# Pyradinodithiazole: An Electron-Accepting Monomer Unit for Hole-Transporting and Electron-Transporting Conjugated Copolymers

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S *Supporting Information*

ABSTRACT: Pyradinodithiazole (**PDTz**) was designed as a new electron-accepting unit. The physical property measurements indicated that the **PDTz** unit has stronger electron-accepting characteristics than thiazolothiazole and benzodithiazole. A donor–acceptor copolymer containing **PDTz** as an acceptor unit was synthesized for hole-transporting semiconductors in organic photovoltaics (OPV). Furthermore, an acceptor–acceptor copolymer containing **PDTz** has also been developed for electron-transporting OPV materials. These copolymer-based blend films showed expected photovoltaic characteristics in individual OPV devices.
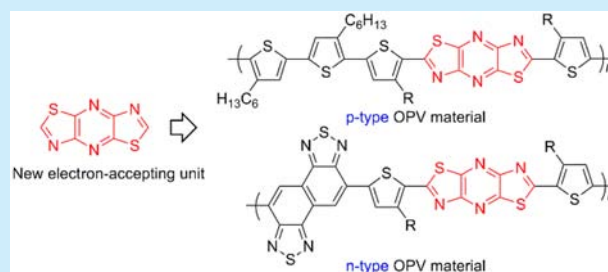
Organic semiconducting materials based on π-conjugated systems have attracted great attention due to their application to electronic devices such as organic light-emitting diodes, organic field-effect transistors, and organic photovoltaics (OPVs).[1] The availability of both hole-transporting (p-type) and electron-transporting (n-type) semiconductors is essential for the accomplishment of high device performance in such applications. Considering the development of OPVs, it is generally accepted that p-type materials should exhibit not only the semiconducting carrier-transport characteristics but also a reduced optical energy gap for the effective utilization of a wide range of solar light and a low-lying highest occupied molecular orbital (HOMO) energy level for gaining a high open-circuit voltage (V_{OC}).[2] As a result of active investigations, π-conjugated copolymers composed of alternating electron-donor (D) and electron-acceptor (A) units have been established as a rational materials design to fulfill these requirements.[2] However, the acceptor units that can be applicable to D–A copolymers are still limited due to the difficulty of molecular design for lowering the lowest unoccupied molecular orbital (LUMO).[3] Moreover, owing to the same difficulty, the development of n-type OPV polymer materials based on electron-accepting π-conjugated units has largely lagged behind that of p-type OPV materials.[4] Under this situation, therefore, the development of new acceptor units is still of significance for constructing both the p-type and n-type semiconducting materials.

Thiazole is an electron-deficient aromatic heterocycle, and its-containing π-extended derivatives such as bithiazole, carbonyl-bridged bithiazole,[5a,b] biscarbonyl-bridged phenylene-inserted bithiazole,[5c–e] thiazolothiazole (**TzTz**),[6–13] and benzodithiazole (**BDTz**)[14–18] were utilized as acceptor units in semiconducting materials (Figure 1a). Among them, the **TzTz** or **BDTz** units were incorporated into D–A copolymers to function as p-type materials in OPVs.[8b,11–13,15b,18b] We anticipated that the exploration of new thiazole-fused derivatives having stronger

electron-accepting ability than **TzTz** and **BDTz** leads to the decreased optical energy gap and lowered HOMO energy level of resulting D–A copolymers. In addition, such units can also be expected to access to n-type polymers. Based on this hypothesis, we designed pyradinodithiazole (**PDTz**) as a new accepting unit by the replacement of the benzene ring in **BDTz** with an electron-deficient pyrazine ring (Figure 1a). The theoretical molecular-orbital calculations of these units, performed by density functional theory (DFT) at the B3LYP/6-31 G(d,p) level, support our molecular design that **PDTz** possesses a low-lying LUMO energy level compared with both **TzTz** and **BDTz** as shown in Figure 1b. Since **PDTz** has not been synthesized so far, we first synthesized a bis(3-dodecylthiophene)-substituted unit derivative, **PDTz-T$_{12}$**, and compared the properties of this compound with those of **TzTz-T$_{12}$**[10] and **BDTz-T$_{12}$**[15b] (Figure 1a). In contrast to **PDTz**, **TzTz**, and **BDTz**, these thiophene-connected systems showed similar HOMO and LUMO frontier orbitals owing to the extension of conjugation (Figure S1, Supporting Information). Then, we report on the synthesis, properties, and OPV performance of new D–A and A–A copolymers **PDTz-T$_{DT}$-HH** and **P-PDTz-T$_{DT}$-NTz**, which have an alternative combination of **PDTz-T$_{DT}$** with 4,4′-dihexyl-2,2′-bithiophene (**HH**) or naphtho[1,2-*c*:5,6-*c*′]bis[1,2,5]thiadiazole (**NTz**), respectively (Figure 1c).

Synthesis of **PDTz-T$_{12}$** and **3b** (dibromo derivative of **PDTz-T$_{DT}$**) is shown in Scheme 1. In general, the **BDTz** framework was obtained by the acid-catalyzed condensation of 2,5-diamino-1,4-benzenedithiol with 2 equiv of aldehyde.[15b] However, this reaction cannot be applied to the synthesis of **PDTz** because of the difficulty of obtaining 3,6-diaminopyrazine-2,5-dithiol. We have thus planned another synthetic route based on the
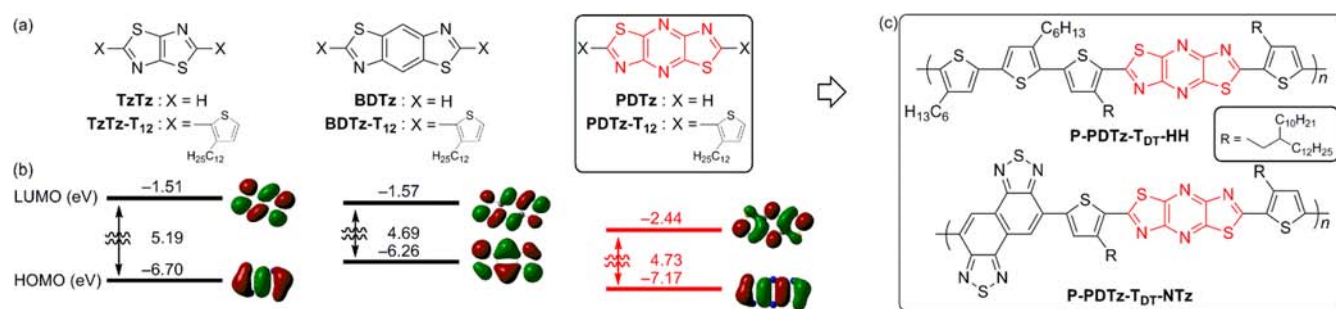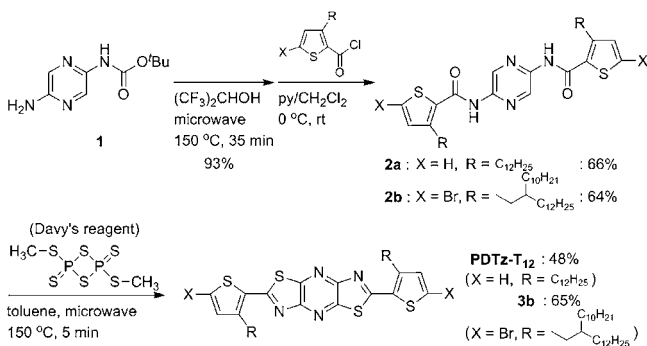
Figure 1. (a, c) Chemical structures used in this study. (b) Calculated frontier orbitals and their energies of **TzTz**, **BDTz**, and **PDTz**.

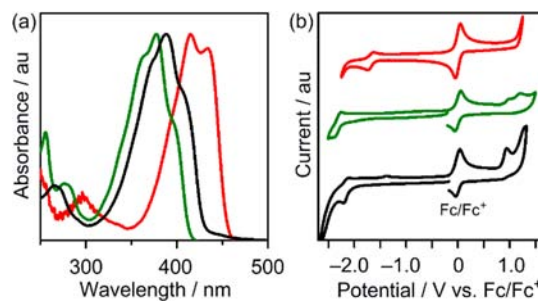**Scheme 1. Synthesis of PDTz-T₁₂ and 3b**

Figure 2. (a) UV−vis absorption spectra of **PDTz-T₁₂** (red), **TzTz-T₁₂** (black), and **BDTz-T₁₂** (green) in CF. (b) Cyclic voltammograms in *o*-DCB/CH₃CN containing 0.1 M TBAPF₆.

intramolecular construction of thiazole ring via the thioamide derivative generated in situ from the corresponding amide.[19] The (*tert*-butyloxy)carbonyl group in compound **1** was deprotected in 1,1,1,3,3,3-hexafluoroisopropyl alcohol under microwave irradiation conditions to afford 2,5-diaminopyrazine,[20] which was subsequently reacted with the thiophenecarbonyl chlorides to give amide compounds **2**. Finally, the reaction of **2** with an excess amount of Davy's reagent gave **PDTz-T₁₂** in 48% yield and **3b** in 65% yield. It should be mentioned that the treatment with sodium hypochlorite during the isolation of **PDTz-T** and **3b** is crucial to remove a trace of sulfur-containing impurities derived from Davy's reagent; otherwise, the following polymerization reactions result in the formation of low-molecular-weight copolymers. The experimental details and characterization data are shown in the Supporting Information.

The photophysical and electrochemical properties of **PDTz-T₁₂** and reference compounds **TzTz-T₁₂** and **BDTz-T₁₂** were examined by UV−vis absorption spectroscopy in chloroform (CF) solutions and cyclic voltammetry (CV) measurements, respectively, and the data obtained are summarized in Table 1. As shown in Figure 2a, the absorption spectrum of **PDTz-T₁₂** displayed significant bathochromic shift compared to those of **TzTz-T₁₂** and **BDTz-T₁₂**; therefore, the optical HOMO−LUMO energy gap (ΔE_g^{opt}) of **PDTz-T₁₂** (2.69 eV), extracted from the absorption onset, is smaller than those of **TzTz-T₁₂** (2.87 eV) and **BDTz-T₁₂** (2.95 eV). CV was performed in *o*-

Table 1. Photophysical and Electrochemical Properties

compd	λ_{max}^{a} (nm)	$\Delta E_g^{opt\,b}$ (eV)	$E^{red}_{1/2}{}^{c}$ (V)	$E^{ox}_{p.a.}{}^{d}$ (V)
PDTz-T₁₂	415, 434	2.69	−1.79	nd[e]
TzTz-T₁₂	388	2.87	−2.15	0.93
BDTz-T₁₂	378	2.95	−2.31	0.95, 1.20

[a]In CF. [b]$\Delta E_g^{opt} = 1240/\lambda_{onset}$. [c]In *o*-DCB/CH₃CN containing 0.1 M TBAPF₆. V vs Fc/Fc⁺. [d]Irreversible. [e]Not detected.

dichlorobenzene (*o*-DCB)/CH₃CN solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The redox potentials were referenced against the ferrocene/ferrocenium (Fc/Fc⁺) couple as an internal standard. As shown in Figure 2b, **TzTz-T₁₂** and **BDTz-T₁₂** exhibited oxidation waves, whereas within the potential window, no oxidation wave could be detected for **PDTz-T₁₂**. On the other hand, reversible reduction waves were observed for all three compounds. The half-wave reduction potential ($E^{red}_{1/2}$) of **PDTz-T₁₂** (−1.79 V) is observed at a more positive potential than those of **TzTz-T₁₂** (−2.15 V) and **BDTz-T₁₂** (−2.31 V), manifesting the more electron-accepting characteristics of the **PDTz** unit than **TzTz** and **BDTz** as predicted from the theoretical calculations: this trend is qualitatively in agreement with the theoretical calculations of thiophene-connected model compounds (Figure S1, Supporting Information). These results imply the potential of **PDTz** as an acceptor unit in both D−A and A−A copolymers for OPVs.

We first attempted the synthesis of copolymer **P-PDTz-T₁₂-HH** (structure shown in Figure S2, Supporting Information). However, the number-average molecular weight (M_n) of this copolymer was low (M_n = 4.3 kDa), owing to its low solubility. Thus, in place of dodecyl groups, branched 2-decyltetradecyl groups were incorporated into the monomer unit, and thus, D−A type copolymer **P-PDTz-T_DT-HH** was synthesized via a Stille coupling reaction of **3b** with distannylbithiophene **4** under microwave irradiation (Scheme 2). The synthesized copolymer was purified using a Soxhlet apparatus by successive washing with methanol and hexane to remove low molecular weight compounds and finally by extracting with CF. Analytical gel-permeation chromatography (GPC) using a polystyrene standard with CF as eluent at 40 °C determined the M_n of **P-PDTz-T_DT-HH** to be 13.5 kDa with molecular weight dispersity ($Đ_M$) of 1.2. On the other hand, since the preparation of strongly electron-deficient **NTz** and its diboronic ester **5** have been

Scheme 2. Synthesis of Copolymers
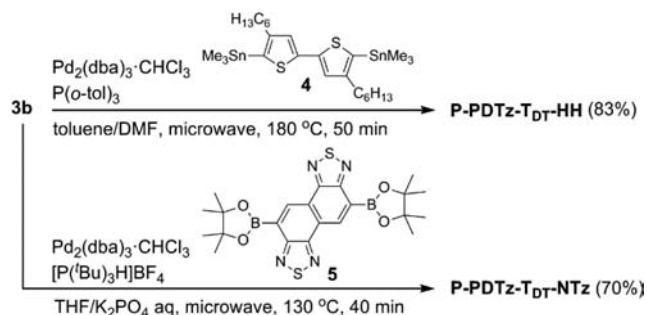
reported recently,[21] **3b** was copolymerized with **5** under Suzuki coupling conditions to generate A−A-type copolymer **P-PDTz-T_{DT}-NTz**, which was collected by Soxhlet extraction with CF (M_n = 46.8 kDa, D_M = 4.3). These synthetic results imply that the nitrogen atoms on the pyrazine in the **PDTz** unit do not disturb the transition-metal-catalyzed coupling reactions. Thanks to the branched long alkyl chains, both the copolymers were soluble in chlorinated solvents such as CF, chlorobenzene, and o-DCB, enabling physical property measurements in the solution state and device fabrications using a solution process. Thermogravimetric analysis (TGA) indicated the moderate thermal stability of **P-PDTz-T_{DT}-HH** and **P-PDTz-T_{DT}-NTz** with 5% weight loss temperatures (T_d) of 191 and 250 °C, respectively (Figure S3a, Supporting Information). Note that TGA of **P-PDTz-T_{12}-HH** showed high T_d of 384 °C, indicating that the **PDTz** unit intrinsically has a thermal stability. Differential scanning calorimetry (DSC) analysis revealed no noticeable thermal transition in the range of 50−300 °C for both the copolymers (Figure S3b, Supporting Information).

The UV−vis absorption spectra of **P-PDTz-T_{DT}-HH** and **P-PDTz-T_{DT}-NTz** in CF solutions and films are shown in Figure 3,
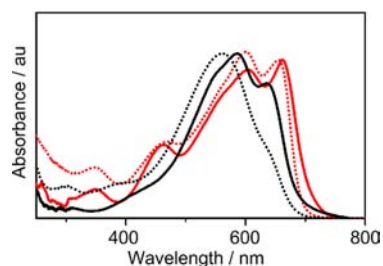

Figure 3. UV−vis absorption spectra of **P-PDTz-T_{DT}-HH** (black) and **P-PDTz-T_{DT}-NTz** (red) in CF solution (dashed line) and as films (solid line).

and their key data are collected in Table 2. Both of the copolymers showed two absorption bands. The high energy bands (400−500 nm) are attributed to π−π* transitions, and the low energy bands (500−700 nm) are attributed to intramolecular charge transfer (ICT) between the neighboring units in the

Table 2. Characteristics and Properties of Copolymers

compd	λ_{max}^{a} (nm)	$\Delta E_g^{opt\,b}$ (eV)	E_{HOMO}^{c} (eV)	E_{LUMO}^{d} (eV)
P-PDTz-T_{DT}-HH	587, 640	1.75	−5.59	−3.84
P-PDTz-T_{DT}-NTz	604, 661	1.73	−5.89	−4.16

^{a}In film. $^b\Delta E_g^{opt}$ = 1240/λ_{onset}. ^{c}Determined by PESA. $^d E_{LUMO}$ = E_{HOMO} + ΔE_g^{opt}.

copolymers. Even in the case of A−A copolymer **P-PDTz-T_{DT}-NTz**, differences in electron-accepting strength between **PPDTz** and **NTz** led to the appearance of ICT: as shown in Figure S4 (Supporting Information), DFT calculations reveal that the LUMO of model compound for **P-PDTz-T_{DT}-NTz** is localized on the **NTz** moiety, while the HOMO is delocalized over the whole conjugated backbone. The absorption spectra of all the copolymer films were slightly red-shifted compared to those in solutions, which is ascribed to intermolecular interaction between conjugated backbones. ΔE_g^{opt} of **P-PDTz-T_{DT}-HH** and **P-PDTz-T_{DT}-NTz** deduced from the absorption onsets of the films are 1.75 and 1.73 eV, respectively. The ionization potentials of the thin films were measured using photoelectron spectroscopy in air (PESA) to determine the HOMO energy levels (E_{HOMO}). From the onsets of the PESA results, the E_{HOMO}s of **P-PDTz-T_{DT}-HH** and **P-PDTz-T_{DT}-NTz** were determined to be −5.59 and −5.89 eV, respectively (Figure S5, Supporting Information). On the basis of these E_{HOMO} and E_g^{opt} values, the LUMO energy levels (E_{LUMO}) were calculated to be −3.84 eV for **P-PDTz-T_{DT}-HH** and −4.16 eV for **P-PDTz-T_{DT}-NTz**. These values, summarized in Table 2, fall under those of promising p-type or n-type OPV polymer materials as shown in Figure S6 (Supporting Information).

The charge-transporting characteristics of these copolymers were measured by the space-charge-limited currents (SCLC) method. D−A copolymer **P-PDTz-T_{DT}-HH** showed both hole and electron mobilities of 10^{-6} cm^2 V^{-1} s^{-1} order. A−A copolymer **P-PDTz-T_{DT}-NTz** also showed bipolar characteristics, while the electron mobility (3.4×10^{-5} cm^2 V^{-1} s^{-1}) is one magnitude higher than hole mobility (1.3×10^{-6} cm^2 V^{-1} s^{-1}) (Figure S7, Supporting Information).

In order to evaluate the OPV performance of these copolymers, bulk heterojunction (BHJ) solar cells were fabricated with an inverted structure of glass/indium tin oxide (ITO)/ZnO/active layer/MoOx/Ag. Note that we avoided a conventional device structure to prevent the influence of interaction between acidic poly(3,4-ethylenedioxy-thiophene:poly(styrenesulfonate) (PEDOT:PSS) and basic **PDTz**.[22] To test the p-type characteristics of **P-PDTz-T_{DT}-HH**, the active layer was fabricated under the combination with [6,6]phenyl-C_{61}-butyric acid methyl ester (PC$_{61}$BM) as an n-type semiconductor. On the other hand, electron-accepting **P-PDTz-T_{DT}-NTz** was blended with energetically matched poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]-dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]-thieno[3,4-b]thiophenediyl]] (PTB7) as the p-type semiconductor (Figure S6, Supporting Information). Optimized conditions are summarized in the Supporting Information. As we expected, both devices showed photovoltaic responses. The current density (J)−voltage (V) curves are shown in Figure 4a. The **P-PDTz-T_{DT}-HH**/PC$_{61}$BM-based device exhibited a power conversion efficiency (PCE) of 1.82% (V_{OC} = 0.83 V; short-circuit current (J_{SC}) = 4.86 mA cm^{-2}; fill factor (FF) = 0.45); this PCE value is comparable to those for the reported OPV devices based on the corresponding **TzTz**- or **BDTz**-incorporated copolymers with PC$_{71}$BM.[13b,15b] The increased electron-accepting characteristics of **PDTz** unit compared to those of **TzTz** and **BDTz** caused the decrease of HOMO energy level of the copolymer, reflected in the relatively high V_{OC}.[13b,15b] The appearance of OPV characteristics in **P-PDTz-T_{DT}-NTz**-based device indicates that **PDTz** unit can be installed in n-type OPV materials. However, small J_{SC} and FF values resulted in a moderate PCE of 0.33% (Table S1, Supporting Information).
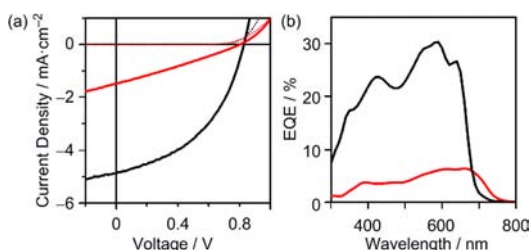
Figure 4. (a) *J*–*V* curves under illumination (solid line) and dark (dashed line). (b) EQE spectra of the **P-PDTz-T$_{DT}$-HH**/PC$_{61}$BM (black) and PTB7/**P-PDTz-T$_{DT}$-NTz** (red) OPV devices.

The external quantum efficiency (EQE) spectra of these devices are shown in Figure 4b, which are in good agreement with the observed J_{sc} values. The surface morphology images of the blend films, observed by atomic force microscopy (AFM), showed nanometer-scale aggregated domain with average roughness (R_a) of 3.6 and 1.4 nm for **P-PDTz-T$_{DT}$-HH**/PC$_{61}$BM and PTB7/**P-PDTz-T$_{DT}$-NTz**, respectively (Figure S8, Supporting Information). X-ray diffraction (XRD) measurements of both the pristine copolymer films and blend films did not show distinct diffraction peaks (Figure S9, Supporting Information), indicative of amorphous natures in the solid state.

In summary, **PDTz**, an electron-deficient multifused heteroaromatic compound composed of pyrazine and thiazole, has been designed and successfully synthesized by the formation of thiazole rings from the pyradine bisthioamide compound as a key reaction. The photophysical and electrochemical properties of **PDTz-T$_{12}$** were measured and compared with those of **BDTz-T$_{12}$** and **TzTz-T$_{12}$**, which indicates that the **PDTz** unit has stronger electron-accepting characteristics than **BDTz** and **TzTz**. To evaluate the potential of **PDTz** as an electron-accepting unit for conjugated copolymers, donor–acceptor type copolymer **P-PDTz-T$_{DT}$-HH** and acceptor–acceptor type copolymer **P-PDTz-T$_{DT}$-NTz** were synthesized, and their properties and charge-transporting characteristics were investigated. OPV devices based on the blend of **P-PDTz-T$_{DT}$-HH**/PC$_{61}$BM and PTB7/**P-PDTz-T$_{DT}$-NTz** showed photovoltaic responses with PCEs of 1.82% and 0.33%, respectively. This result indicates that **P-PDTz-TDT-HH** and **P-PDTz-TDT-NTz** act as p-type and n-type OPV materials, respectively, and **PDTz** has a potential of an electron-deficient unit for semiconducting polymers. Toward the improvement of semiconducting performance, further exploration of conjugated copolymers containing **PDTz** by the alkyl side-chain engineering and fine-tuning of D and/or A units is currently underway in our group.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02306.

TGA, DSC, PESA, SCLC, AFM images, XRD, synthetic details, NMR spectra, device fabrication, and calculation (PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) (a) Facchetti, A. *Chem. Mater.* **2011**, *23*, 733−758. (b) Holliday, S.; Donaghey, J. E.; McCulloch, I. *Chem. Mater.* **2014**, *26*, 647−663.

(2) Zhou, H.; Yang, L.; You, W. *Macromolecules* **2012**, *45*, 607−632.

(3) Zhang, Z.-G.; Wang, J. *J. Mater. Chem.* **2012**, *22*, 4178−4187.

(4) Facchetti, A. *Mater. Today* **2013**, *16*, 123−132.

(5) (a) Ie, Y.; Nitani, M.; Karakawa, M.; Tada, H.; Aso, Y. *Adv. Funct. Mater.* **2010**, *20*, 907−913. (b) Nitani, M.; Ie, Y.; Tada, H.; Aso, Y. *Chem. - Asian J.* **2011**, *6*, 2352−2361. (c) Ie, Y.; Ueta, M.; Nitani, M.; Tohnai, N.; Miyata, M.; Tada, H.; Aso, Y. *Chem. Mater.* **2012**, *24*, 3285−3293. (d) Ie, Y.; Sato, C.; Nitani, M.; Tada, H.; Aso, Y. *Chem. Lett.* **2014**, *43*, 1640−1642. (e) Ie, Y.; Sato, C.; Nitani, M.; Tada, H.; Aso, Y. *Chem. - Eur. J.* **2014**, *20*, 16509−16515.

(6) (a) Ando, S.; Nishida, J.-i.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Mater. Chem.* **2004**, *14*, 1787−1790. (b) Ando, S.; Nishida, J.-i.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 5336−5337.

(7) Peng, Q.; Peng, B.; Kang, T.; Neoh, K. G.; Cao, Y. *Macromolecules* **2005**, *38*, 7292−7298.

(8) (a) Osaka, I.; Sauvé, G.; Zhang, R.; Kowalewski, T.; McCullough, R. D. *Adv. Mater.* **2007**, *19*, 4160−4165. (b) Osaka, I.; Saito, M.; Mori, H.; Koganezawa, T.; Takimiya, K. *Adv. Mater.* **2012**, *24*, 425−430.

(9) Naraso; Wudl, F. *Macromolecules* **2008**, *41*, 3169−3174.

(10) Mishra, S. P.; Palai, A. K.; Kumar, A.; Srivastava, R.; Kamalasanan, M. N.; Patri, M. *Macromol. Chem. Phys.* **2010**, *211*, 1890−1899.

(11) Jung, I. H.; Yu, J.; Jeong, E.; Kim, J.; Kwon, S.; Kong, H.; Lee, K.; Woo, H. Y.; Shim, H.-K. *Chem. - Eur. J.* **2010**, *16*, 3743−3752.

(12) Shi, Q.; Fan, H.; Liu, Y.; Hu, W.; Li, Y.; Zhan, X. *J. Phys. Chem. C* **2010**, *114*, 16843−16848.

(13) (a) Subramaniyan, S.; Xin, H.; Kim, F. S.; Shoaee, S.; Durrant, J. R.; Jenekhe, S. A. *Adv. Energy Mater.* **2011**, *1*, 854−860. (b) Subramaniyan, S.; Xin, H.; Kim, F. S.; Murari, N. M.; Courtright, B. A. E.; Jenekhe, S. A. *Macromolecules* **2014**, *47*, 4199−4209.

(14) Wolfe, J. F.; Loo, B. H.; Arnold, F. E. *Macromolecules* **1981**, *14*, 915−920.

(15) (a) Osaheni, J. A.; Jenekhe, S. A. *Chem. Mater.* **1992**, *4*, 1282−1290. (b) Ahmed, E.; Subramaniyan, S.; Kim, F. S.; Xin, H.; Jenekhe, S. A. *Macromolecules* **2011**, *44*, 7207−7219.

(16) Mamada, M.; Nishida, J.-i.; Tokito, S.; Yamashita, Y. *Chem. Lett.* **2008**, *37*, 766−767.

(17) Osaka, I.; Takimiya, K.; McCullough, R. D. *Adv. Mater.* **2010**, *22*, 4993−4997.

(18) (a) Mike, J. F.; Intemann, J. J.; Cai, M.; Xiao, T.; Shinar, R.; Shinar, J.; Jeffries-EL, M. *Polym. Chem.* **2011**, *2*, 2299−2305. (b) Bhuwalka, A.; Ewan, M. D.; Mike, J. F.; Elshobaki, M.; Kobilka, B.; Chaudhary, S.; Jeffries-EL, M. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 1533−1540.

(19) Fruit, C.; Turck, A.; Plé, N.; Quéguiner, G. *J. Heterocycl. Chem.* **2002**, *39*, 1077−1082.

(20) Choy, J.; Jaime-Figueroa, S.; Jiang, L.; Wagner, P. *Synth. Commun.* **2008**, *38*, 3840−3853.

(21) Kawashima, K.; Miyazaki, E.; Shimawaki, M.; Inoue, Y.; Mori, H.; Takemura, N.; Osaka, I.; Takimiya, K. *Polym. Chem.* **2013**, *4*, 5224−5227.

(22) Ratcliff, E. L.; Bakus, R. C., II; Welch, G. C.; van der Poll, T. S.; Garcia, A.; Cowan, S. R.; MacLeod, B. A.; Ginley, D. S.; Bazan, G. C.; Olson, D. C. *J. Mater. Chem. C* **2013**, *1*, 6223−6234.