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Morphology Driven by Molecular Structure of Thiazole-Based Polymers for Use in Field-Effect Transistors and Solar Cells

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Abstract: We study the effects of molecular structure in thiazolebased polymers on active layer morphologies and device performances of electronic and photovoltaic devices. Therefore, thiazole-based conjugated polymers with a novel thiazole-vinylenethiazole (TzVTz) structure are designed and synthesized. We introduce the TzVTz structure to extend the π -conjugation and coplanarity of the polymer chains. By combining alkylthienylsubstituted BDT or DTBDT electron-donating units and a TzVTz electron-accepting unit, enhanced intermolecular interactions and charge transport are obtained from the novel polymers, BDT-TzVTz and DTBDT-TzVTz. With a view to using the polymers in transistor and photovoltaic applications, molecular self-assembly in and the nanoscale morphologies of the BDT-TzVTz and DTBDT-TzVTz thin films are controlled via thermal annealing to enhance molecular packing and by introducing a diphenyl ether solvent additive to improve miscibility between polymer donors and PCBM acceptors, respectively. The morphology characterization on the photoactive layers reflects that a higher degree of m-electron delocalization and more favorable molecular packing of DTBDT-TzVTz than those of BDT-TzVTz lead to distinctly higher performances in transistor and photovoltaic devices. The superior performance of photovoltaic device incorporating DTBDT-TzVTz is obtained from superior miscibility of DTBDT-TzVTz with PCBM and improved crystallinity of DTBDT-TzVTz in nano-fibrillar structure.

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Introduction

Extensive research has examined solution-processed organic electronic devices in view of their advantages, which include light weight, flexibility, and semi-transparency, as well as low fabrication costs in mass production.^[1-4] A variety of organic semiconductors have been designed and synthesized, and their optical, electrical, and chemical properties have been investigated in an effort to realize efficient organic electronic devices.[5-8] Significant research efforts have been devoted toward developing donor-acceptor (D-A)-type copolymers with a broad light absorption spectrum and a high charge carrier mobility.^[5,7,9,10] Benzo[1,2-b:4,5-b']dithiophene (BDT) and dithieno[2,3-d:2',3'd']-benzo[1,2-b:4,5-b']dithiophene (DTBDT) derivatives have been widely used as electron-donating units in polymer semiconductors.^[7,8,10-12] Composed of fused aromatic and planar core units, these derivatives display high charge charier mobilities.^[10,11,13] Copolymers consisting of BDT and DTBDT have been synthesized with a variety of electron-accepting units, including thieno[3,4-b]thiophene (TT), diketopyrrolopyrrole (DPP), thienopyrroledione (TPD), thazole, and benzodithiazole (BT).[10,12-^{16]} The thiazole acceptor unit, featuring an electron-withdrawing nitrogen on the imine, displayed a high planarity and efficient π - π stacking.^[17-19] Therefore, the superior charge transport properties of copolymers that incorporate a thiazole unit have been reported previously in the context of organic photovoltaic (OPV) device applications.^[20-22] However, bithiazole-based polymers have struggled to show high performance due to the large-scale phase separation between polymer donors and [6,6]phenyl-C71-butyric acid methyl ester (PC71BM) acceptors.[15,23] Therefore, designing thiazole-based polymers having better miscibility with PC71BM and along with high crystallinity is required.

Here, we designed two copolymers, poly[(E)-5-(4,8-bis(4,5didecylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-2-(2-(thiazol-2-yl)vinyl)thiazole] (BDT-TzVTz) or poly[(E)-5-(5,10bis(4,5-didecylthiophen-2-yl)benzo[1,2-b:4,5-b'] dithieno[3.2b]thiophene)-2-(2-(thiazol-2- yl)vinyl)thiazole] (DTBDT-TzVTz), for use in organic field-effect transistor (OFET) and OPV devices. These two copolymers have alkylthienyl-substituted BDT or DTBDT units as electron-donating units to improve miscibility with PC71BM, and thiazole-vinylene-thiazole (TzVTz) as the electronaccepting unit. We used alkylthienyl -substituted BDT or DTBDT units, because the two-dimensional (2D) conjugated structure can enhance light absorption and charge carrier transport properties.^[24] The molecular structures of BDT-TzVTz and DTBDT-TzVTz are depicted in Scheme 1. The bithiazole-based polymer device performances were improved by introducing a novel TzVTz structure that provided appropriate electron-

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withdrawing properties and long planar conjugated systems. This structure, which featured vinylene groups between two thiazole units, could extend the π -conjugation and coplanarity of the polymer chains because the vinylene bonds between the two thiazole units reduced steric hindrance on the conformation of the rest of the polymer chain. By combining alkylthienyl-substituted BDT or DTBDT electron-donating units and a TzVTz electron-accepting unit, intermolecular interactions and charge transport in copolymers and miscibility with PC₇₁BM acceptor were expected to improve.

For transistor and photovoltaic applications, molecular selfassembly in and the nanoscale morphologies of the TzVTz-based polymer or TzVTz-based polymer:PC₇₁BM thin films were controlled via thermal annealing and by introducing a diphenyl ether (DPE) solvent additive, respectively. The self-assembly behaviors and active layer morphologies of films prepared from the TzVTz-based polymers were investigated to understand the relationship between the molecular structure and device performance. In OFET and OPV devices, distinctly higher performances were obtained from DTBDT-TzVTz, which displayed a higher degree of π -electron delocalization, stronger crystallinity and better miscibility with PC₇₁BM.

Results and Discussion

Materials Synthesis

The synthetic schemes used to produce the monomer and polymers are depicted in Scheme 1. The new acceptor (E)-1,2-bis(5-bromothiazol-2-yl)ethene was obtained by bromination of TzVTz which was synthesized through a Stille coupling reaction of (2-tributylstannyl)thiazole and 1,2-dichloroethene. The polymerization was carried out through a Stille coupling reaction in dichlorobenzene using $Pd_2(dba)_3$ and $P(oTol)_3$. The synthesized BDT-TzVTz and DTBDT-TzVTz polymers were purified by Soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform. The extracted chloroform solution was condensed and precipitated in methanol. The structures of the monomers were characterized by H-NMR, ¹³C-NMR, and mass spectroscopies (Figure S1–S6).

Material Properties

The polymers were soluble in common organic solvents, such as chloroform and dichlorobenzene, after slightly heating the polymer solutions. The molecular weights of the polymers were measured by gel permeation chromatography (GPC) using a polystyrene standard in tetrahydrofuran solvent. The weight average molecular weights (M_w) of the BDT-TzVTz and DTBDT-TzVTz polymers were 86.9k and 104k, with polydispersity indices (PDIs) of 2.53 and 1.56, respectively. The thermal properties of BDT-TzVTz and DTBDT-TzVTz were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), as shown in Figure S7. BDT- TzVTz and DTBDT-TzVTz were found to exhibit good thermal stabilities, losing less than 5% of their weight at 431 °C, and 455 °C, respectively, as determined by TGA under a nitrogen atmosphere. The DSC plots of both polymers did not reveal melting or crystalline transitions under 300 °C.

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Scheme 1. Synthetic routes to BDT-TzVTz and DTBDT-TzVTz.

The UV-vis absorption spectra of the polymers in dilute chloroform solutions and as thin films were recorded, as shown in Figures 1a and 1b, respectively, to investigate the optical properties, as summarized in Table 1. The maximum absorption bands attributed to intramolecular charge transfer were observed at 535 and 571 nm for BDT- TzVTz in chloroform solution and at 552 and 588 nm for DTBDT-TzVTz, respectively. In the film state, the absorption maxima were observed at 541 and 580 nm for BDT-TzVTz and 548 and 587 nm for DTBDT-TzVTz, reflecting that both polymers could form aggregates in solutions and displayed good intermolecular interactions in the solution state as well as in the solid state.^[25-27] The optical band gaps of BDT-TzVTz and DTBDT-TzVTz, estimated from the absorption onset, were 1.95 and 1.94 eV, respectively. The electrochemical properties were studied using cyclic voltammetry (CV) in a chloroform solution to determine the oxidation potentials and highest occupied molecular orbital (HOMO) energy levels (Figure 1c). The HOMO levels were calculated to be -5.28 eV for BDT-TzVTz and -5.29 eV for DTBDT-TzVTz, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the HOMO levels and the optical band gaps.^[28,29] The BDT-TzVTz and DTBDT-TzVTz polymers provided LUMO levels of -3.33 and -3.35 eV, respectively. The effects of introducing a vinylene group between the thiazole units were investigated by obtaining the HOMO and LUMO surface plots through density functional theory (DFT) calculations using the B3LYP 6-311G** basis set for two repeating units of each of BDT-TzVTz, DTBDT-TzVTz, BDT-TzTz, and DTBDT-TzTz (Figure S8). The theoretical results predicted that the new acceptor TzVTz-based units showed deeper LUMO level and narrower band gaps than those in the TzTz-based units because the presence of TzVTz favored the formation of a planar conjugated structure and extended π -conjugation...

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Figure 1. Normalized UV-vis-NIR absorption spectra of the TzVTz-based polymers (a) in a CHCl₃ solution, and (b) in a thin film. (c) Cyclic voltammograms of the polymers.

Table 1. polymers	Optical a	nd electro	chemical	properties	of the Ta	zVTz-based
Polym er	λ _{max} (nm) solutio	λ m (nm)	λ ax onset (nm)	E _{g^{opt[a]} (eV)}	HOMO	[LUMO[c]

CI	n	film	film	(01)	(eV)	(eV)
BDT- TzVTz	535 571(s) ^[d]	541 580 (s) ^[d]	634	1.95	-5.28	-3.33
DTBDT -TzVTz	552 588(s) ^[d]	548 587 (s) ^[d]	637	1.94	-5.29	-3.35

[a] Estimated from the absorption edge in the film state (E_g^{opt} =1240/ λ onset). [b] Estimated from the onset oxidation potential. [c] Determined by the HOMO + E_g^{opt} .^[26,27]. [d] Peak positions of shoulders in absorption spectra.

Active Layer Morphology

Morphological analyses were conducted to understand the relationship between molecular structure and aggregation behavior of TzVTz-based polymers. The surface morphology of the TzVTz-based polymer thin film was characterized using atomic force microscopy (AFM) as shown in Figure S9. Although the two polymers gave similar morphological features, DTBDT-TzVTz displayed a more aggregated surface morphology with a higher surface roughness. The root-mean-square (RMS) roughness values of the BDT-TzVTz and DTBDT-TzVTz thin films were 0.54 and 1.18 nm, respectively. Greater aggregation within the DTBDT-TzVTz polymer was thought to originate from the stronger intermolecular interactions in DTBDT-TzVTz, $^{\left[30,31\right] }$ which featured extended conjugation and a high planarity among the DTBDT units.^[32,33] The longer conjugation length and enhanced molecular packing of DTBDT-TzVTz are expected to result in a more efficient channel for charge carrier transport.

The aggregation and phase separation behaviors of the polymers in polymer:PC₇₁BM bulk heterojunction (BHJ) blend films were characterized using AFM and transmission electron microscopy (TEM). The AFM images shown in Figure 2 reveal strong aggregation in the TzVTz-based copolymers blended with PC₇₁BM. The strong self-assembly properties of the TzVTz-based polymers induced the formation of large domains with a high roughness upon blending with PC₇₁BM. In the BDT-TzVTz:PC₇₁BM blend film, large domains with domain sizes of hundreds of nanometers and rough surfaces with an RMS surface roughness of 17.6 nm were observed. This result indicated inefficient exciton dissociation in the blend films due to the limited interface between the BDT-TzVTz donor and the PC₇₁BM acceptor.^[34-36] To decrease the domain size, DPE processing additive was introduced to polymer:PC₇₁BM blend solutions. Previous studies reported that the DPE additive prevents severe polymer and PC₇₁BM aggregation and forms a bicontinuous network in the blend systems.^[37,38] Processing the BDT-TzVTz:PC₇₁BM blend films with the DPE additive decreased the domain size and surface roughness of the active films, as intended. The DTBDT-TzVTz:PC₇₁BM blend films, although similar trends were observed in the presence of the additive. The surface roughness values decreased from 3.10 to 1.44 nm in the blend films prepared without or with the additive, respectively.



Figure 2. AFM images of polymer:PC $_{71}$ BM blend films spin-coated (a,c) without or (b,d) with the 3% DPE additive.

The TEM measurements revealed the bulk morphologies of the blend films (Figure 3). The large domains observed in AFM images of the BDT-TzVTz:PC71BM film were also observed in TEM images and indicated PC71BM-rich domains. The large domain size and unconnected pathways in the PC71BM-rich domains suggested the presence of unfavorable exciton dissociation and charge transport properties of the BDT-TzVTZ:PC71BM blend film prepared without DPE, which can lead to low photovoltaic performances.^[34,37,39] The addition of DPE to the BDT-TzVTz:PC71BM blends decreased the domain size, thereby increasing the chance of exciton dissociation.^[34-36] The DTBDT-TzVTz:PC71BM blend films displayed homogeneous bulk morphologies compared to that of BDT-TzVTz:PC71BM. Although the DTBDT-TzVTz copolymer displayed a stronger crystallinity, it provided superior miscibility with the PC71BM acceptor compared to BDT-TzVTz. These results may be interpreted in terms of the molecular structures of the two TzVTz-based copolymers. Compared to BDT-TzVTz, the bulky donor units in DTBDT-TzVTz

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are separated by a larger space, and this structure provides adequate space to allow PC₇₁BM intercalation into the polymers. The facile intercalation of PC₇₁BM appears to have contributed to the homogeneous morphology.^[40,41] The addition of DPE to the DTBDT-TzVTz:PC₇₁BM blend film induced the formation of small domains and a nano-fibrillar structure. Within the DPE-containing DTBDT-TzVTz:PC₇₁BM blend film, the photogenerated excitons can have a greater chance of dissociating due to the homogeneously blended morphologies, and the crystalline interpenetrating structure can facilitate charge transport.^[34,37,42]



Figure 3. TEM images of polymer:PC $_{71}BM$ blend films processed (a,c) without or (b,d) with the 3% DPE additive.

Photoluminescence (PL) measurements were carried out to measure the exciton dissociation properties in the four polymer:PC₇₁BM blend films (Figure S10). The PL spectra of the DTBDT-TzVTz:PC₇₁BM blends exhibit higher photoluminescence quenching efficiencies (PLQE) with lower PL intensities compared to the BDT-TzVTz blends and indicate that the excitons were well-dissociated into charge carriers in the blend films as the emission was efficiently quenched due to the larger interface between the DTBDT-TzVTz and PC₇₁BM.^[43,44] The PL spectra of the DPE-containing blend films, which displayed low PL intensities, showed that exciton dissociation was more efficient in the blend films prepared with DPE, as expected from the AFM and TEM measurements.

The crystalline structures of the TzVTz-based polymers in the polymer:PC₇₁BM blend films were investigated in search of a deeper understanding of the structural effects on the blend films morphologies and photovoltaic characteristics. Grazing incidence wide angle x-ray scattering (GIWAXS) studies were performed, as shown in Figure 4. The TzVTz-based polymer peaks in the 2D-GIWAXS patterns indicated that the edge-on orientation was dominant for the polymers in blend films, whereas randomly oriented crystals were evident in the scattering patterns. Line-cut

profiles in the in-plane direction were extracted to compare the peak position and intensity (Figure S12). The amorphous halo at q ≈ 1.31 Å⁻¹ was attributed to the PC₇₁BM domains.^[45,46] The (*h*00) peaks in the scattering patterns of the BDT-TzVTz:PC₇₁BM blend films prepared with or without the DPE additive appeared at q ≈ 0.32 and 0.65 Å⁻¹, giving a *d*-spacing of 1.93 nm. The (010) π-π stacking peak was observed at q ≈ 1.86 Å⁻¹, and the π-π stacking distance was 3.38 Å. In the DTBDT-TzVTz:PC₇₁BM blend films prepared with or without the DPE additive, the (*h*00) peaks were observed at q ≈ 0.29 and 0.59 Å⁻¹, giving a d-spacing of 2.13 nm. The increased *d*-spacing of DTBDT-TzVTz seems to originate from the larger core of DTBDT than BDT. The π-π stacking peak was observed at q ≈ 1.84 Å⁻¹, indicating a π-π stacking distance of 3.41 Å.

The (h00) peaks displayed an slightly enhanced intensity in the case of the DTBDT-TzVTz:PC71BM films compared to the BDT-TzVTz:PC71BM films. The maintenance of crystallinity in the DTBDT-TzVTzPC71BM blends which exhibited better miscibility with PC71BM compared to those of BDT-TzVTz:PC71BM blends was attributed to the copolymer design strategy. The extended conjugated core and improved planarity of the backbone in the DTBDT-TzVTz polymer facilitated crystallization. These results agreed with the higher photovoltaic performances measured in the DTBDT-TzVTz:PC71BM photovoltaic devices compared to the performances in the BDT-TzVTz-based devices, in that the improved miscibility and maintained crystallinity improve the photovoltaic properties.^[3,34,37] In addition, the (100) and (200) polymer peaks in the scattering patterns of the blend films processed with the DPE additive were slightly stronger in intensity, indicating a stronger degree of crystallinity. The enhanced crystallinity of the BDT-TzVTz and DTBDT-TzVTz polymers in the DPE-containing blend films may improve the charge transport properties of the DPE-containing device.

A morphological analysis revealed the superior miscibility between DTBDT-TzVTz and $PC_{71}BM$ and the greater crystallinity in the DTBDT-TzVTz film. The polymer: $PC_{71}BM$ active layers optimized with the DPE additive exhibited a better miscibility and stronger crystallinity, which can result in efficient exciton dissociation and charge carrier transport. The small domains and nano-fibrillar crystalline structures of the DPE-added DTBDT-TzVTz: $PC_{71}BM$ device accounted for the promising photovoltaic performance of the TzVTz-based polymer discussed below.

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Figure 4. 2D-GIWAXS patterns obtained from the polymer:PC71BM blend films processed (a,c) without or (b,d) with the DPE additive.

Organic Field-Effect Transistor Properties

The charge transport properties of the BDT-TzVTz and DTBDT-TzVTz polymers and the potential utility of the TzVTz-based polymers as active materials in OFET devices were explored by fabricating BDT-TzVTz and DTBDT-TzVTz-based OFETs using a spin-coating method. The extracted OFET parameters are summarized in Table 2. As shown in Figure 5 and Figure S11, the devices displayed typical p-channel transfer characteristics. Initially, the field-effect mobility (μ_h) of the as-spun BDT-TzVTz film was $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} (I_{on}/I_{off} = 1.0 \times 10^5)$ in the saturation regime. Its hole mobility increased to 2.5 \times 10⁻³ cm² V⁻¹ s⁻¹ (I_{on}/I_{off} = 9×10^4) as the annealing temperature increased to 200 °C. For the DTBDT-TzVTz-based OFET, the mobility values of the asspun film and the annealed film at 150 °C were 2.58 \times 10⁻² cm² $V^{-1} s^{-1} (I_{on}/I_{off} = 1 \times 10^4)$ and 3.68 × 10⁻² cm² V⁻¹ s⁻¹ (I_{on}/I_{off} = 2 × 10³), respectively. These OFET performances of BDT-TzVTz and DTBDT-TzVTz dovetailed with the UV-vis absorption spectra and AFM data. The longer conjugation length of the DTBDT unit compared to the BDT unit provided a higher degree of m-electron delocalization and more favorable molecular packing in the DTBDT-TzVTz film than in the BDT-TzVTz film.^[33,47]



Figure 5. (a, b) Output, and (c, d) transfer characteristics of the best performed OFET devices incorporating (a, c) BDT-TzVTz and (b, d) DTBDT-TzVTz.

Table 2. OFET device characteristics of the TzVTz-based polymers.						
Polymer	Annealing temp. (°C)	μ _{avg} (cm² V ⁻¹ s ⁻¹)	µ _{max} (cm² V⁻¹ s⁻¹)	on/off ratio	V _{th} (V)	
	As cast	0.0011	0.0012	1 × 10 ⁵	-14	
BDT-	100	0.0012	0.0013	2 × 10 ⁴	-9	
TzVTz	150	0.0018	0.0019	3 × 10 ⁴	-10	
	200	0.0022	0.0025	9 × 10 ⁴	-10	
	As cast	0.0215	0.0258	1 × 10 ⁴	8	
DTBDT-	100	0.0234	0.0295	4 × 10 ³	3	
TzVTz	150	0.0315	0.0368	2 × 10 ³	0	
	200	0.0153	0.0201	7 × 10 ³	29	

Photovoltaic Characteristics

The photovoltaic properties of the TzVTz-based polymers were explored in conventional solar cells using a device configuration comprising glass/indium tin oxide (ITO)/poly(3,4ethylenedioxythiophene):poly(styrene-sulfonate)

(PEDOT:PSS)/polymer:PC71BM/LiF/Al. The photovoltaic performances are summarized in Figure 6 and Table 3. An active layer composed of TzVTz-based polymers and PC71BM was optimized at a blend ratio of 1:4 (w/w) as shown in Figure S13 and Table S1 and a concentration of 30 mg ml⁻¹ in chlorobenzene. The photovoltaic devices processed with 3% (v/v) DPE additive provided improved PCEs with a higher short-circuit current (J_{sc}) and fill factor (FF). The BDT-TzVTz:PC71BM device prepared without DPE showed an average PCE of 1.31% with an opencircuit voltage (V_{oc}) of 0.78 V, a J_{sc} of 3.93 mA cm⁻², and a FF of

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0.43. The BDT-TzVTz photovoltaic device prepared with DPE exhibited an average PCE of 1.99% with a V_{oc} of 0.77 V, a J_{sc} of 5.53 mA cm⁻², and a FF of 0.47. The higher J_{sc} and FF values measured in the photovoltaic devices prepared with DPE agreed well with the improved morphologies of the BDT-TzVTz:PC71BM blend films discussed above. As the DPE additive alleviate the severe phase separation between polymer donor and PC71BM acceptor, which can limit the exciton diffusion to the interface, the higher device performances were achieved. The DTBDT-TzVTz device prepared without DPE showed an average PCE of 4.27% with a $V_{\rm oc}$ of 0.79 V, a $J_{\rm sc}$ of 8.74 mA cm⁻², and a FF of 0.62. As with the BDT-TzVTz device, a distinctly higher performance was achieved in the DTBDT-TzVTz device processed with the DPE additive. This device displayed an average PCE of 6.58%, a $V_{\rm oc}$ of 0.79, a J_{sc} of 13.17 mA cm⁻², and a FF of 0.64. The highest PCE obtained from the DTBDT-TzVTz:PC71BM device was 6.73%. This PCE value is among the highest yet recorded in OPVs that incorporate thiazole-based copolymers. The superior photovoltaic performances of DTBDT-TzVTz compared to those of BDT-TzVTz, particularly the higher J_{sc} and slightly increased FF, appeared to derive from the active layer morphology and higher hole mobility of DTBDT-TzVTz, considering that the two TzVTz-based copolymers displayed comparable light absorption properties and energy levels. The homogeneous morphology of DTBDT-TzVTz:PC71BM blend films efficient for exciton dissociation is considered to be the main factor underlying the superior performance of the DTBDT-TzVTz:PC71BM photovoltaic device. The moderate domain size and nano-fibrallar structure in DTBDT-TzVTz:PC71BM devices processed with DPE are in agreement with photovoltaic characteristics. The external quantum efficiency (EQE) curves of TzVTz-based photovoltaic devices shown in Figure 6b exhibited photoresponse from the wave length of 300 to 700 nm. The photovoltaic devices showed balanced photoresponse to the wavelength of 650 nm, but the limited photoresponse in longer wavelength region can be responsible for the limited overall EQE and J_{sc} values of the devices. As the EQE curves were obtained from the devices with polymer:PC71BM blend ratio of 1:4, the photoresponse in light absorption region of PC71BM were slightly prominent. The two TzVTz-based polymers showed similar trend of EQE curves as a function of the wavelength, which indicates similar light absorption properties of TzVTz-based devices. The distinctly increased intensity in EQE curves of DTBDT-TzVTz-based devices reflects that the charge carrier generation was more efficient in these devices as discussed above. The EQE also increased as a result of introducing DPE, and the curves according to the wavelength revealed that the DPE additive affected charge transfer or transport rather than light absorption characteristics.



Figure 6. (a) *J-V* characteristics of the polymer:PC₇₁BM BHJ solar cells processed without or with the DPE additive, and (b) EQE spectra obtained from the corresponding devices.

Table 3. Photovoltaic characteristics of the TzVTz-based polymer:PC71BM
BHJ solar cells.

Polymer	Additive	Voc (V)	J₅c (mA cm ⁻²)	FF	PCE _{avg} (%)	PCE _{max} (%)
BDT-	w/o DPE	0.78 ± 0.01	3.93 ± 0.18	0.43 ± 0.01	1.31 ± 0.10	1.41
TzVTz	w DPE	0.77 ± 0.01	5.53 ± 0.22	0.47 ± 0.01	1.99 ± 0.11	2.11
DTBDT-	w/o DPE	0.79 ± 0.01	8.74 ± 0.14	0.62 ± 0.01	4.27 ± 0.08	4.40
TzVTz	w DPE	0.79 ± 0.01	13.17 ± 0.21	0.64 ± 0.01	6.58 ± 0.18	6.73

The average values and standard deviations were obtained from 8 devices.

Conclusions

To investigate the effects of molecular structure in thiazole-based polymers on the crystalline behavior and device characteristics, a series of copolymers with thiazole-vinylene-thiazole as the electron-accepting unit, combined with BDT or DTBDT electrondonating units, was synthesized. The extended coplanarity of the TzVTz-based copolymers enhanced the intermolecular interactions and charge transport properties investigated in OFET and OPV devices. As DTBDT-TzVTz showed higher degree of πelectron delocalization and better molecular packing than BDT-TzVTz, higher hole mobilities were obtained from DTBDT-TzVTz. The BDT-TzVTz and DTBDT-TzVTz polymers exhibited charge carrier mobilities of 2.5 x 10^{-3} cm² V⁻¹ s⁻¹ and 3.7 x 10^{-2} cm² V⁻¹ s⁻¹ in OFET devices, respectively. The active layer of OPV devices prepared with the TzVTz-based polymers and PC71BM were optimized by adding the DPE solvent additive. The DPE additive prevented the formation of large domains favored by the planar structure and strong aggregation behaviors of the polymers, thereby improving the device performances. The TzVTz-based OPV devices gave the highest PCEs of 2.11% for BDT-TzVTz and 6.73% for DTBDT-TzVTz. The morphological characteristics suggested that the distinctly better performance of the DTBDT-TzVTz film arose from its stronger crystallinity and superior miscibility with PC71BM in the active layer.

Experimental Section

OFET Device Fabrication and Mobility Measurements

OFETs based on BDT-TzVTz and DTBDT-TzVTz were fabricated using heavily N-doped silicon with a 300 nm thick thermally grown SiO₂ dielectric layer. All OFET devices employed a bottom-gate/top-contact configuration, and polymer films were deposited onto ODTS-modified Si/SiO₂ substrates along with gold source/drain electrodes (with a channel region 50 μ m in

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length and 1000 μ m in width). Before modifying the silicon oxide surface with ODTS, the silicon oxide surface was cleaned with piranha solution (H₂O₂ (40 mL)/ concentrated H₂SO₄ (60 mL)) for 20 min at 250 °C, rinsed with distilled water several times, and ozone-treated for 20 min. BDT-TzVTz and DTBDT-TzVTz polymers were deposited onto the chemically modified SiO₂ surfaces by spin-coating at 2000 rpm from 0.2 wt% 1,2-dichlorobenzene solutions. The OFET devices were annealed for 10 min under a nitrogen atmosphere. The electrical characteristics of the fabricated OFETs were measured in air using Keithley 2400 and 236 source/measure units. Field-effect mobility values were extracted in the saturation regime from the slope of the source-drain current.

Photovoltaic Device Fabrication and Characterization

The photovoltaic devices were fabricated to have a structure of glass/ITO/PEDOT:PSS/polymer:PC71BM/LiF/Al. The patterned ITO substrates were pre-cleaned with detergent, deionized water, acetone, and isopropyl alcohol in an ultrasonic bath. After residual solvents were removed using pressurized nitrogen, the substrates were exposed to UVozone for 30 min. A PEDOT:PSS layer was then deposited onto the substrate by spin-coating at 4000 rpm for 60 s and baking at 120 °C for 30 min. The active solutions were prepared at a weight ratio of 1:4 and a concentration of 30 mg mL⁻¹ in chlorobenzene with 3% (v/v) DPE. The solutions were stirred overnight in nitrogen-filled glove box, filtered through a 5 µm-polytetrafluoroethylene (PTFE) filter, and spin-coated onto the PEDOT:PSS layer to have a film thickness of ca. 100 nm. Subsequently, 0.8 nm LiF and 100 nm Al layers were deposited as the top electrode by thermal evaporation under 3×10⁻⁶ Torr. The J-V characteristics were measured using a Keithley Model 2400 source measurement unit, and a 450W Xenon lamp (Oriel) with an AM 1.5 G filter was used as the solar simulator. The light intensity was calibrated to 100 mW cm⁻² using a silicon cell calibrated with a KG5 filter, which was traced to the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) curves were obtained using a photomodulation spectroscopy setup (model Merlin, Oriel).

Instruments and Characterization

The ¹H-NMR and ¹³C-NMR spectra were recorded using a Bruker AM-300 spectrometer and 500 Spectrometer. The thermal analysis was performed on a TA TGA 2100 thermogravimetric analyzer under nitrogen on a TA instrument 2100 DSC. The sample was heated at 20 °C min-1. Differential scanning calorimetry was conducted under nitrogen using a TA instrument 2100 DSC. The sample was heated at 20 °C min⁻¹ from 0 °C to 300 °C. UV-vis absorption studies were carried out using a Perkin-Elmer LAMBDA-900 UV/VIS/IR spectrophotometer. Cyclic voltammetry (CV) was performed on an EG and G Parc model 273 Å potentiostat/galvanostat system with a three-electrode cell in a solution of Bu4NCIO4 (0.1 M) in chloroform solvent at a scan rate of 100 mVs⁻¹. A Pt wire was used as the counter electrode, and an Ag/AgNO3 (0.1 M) electrode was used as the reference electrode. For AFM and GIWAXS measurements, polymer of polymer:PC71BM thin films were prepared on SiO2/PEDOT:PSS substrates. The AFM images were obtained using a Digital Instruments Multimode IIIa operated in the tapping mode, and GIWAXS studies were conducted at the 3C SAXS I beamline of the Pohang Accelerator Laboratory (PAL) in Korea. PL and TEM measurement were conducted by depositing the polymer:PC71BM thin films by spin-coating onto the top of the glass/PEDOT:PSS substrate. The PL spectra were obtained using an FP 6500, JASCO spectrophotometer. The active thin films used for the TEM measurements were floated on deionized water and then transferred to 200-mesh grids. TEM measurements were performed using a HITACHI 7600 operated at 100 kV..

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Keywords: Thiazole-based copolymer • Intermolecular interaction • Bulk heterojunction morphology • Organic field-effect transistor • Polymer solar cell

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We studied the effects of molecular structure in thiazole-based polymers on active layer morphologies and device performances of electronic and photovoltaic devices

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Morphology Driven by Molecular Structure of Thiazole-Based Polymers for Use in Field-Effect Transistors and Solar Cells