV-visible absorption and PL emission spectra of the polymers (a) in chloroform solution and (b) as films.

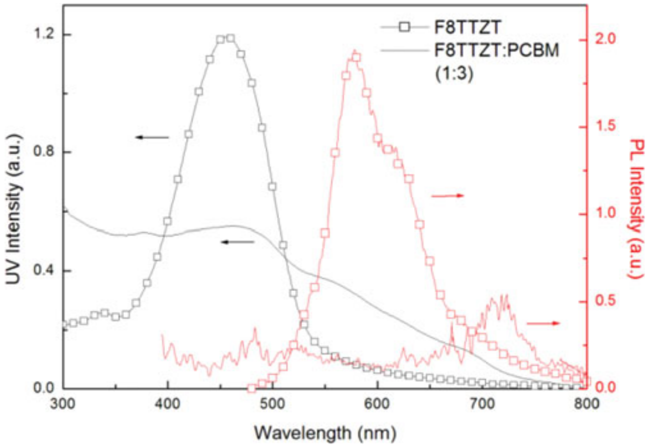


Figure 2. UV-visible absorption and PL emission spectra of the **F8TTZT**:$PC_{71}BM$ blend film.

3.2. *Photovoltaic properties of the polymers*

OPV cells were fabricated with the configuration ITO/PEDOT:PSS/polymer:$PC_{71}BM$/LIF/Al. Figure 3 shows the current density versus voltage (J–V) curves for photovoltaic devices measured in air under white light AM 1.5 G illumination (100 mW/cm^2). The photovoltaic properties of the blend films are summarized in Table 2. The devices were fabricated using various blending ratios and annealing temperatures. The optimized performances were obtained at a ratio of 1:3 (D:A) and annealing temperature of 80°C. Table 2 shows the photovoltaic parameters of the **F8TTZT**:$PC_{71}BM$ blend films at various annealing temperatures. The difference caused by the annealing temperature was mostly attributed to the short-circuit current (J_{SC}). A J_{SC} of 1.92 mA/cm^2, more than twice that of pristine cells (0.83 mA/cm^2), is obtained when the **F8TTZT**:$PC_{71}BM$ blend films are annealed at 80°C, probably owing to the higher degree of molecular aggregation induced by annealing.[11] However, the device performance (in particular, J_{SC}) is decreased when the films are annealed at 120°C, suggesting the importance of optimizing the fabrication conditions for OPVs. Furthermore, to investigate the effect of increased planarity of the polymers on the device performance, the OPV

Table 1. Physical properties of the polymers.

	F8TBTT	F8TTZT
M_w [a]	189,000	137,400
M_n [a]	70,400	52,000
PDI (M_w/M_n)	2.68	2.64
UV (λ_{max}, nm)		
Solution	451	452
Film	455	457
PL (λ_{max}, nm)		
Solution	566	530,560
Film	582	576
E_{onset} (V *vs.* SCE) [b]	1.31	1.28
HOMO (eV)[b]	−5.70	−5.67
LUMO (eV)[c]	−3.38	−3.33
E_g, eV (λ_{onset}, nm)[d]	2.32 (532)	2.34 (530)

[a] M_n and M_w are the number-average and weight-average molecular weights, respectively, determined by GPC.
[b] E_{onset} is the onset potential of oxidation
[c] Calculated using the empirical equations: $I_p(HOMO) = -(E_{onset} + 4.39)$ and $E_g = I_p(LUMO) - I_p(HOMO)$
[d] Optical gaps, E_g, determined from the absorption onsets (value in parentheses) of the UV-visible spectrum of the polymer film ($E_g = 1240/\lambda_{onset}$).

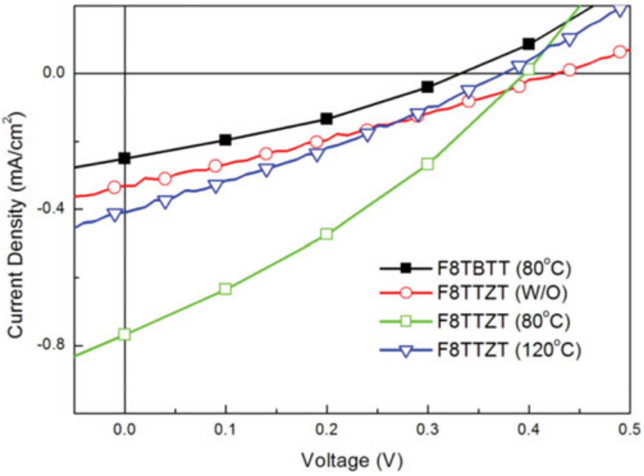


Figure 3. *J–V* curves for the polymer:$PC_{71}BM$ blend films.

Table 2. Photovoltaic properties of the polymers[a,b].

Donor	Annealing temperature	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
F8TBTT	80°C	0.27	1.00	27.5	0.07
F8TTZT	w/o	0.43	0.83	28.4	0.10
	80°C	0.40	1.92	31.2	0.24
	120°C	0.37	1.03	29.3	0.11

[a] D:A = 1:3, chlorobenzene.

[b] V_{OC}, open-circuit voltage; J_{SC}, short-circuit current; FF, fill factor; PCE, power conversion efficiency.

cell based on the **F8TBTT**:$PC_{71}BM$ blend film was fabricated under the same conditions. Interestingly, the device made of **F8TTZT**:$PC_{71}BM$ showed a PCE of 0.24%, which is three times higher than that of **F8TBTT**:$PC_{71}BM$ (0.07%), and this improvement is attributed to the higher J_{SC}. Replacement of the relatively flexible bithiazole moiety in **F8TBTT**with a fused thiazolothiazole moiety yielded a polymer (**F8TTZT**) with a higher degree of planarity and rigidity.[4] The increased planarity of **F8TTZT** induced by the fused thiazolohthiazole results in improved intermolecular charge transport and higher J_{SC} in the OPVs.

4. Conclusions

We synthesized two fluorene- and thiazole-based copolymers for OPVs. The fused thiazolothiazole-based copolymer **F8TTZT** had an enhanced PCE of 0.24% compared to the bithiazole-based copolymer **F8TBTT**. This was attributed to the improved intermolecular charge transport and higher J_{SC} in the OPVs arising from the more planar structure of **F8TTZT** compared to **F8TBTT**. Further improvements of the photovoltaic characteristics could be achieved by molecular engineering and/or optimizing the fabrication conditions.

Acknowledgment

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