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Donor–acceptor-Type Polymers Based on Dithieno[2,3-*b*;7,6-*b*]carbazole Unit for Photovoltaic Applications

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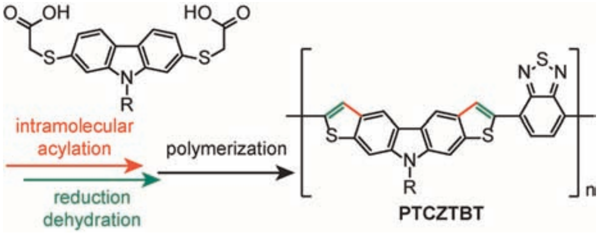
ABSTRACT



Dithieno[2,3-*b*;7,6-*b*]carbazole (TCZT), a type of heteropentacene with nitrogen and sulfur atoms, was synthesized with a focus on the unique reactivity of carbazole via double intramolecular Friedel–Crafts acylation. A donor–acceptor-type polymer (PTCZTBT) was also synthesized, and its physicochemical properties are reported.

Solution-processed organic photovoltaic (OPV) devices consist of a bulk heterojunction with a π-conjugated polymer (electron donor) and a fullerene derivative (electron acceptor). In the past decade, these devices have attracted increasing research interest from the viewpoint of their many applications. Many studies have attempted to fabricate optimized photovoltaic devices based on poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PC$_{61}$BM); however, these devices showed a maximum photoconversion efficiency of only $\sim$5%.[1] This is because P3HT shows an absorption band at around 550 nm with a HOMO energy level of -4.89 eV. As a result, the poor light absorbing property at longer wavelengths prevents efficient exciton (excited state) formation, which is the origin of the short circuit current (J_{sc}) in photovoltaic devices. In order to improve the light absorbing property, Janssen proposed a new class of donor–acceptor-type low-bandgap conjugated polymers that consist of an electron-sufficient backbone and an electron-deficient one.[2] Broad light absorption has been achieved by exploiting the intramolecular charge transfer (CT) transition between these two backbones. This design strategy has driven research on the use of π-conjugated polymers for producing photovoltaic devices having high photoconversion efficiency.

Poly(2,7-carbazole-*alt*-dithienylbenzothiadiazole) (**PCDTBT**, Figure 1), which was first reported by Leclerc, is considered one of the most promising donor–acceptor-type low-bandgap polymers.[3] In attempts to synthesize a new

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(1) (a) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617. (b) Dang, M. T.; Hirsch, L.; Wants, G. *Adv. Mater.* **2011**, *23*, 3597.

(2) (a) van Duren, J. K. J.; Dhanabalan, A.; van Hal, P. A.; Janssen, R. A. J. *Synth. Met.* **2001**, *121*, 1587. (b) Dhanabalan, A.; van Duren, J. K. J.; Van Hal, P. A.; Van Dongen, J. L. J.; Janssen, R. A. J. *Adv. Mater.* **2001**, *11*, 255.

(3) (a) Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* **2007**, *19*, 2295. (b) Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletête, M.; Durocher, G.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2008**, *130*, 732. (c) Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297.

(4) (a) Chen, C. P.; Chan, S. H.; Chao, T. C.; Ting, C.; Ko, B. T. *J. Am. Chem. Soc.* **2008**, *130*, 12828. (b) Wu, J. S.; Cheng, Y. J.; Dubosc, M.; Hsieh, C.-H.; Chang, C. Y.; Hsu, C. S. *Chem. Commun.* **2010**, *46*, 3259. (c) Chen, C. H.; Cheng, Y. J.; Dubosc, M.; Hsieh, C. H.; Chu, C. C.; Hsu, C. S. *Chem. Asian J.* **2010**, *5*, 2483. (d) Zheng, Q.; Jung, B. J.; Sun, J.; Katz, H. E. *J. Am. Chem. Soc.* **2010**, *132*, 5394. (e) Zhang, Y.; Zou, J.; Yip, H. L.; Chen, K. S.; Zeigler, D. F.; Sun, Y.; Jen, A. K. Y. *Chem. Mater.* **2011**, *23*, 2289. (f) Cheng, Y. J.; Wu, J. S.; Shih, P. I.; Chang, C. Y.; Jwo, P. C.; Kao, W. S.; Hsu, C. S. *Chem. Mater.* **2011**, *23*, 2361. (g) Bronstein, H.; Leem, D. S.; Hamilton, R.; Woebkenberg, P.; King, S.; Zhang, W.; Ashraf, R. S.; Heeney, M.; Anthopoulos, T. D.; de Mello, J.; McCulloch, I. *Macromolecules* **2011**, *44*, 6649. (h) Cheedarala, R. K.; Kim, G. H.; Cho, S.; Lee, J.; Kim, J.; Song, H. K.; Kim, J. Y.; Yang, C. *J. Mater. Chem.* **2011**, *21*, 843.

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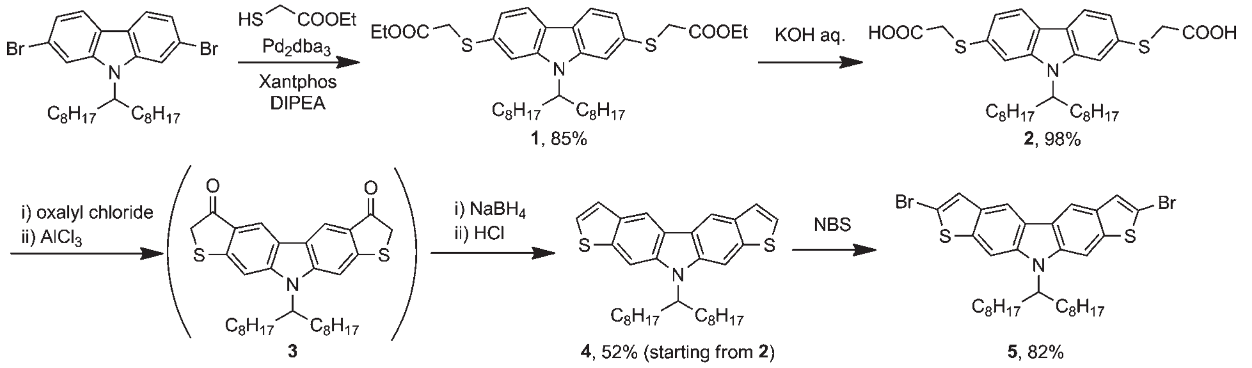
Scheme 1. Synthesis of Dibromodithienocarbazole (**5**) via Intramolecular Acylation



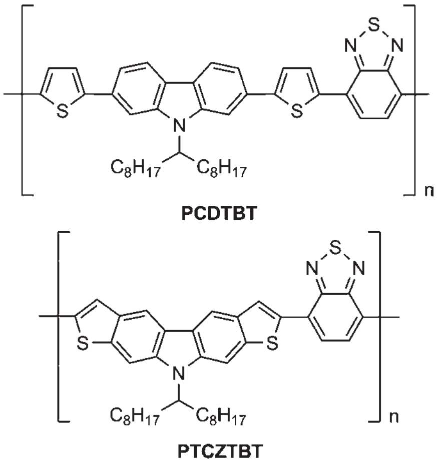


Figure 1. Chemical structure of **PCDTBT** and **PTCZTBT**.

class of low-bandgap polymers, the incorporation of a planar building block is potentially promising because (a) the interchain interaction supported by the overlapping of the π orbital between planar aromatic moieties would facilitate the charge transport between the polymer chains and (b) interchromophore interaction would allow wide absorption as in the case of P3HT. Indeed, various π-conjugated polymers containing ring-fused aromatic compounds such as heteroacene have been synthesized for developing organic electronic devices.[4,5] However, few attempts have been made to incorporate them into low-bandgap polymers with the objective of developing OPV devices.[4] In these studies, the most popular approach for constructing the fused aromatic system has been to bridge two aromatic rings by the sp^3 carbon using intramolecular annulation through the acid-mediated Friedel–Crafts reaction. For example, Hsu reported the synthesis of coplanarized **PCDTBT** by the sp^3 carbon (poly(carbazole-dicyclopentathiophene-*alt*-benzothiadiazole, **PCDCTBT**, Figure S9, Supporting Information).[4b,f] In a recent study, the presence of a quaternary carbon atom was found to suppress the device stability against photoirradiation.[6] As a new polymer design, we designed a copolymer of dithieno-[2,3-*b*;7,6-*b*]carbazole (**TCZT**), a type of heteropentacene, and benzothiadiazole (**PTCZTBT**, Figure 1), a model polymer of **PCDTBT**, by direct ring fusion using the sp^3-carbon-free aromatic backbone, which cannot be achieved via the traditional strategy using Friedel–Crafts reaction. Herein, we report the direct ring formation procedure of **TCZT** via intramolecular acylation and the synthesis and physicochemical properties of **PTCZTBT**.

The synthesis of the key building block is shown in Scheme 1. Mohanakrishnan[7] first reported the construction of the **TCZT** backbone via 1,5-sigmatropic rearrangement followed by electrocyclization and subsequent aromatization (Scheme S1, Supporting Information). Another synthetic approach, which serves as a fundamental method to construct thiophene-fused aromatic backbones, involves the ring-closure reaction of 3,6-diethynyl-2,7-dibromocarbazole in the presence of sodium sulfide at very high temperature (Scheme S2, Supporting Information).[5d] We focused on the direct intramolecular ring formation via Friedel–Crafts acylation. An attempt to construct the thiophene-fused aromatic system via an intramolecular acylation approach was made to synthesize thieno[3,2-*b*]thiophene, which was obtained from 3-(carboxymethylsulfanyl)thiophene as a starting compound.[8] This approach is supported by the electronic feature of the thiophene ring,

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(5) (a) Youn, J.; Chen, M. C.; Liang, Y. J.; Huang, H.; Ortiz, R. P.; Kim, C.; Stern, C.; Hu, T. S.; Chen, L. H.; Yan, J. Y.; Facchetti, A.; Marks, T. J. *Chem. Mater.* **2010**, *22*, 5031. (b) Ahmed, E.; Earmme, T.; Ren, G.; Jenekhe, S. A. *Chem. Mater.* **2010**, *22*, 5786. (c) Zheng, Q.; Chen, S.; Zhang, B.; Wang, L.; Tang, C.; Katz, H. E. *Org. Lett.* **2011**, *13*, 324. (d) Chen, Y.; Tian, H.; Yan, D.; Geng, Y.; Wang, F. *Macromolecules* **2011**, *44*, 5178.

(6) Manceau, M.; Bundgaard, E.; Carlé, J. E.; Hagemann, O.; Helgesen, M.; Søndergaard, R.; Jørgensen, M.; Krebs, F. C. *J. Mater. Chem.* **2011**, *21*, 4132.

(7) (a) Mohanakrishnan, A. K.; Dhayalan, V.; Clement, J. A.; Balamurugan, R.; Sureshbabu, R.; Kumar, N. S. *Tetrahedron Lett.* **2008**, *49*, 5850. (b) Dhayalan, V.; Clement, J. A.; Jagan, R.; Mohanakrishnan, A. K. *Eur. J. Org. Chem.* **2009**, 531.

(8) Leriche, P.; Raimundo, J. M.; Turbiez, M.; Monroche, V.; Allain, M.; Sauvage, F. X.; Roncali, J.; Frére, P.; Skabara, P. J. *J. Mater. Chem.* **2003**, *13*, 1324.

which can be easily functionalized by electrophilic aromatic substitution at its 2,5-positions (*ortho* position from the sulfur atom). We adopted this strategy to construct the thiophene-fused aromatic system based on unique reactivity of the carbazole backbone and designed a synthetic scheme that involves intramolecular Friedel–Crafts acylation. Compound **1** was prepared by palladium-catalyzed carbon–sulfur bond formation[9] of *N*-alkyl-2,7-dibromocarbazole[3a] using Xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) as a ligand and *N*,*N*-diisopropylethylamine (DIPEA) as a base with 85% yield. After hydrolysis, thioglycolic acid (**2**, 98% yield) was converted into acid chloride by oxalyl chloride, followed by ring closure to form dihydrothiophenone-fused carbazole **3** using double intramolecular Friedel–Crafts acylation. Because of the strong electron-rich property of the nitrogen atom in the carbazole backbone, acylation is favored at the 3- and 6-position of the carbazole ring (*para* position from the nitrogen atom) to result in regioselective cyclization.[10] The reduction and dehydration of **3** without purification allows the successful formation of *N*-9′-heptadecanyl-dithieno[2,3-*b*;7,6-*b*]carbazole **4** (52% yield, starting from **2**). The characteristic signal around 3.8 ppm attributed to the thiomethyl proton disappeared after the formation of the fused thiophene ring (Figure 2). Compound **4** was allowed to react with *N*-bromosuccinimide (NBS) to yield **5** as a colorless powder with 82% yield. The overall yield for our method to obtain the sp^3-carbon-free **TCZT** backbone starting from N-alkyl-2,7-dibromocarbazole was 43%, whereas that reported in the literature[5d] was 29%. The peculiarity of our synthetic procedure is that the target thiophene-fused aromatic system can be obtained under mild reaction conditions in good overall yield.

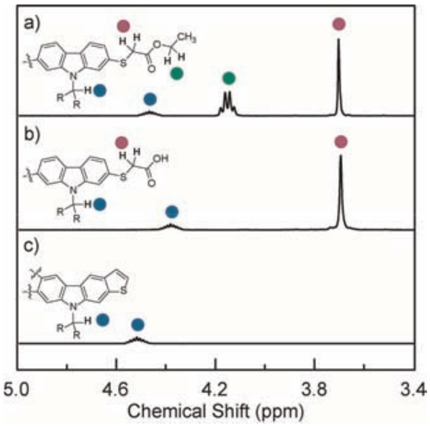
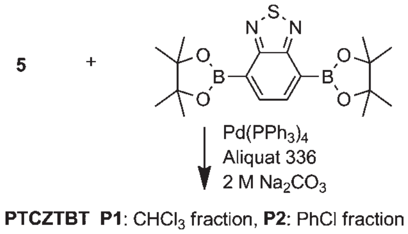


Figure 2. Magnified view of ^{1}H NMR spectra of (a) **1**, (b) **2**, and (c) **4** (400 MHz, 293 K $CDCl_3$).

Scheme 2. Synthesis of **PTCZTBT** (**P1** and **P2**)



The target copolymer, **PTCZTBT** was synthesized by a Suzuki coupling reaction between **5** and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) in toluene (Scheme 2). The crude polymer was purified using Soxhlet extraction to obtain a chloroform-soluble fraction (**P1**) and a chlorobenzene-soluble one (**P2**) as black powders. The yields of **P1**, **P2**, and the insoluble part were 35%, 11%, and 47%, respectively. The formation of a large amount of insoluble fraction is due to the intrinsic low solubility of **5** with a planar aromatic structure, despite the introduction of branched long alkyl chains. The number- (M_n) and weight-average (M_w) molecular weights of **P1** and **P2** as determined by gel permeation chromatography (GPC) with polystyrene as the standard are summarized in Table S1 (Supporting Information). **P1** has M_w of 21 kDa, with a polydispersity index (PDI) of 3.9; **P2** has M_w of 28 kDa, with PDI of 4.2.

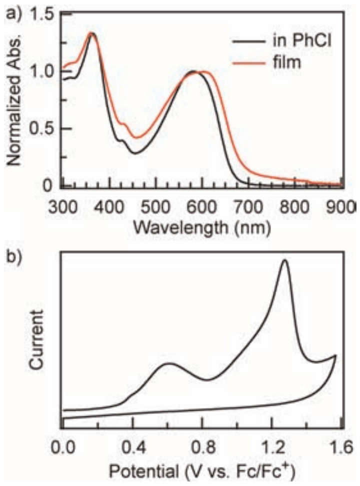


Figure 3. (a) UV–vis absorption spectra of **P1** in chlorobenzene and film prepared by spin-coating from chlorobenzene solution (normalized at λ_{max} in visible region). (b) Cyclic voltammogram of the cast film of **P1** measured in acetonitrile at scan rate of 100 mV/s with Bu_4NPF_6 (0.1 mol/L) as electrolyte. The film was prepared by spin-coating chlorobenzene solution on the working electrode.

The normalized UV–vis absorption spectra of **P1** in chlorobenzene are shown in Figure 3a. A characteristic absorption at around 600 nm is attributed to intramolecular CT transition between the electron-sufficient

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[9] Itoh, T.; Mase, T. *Org. Lett.* **2004**, *6*, 4587.

[10] Velasco, D.; Castellanos, S.; López, M.; López-Calahorra, F.; Brillas, E.; Juliá, L. *J. Org. Chem.* **2007**, *72*, 7523.

TCZT and the electron-deficient benzothiadiazole unit. **P1** and **P2** show quite similar absorption spectra with absorption maxima (λ_{max}) at 578 and 586 nm, respectively (Figure S10a, Supporting Information). The difference in λ_{max} is due to the degree of π-conjugation with different molecular weights. On the other hand, a broader absorption of the cast film of **P1** and **P2** was observed at around 600 nm, whereas the absorption of chlorobenzene solution shows a narrow spectral shape. The absorption spectrum of the **PCDTBT** film, which has an analogous structure to **P1** and **P2**, shows slight broadening of the spectral shape. These results suggest that in the solid states thin film crystallization and subsequent backbone planarization occur due to strong $\pi-\pi$ interaction between the planar **TCZT** units. The optical bandgap of **P1** and **P2** is 1.80 and 1.78 eV, respectively, as estimated from the absorption onset (689 and 695 nm, respectively). Narrow bandgap and broad absorption of **PTCZTBT** was observed by incorporating the planar electron-rich **TCZT** backbone instead of the carbazole unit in **PCDTBT** (optical bandgap: 1.87 eV).[3a] On the other hand, the wider bandgap than that of **PCDCTBT** (1.68 eV)[5c] is probably due to the stronger electron-donating property of the heteroheptacene unit supported by the extended aromatic system.

The electrochemical properties of **P1** and **P2** were studied by cyclic voltammetry (Figure 3b, Figures S10b and S11, Supporting Information). The HOMO and LUMO values were determined from the onset values of the oxidation and reduction potential with respect to ferrocene (Fc), respectively, as shown in Table S2 (Supporting Information). Both polymers showed oxidation waves attributed to the oxidation of **TCZT** at 0.6 and 1.3 V vs Fc/Fc^+. We estimated the HOMO and LUMO values to be -5.1 and -3.7 eV, respectively, for both **P1** and **P2**. Considering that the HOMO level of **PCDTBT** is -5.5 eV,[3a] the increased HOMO of **PTCZTBT** is due to the electron richness of the **TCZT** unit. We also evaluated the ionization potential (IP), which corresponds to the HOMO energy level of the polymers in thin film by photoelectron spectroscopy in air. The IPs estimated from the onset of the spectra are 5.1 eV for both **P1** and **P2** (Figure S12, Supporting Information), which agrees with the HOMO energy levels estimated by cyclic voltammetry.

Preliminary bulk heterojunction-type OPV devices were fabricated with a device structure of ITO/Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)/polymer:$PC_{61}BM$/Al. The devices were measured under the simulated AM 1.5 G illumination condition (100 mW/cm^2) (Figure S13 and Table S3, Supporting Information). The photoconversion efficiency of the best device was 0.35%. A current density (J_{SC}) was obtained (2.06 mA/cm^2) along with a fill factor (FF; 0.30) and open-circuit voltage ($V_{OC} = 0.60$ V). The V_{OC} value agrees with the calculated V_{OC} (0.5 V) determined from electrochemical data.[11] We believe that the device performance can be further improved by optimizing the processing conditions to form a suitable bulk heterojunction morphology.

In summary, a new direct strategy for synthesizing **TCZT**, a heteropentacene, via double-intramolecular Friedel–Crafts acylation has been proposed, and **TCZT** has been developed as a new class of low-bandgap polymers. We investigated the basic optoelectronic properties of **PTCZTBT**, and we used it to produce an OPV device. The optimization of OPV device fabrication is currently under investigation.

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Supporting Information Available. Detailed experimental procedures and characterization data for **1–5**, **P1**, and **P2**. This material is available free of charge via Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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(11) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. K. *Adv. Mater.* **2006**, *18*, 789.