# Macromolecules

## Dithienylbenzodipyrrolidone: New Acceptor for Donor–Acceptor Low Band Gap Polymers

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**Supporting Information** 

**ABSTRACT:** An analogue of DPP, dithienylbenzodipyrrolidone (DTBDPD), was successfully synthesized. Several D–A copolymers, with different electron donating capability donor unit (fluorene, difluorene, dithienosilole, and dithienopyrrole) and DTBDPD acceptor, were prepared by means of Suzuki and Stille coupling reaction. The optical and electrochemical properties were demonstrated through UV–vis–NIR absorption and cyclic voltammetry (CV). All polymers showed near-infrared or even infrared absorption and deeper LUMO levels, as low as –3.80 eV.

### 1. INTRODUCTION

Conjugated polymers have received increasing attention due to their intriguing electronic and optoelectronic properties for application in a variety of optoelectronic devices, such as polymeric light-emitting diodes (PLEDs),<sup>1</sup> organic thin film transistors (OTFTs),<sup>2</sup> and organic photovoltaics (OPVs).<sup>3</sup> Such applications, inter alia, encourage the continued exploration of conjugated polymers with new structures. Donor-acceptor architecture copolymers are of much interest because of the facile tailoring of electronic structure. The independent selection of electron donating and accepting moieties facilitates the tuning of the HOMO and LUMO energy level, energy band gap, photon absorption, and charge carrier transport (p-type, n-type, or ambipolar).<sup>4-7</sup> D–A copolymers contain acceptors with electron withdrawing moieties such as imides or lactams, e.g., rylene bisimides<sup>8</sup> and diketopyrrolopyrrole (DPP). The latter have been extensively explored and were found to exhibit large electron affinity (EA > 3.4 eV), near-infrared absorption, and good charge carrier transport. During the past decade, incorporation of DPP in polymers,<sup>9–16</sup> oligomers,<sup>17,18</sup> and dendrimers<sup>19</sup> resulted in materials for optoelectronic applications, especially in organic thin film transistors  $(OTFTs)^{10-14}$  and organic photovoltaics (OPVs).<sup>15–19</sup> Hole mobility as high as 10.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> under ambient conditions has been achieved by developing a very high molecular weight DPP-DTT (dithienylthieno[3,2-b]thiophene) polymer,<sup>14g</sup> and power conversion efficiency (PCE) up to 6.71% for a DPP and bithiophene copolymer<sup>16c</sup> have been reported.

Benzodipyrrolidone (BDPD) is a molecule originally prepared as a colorant<sup>20</sup> and is similar in structure to DPP; i.e., a planar, highly conjugated, lactam structure, resulting in strong  $\pi - \pi$  interactions and electron-withdrawing effects with



the additional twist of being a quinodimethane derivative. Benzodipyrrolidone can also be envisioned as an "extended" DPP. It was expected that introduction of alkyl chains to enhance the solubility and adjust the performance of devices would be facile. Moreover, the quinodimethane moiety, in analogy to tetracyanoquinodimethane (TCNQ)<sup>21</sup> and DPP, was expected to exhibit enhanced  $\pi-\pi$  stacking. Other similar colorants with bis-lactam or quinodimethane molecular architecture, dihydropyrroloindoledione (DPID)<sup>22</sup> and benzodifuranone (BDF),<sup>23</sup> have already been successfully used for constructing low band gap polymers. Benzodipyrrolidone and its derivatives should be considered as another interesting building block for donor-acceptor conjugated polymers with promising optoelectronic applications.

In our previous work, several benzodipyrrolidone-based small molecules and polymers were synthesized.<sup>24</sup> Benzodipyrrolidone showed promising electron accepting properties, which made it attractive for constructing new series of n-type and donor-acceptor materials. While the benzodipyrrolidones we described were phenyl, instead of thienyl, interspersed, it was necessary to prepare monomers that were closer to the muchstudied dithienyl DPP. Herein, we report that we successfully developed a method to prepare dithienylbenzodipyrrolidone (DTBDPD). Several D–A copolymers, with different electron donating capability donor unit (fluorene, difluorene, dithienosilole, and dithienopyrrole) and DTBDPD acceptor were prepared by means of Suzuki and Stille coupling reaction (Chart 1). The polymers showed very attractive properties, i.e., near-infrared (NIR) or even infrared (IR) absorption that was

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Chart 1. Structures of Dithienylbenzodipyrrolidone (DTBDPD) D-A Polymers



determined directly by the electron donating ability of the donors as well as deeper LUMO levels, as low as -3.80 eV.

#### 2. EXPERIMENTAL SECTION

**Materials.** Toluene and tetrahydrofuran (THF) were purified through a solvent purification system. Commercially available reagents were used without further purification unless otherwise stated.

General Measurements. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on Varian-NMR 600 spectrometers in  $\text{CDCl}_3$  or  $d_4$ -ODCB with tetramethylsilane (TMS) as internal standard. Mass spectrometry was performed by the UC Santa Barbara Mass Spectrometry Laboratory. GPC measurements were conducted on a Waters 510 system using polystyrene as standard. Electronic absorption spectra were obtained on an Agilent Technologies G1103A UV/vis spectrometer. Thermogravimetric analysis (TGA) was carried out on a TGA Q50 (TA Instruments) at a heating rate of 10 °C min<sup>-1</sup> at a nitrogen flow. Differential scanning calorimetry (DSC) was run on a DSC Q10 (TA Instruments) at a heating/cooling rate of 10/-10 °C min-<sup>1</sup> at a nitrogen flow. Cyclic voltammetry (CV) were performed on a Princeton Applied Research Model 263A potentiostat/galvanostat with a three-electrode cell in a solution 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as supporting electrolyte dissolved in methylene chloride or o-dichlorobenzene at a scan rate of 50 mV/s. A Pt disk was used as working electrode, a Pt wire as the counter electrode, and an Ag electrode as the reference electrode. The potential was calibrated by the ferrocene/ferrocenium standard. HOMO and LUMO energy levels were estimated by the equations HOMO =  $-(4.80 + \Delta E_{\text{oxd}}^{\text{onset}})$  and LUMO =  $-(4.80 - \Delta E_{\text{red}}^{\text{onset}})$ .

*N,N'-Dihexylbenzene-1,4-diamine* (1). To a solution of cyclohexane-1,4-dione (5.60 g, 50.0 mmol) in ethanol (500 mL) was added hexylamine (10.1 g, 100 mmol). The resulting mixture was stirred under bobbling air for 4 h. Solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane:DCM:ethyl acetate = 10:10:1 as eluent yield 1 (8.50 g, 61.5%) as a light yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$  ppm: 6.54 (s, ArH, 4H), 3.15 (br, NH, 2H), 3.03 (tr, J = 7.5 Hz, NCH<sub>2</sub>, 4H), 1.55–1.60 (m, CH<sub>2</sub>, 4H), 1.24–1.40 (m, CH<sub>2</sub>, 12H), 0.83–0.89 (m, CH<sub>3</sub>, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$  ppm 140.96 (2 × ArC), 114.74 (4 × ArCH), 45.42 (2 × NCH<sub>2</sub>), 31.70, 29.78, 26.91, 22.63 (8 × CH<sub>2</sub>), 14.03 (4 × CH<sub>3</sub>). TOF MS (EI+): m/z (%): 276.26 [M]+.

*N*,*N*'-1,4-*Phenylenebis*[2-chloro-*N*-hexyl]acetamide (2). To a solution of chloroacetyl chloride (0.402 g, 3.56 mmol) in THF (5 mL) at 0 °C was added a solution of 1 (0.300 g, 1.19 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.135 g, 1.11 mmol) in THF (10 mL) dropwise. After 1 h, the reaction mixture was quenched with water. The precipitate was collected by filtration. After being washed with water and methanol, the solid was dried in vacuo to yield 2 (0.37 g, 72.5%) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$  ppm: 7.32 (s, ArH, 4H), 3.82 (s, (C=O) CH<sub>2</sub>, 4H), 3.27 (t, *J* = 7.8 Hz, NCH<sub>2</sub>, 4H), 1.53–1.55 (m, CH<sub>2</sub>, 4H), 1.26–1.32 (m, CH<sub>2</sub>, 12H), 0.87–0.88

(m, CH<sub>3</sub>, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$  ppm: 165.64 (2(C=O)), 141.51 (2 × ArC), 129.65 (4 × ArCH), 50.21 (2(C=O)CH<sub>2</sub>), 41.73 (2 × NCH<sub>2</sub>), 31.41, 27.51, 26.31, 22.49 (8 × CH<sub>2</sub>), 13.95 (4 × CH<sub>3</sub>). TOF MS (EI+): *m/z* (%): 428.21[M]+.

1,5-Dihexyl-5,7-dihydro-1H,3H-pyrrolo[2,3-f]indole-2,6-dione (3). A mixture of 2 (5.00 g, 11.6 mmol) and anhydrous aluminum chloride (10.8 g, 81.5 mmol) was heated at 190 °C for 20 min. After cooling, cracked ice was added to quench the reaction. The precipitate formed was collected by filtration. After being washed with water and methanol, the solid was dried and further purified by column chromatography on silica gel with DCM:ethyl acetate = 10:1 as eluent yield 3 (2.88 g, 70%) as a white solid. IR (ATR):  $v_{max}$  (cm<sup>-1</sup>): 3054, 2958, 2929, 2870, 1711, 1677, 1501, 1476, 1350, 1242, 1182, 1127, 948, 843. TOF MS (FI+): m/z (%): 356.25 [M]+. Anal. Calcd for ( $C_{22}H_{32}N_2O_2$ ): C, 74.12; H, 9.05; N, 7.86. Found: C, 74.6; H, 10.1; N, 7.78.

3,3,7,7-Tetrabromo-1,5-dihexyl-5,7-dihydro-1H,3H-pyrrolo[2,3-f]indole-2,6-dione (4). A mixture of 3 (2.88 g, 8.08 mmol), AIBN (0.264 g, 1.62 mmol), and NBS (8.63 g, 48.5 mmol) was added carbon tetrachloride (20 mL). The resulting mixture was heated at reflux for 12 h. After cooling, the mixture was washed with brine and dried over anhydrous MgSO<sub>4</sub>. On removal of solvent, the residue was purified by column chromatography on silica gel with hexane:DCM = 1:2 as eluent to yield 4 (3.12 g, 57%) as a yellow solid. IR (ATR):  $v_{max}$  (cm<sup>-1</sup>): 3048, 2953, 2926, 2860, 1722, 1475, 1341, 1185, 1161, 1132, 879, 802, 702. TOF MS (FI+): m/z (%): 667.88 [M]+. Anal. Calcd for (C<sub>22</sub>H<sub>28</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>2</sub>): C, 39.32; H, 4.20; N, 4.17. Found: C, 39.4; H, 4.48; N, 4.05.

3,7-Dibromo-1,5-dihexyl-1H,5H-pyrrolo[2,3-f]indole-2,6-dione (5). To a suspension of 4 (3.00 g, 4.46 mmol) in CH<sub>3</sub>CN (100 mL) was added sodium iodine (2.00 g, 13.4 mmol). The resulting mixture was stirred at room temperature for 30 min. After the solvent being removed under reduced pressure, the residue was dissolved in DCM. The solution was washed with sodium thiosulfate(aq) and water and dried over anhydrous MgSO<sub>4</sub>. On removal the solvent, the residue was purified by column chromatography on silica gel with hexane:DCM = 1:2 as eluent to yield 5 (2.00 g, 87.7%) as a dark purple solid. IR (ATR):  $v_{max}$  (cm<sup>-1</sup>): 3067, 2955, 2927, 2862, 1727, 1692, 1599, 1578, 1473, 1376, 1326, 1279, 1232, 1155, 1115, 913, 865, 805. TOF MS (FI +): m/z (%): S10.06 [M]+. Unstable during heat, elemental analysis is not available.

1,5-Dihexyl-3,7-dithiophen-2-yl-1H,5H-pyrrolo[2,3-f]indole-2,6dione (6). A mixture of 5 (1.00 g, 1.95 mmol), 2-(tributylstannyl)thiophene (1.60 g, 4.29 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (60 mg), and toluene (20 mL) was heated at reflux for 24 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with toluene. The organic layer was washed with aqueous potassium fluoride and brine and then dried over anhydrous MgSO<sub>4</sub>. On removal of the solvent, the residue was purified by column chromatography on silica gel with hexane:DCM = 1:1 as eluent to yield 6 (0.70 g, 70%) as a dark purple solid with golden reflection. IR (ATR):  $v_{max}$  (cm<sup>-1</sup>): 3108, 3073, 2957, 292, 2859, 1676, 1584, 1563, 1439, 1415, 1376, 1348, 1216, 1192, 1077, 1067, 852, 821, 688. TOF MS (EI+): m/z (%): 518.21 [M]+. Anal. Calcd for (C<sub>30</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>): C, 66.46; H, 6.61; N, 5.40. Found: C, 69.4; H, 6.88; N, 5.35.

1,5-Dihexyl-3,7-dithiophen-2-yl-1H,5H-pyrrolo[2,3-f]indole-2,6dione (7). To a solution of 6 (0.275 g, 0.530 mmol) in THF (50 mL) was added NBS (0.250 g, 1.40 mmol) portionwise. The resulting mixture was stirred at room temperature overnight. To the resulting mixture methanol was added. The precipitate was collected, washed with methanol, and dried in vacuo to yield 7 as a dark purple solid (0.300 g, 84.0%) with golden reflection. IR (ATR):  $v_{max}$  (cm<sup>-1</sup>): 3112, 2956, 2924, 2856, 1675, 1582, 1560, 1414, 1376, 1191, 1073, 1054, 962, 916, 618. TOF MS (FD+): m/z (%): 674.0 [M]+. Anal. Calcd for (C<sub>30</sub>H<sub>32</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>): C, 53.26; H, 4.77; N, 4.14. Found: C, 53.2; H, 4.85; N, 4.13.

Stille Polymerization. PDTBDP-DTSi. A mixture of 7 (0.115 g, 0.148 mmol), 4,4'-bis(2-ethylhexyl)-5,5'-bis(trimethyltin)dithieno-[3,2-b:2',3'-d]silole (0.127 g, 0.170 mmol),  $Pd_2(dba)_3$  (5 mg), (o-tol)<sub>3</sub>P (3.0 mg), and toluene (20 mL) was heated at reflux for 24 h. 2-

#### Scheme 1. Synthetic Route for Dibromobenzodipyrrolidone



Bromothiophene (0.070 g, 0.44 mmol) in toluene (1 mL) was added, and the resulting mixture was stirred for another 12 h. Then after cooling to room temperature, the mixture was dropped into methanol to precipitate. After being filtered and dried, the precipitation was Soxhlet extracted with methanol, acetone, hexane, dichloromethane, and chloroform in succession. The chloroform solution was concentrated and reprecipitated in methanol. The solid was filtered and dried to yield polymer (0.110 g, 79.7%) as a black solid. Anal. Calcd for  $(C_{54}H_{70}N_2O_2S_4Si)_n$ : C, 69.33; H, 7.54; N, 2.99. Found: C, 69.2; H, 7.34; N, 3.05.

PDTBDPD-DTPy. The same procedure as preparing DTBDPD-DTSi was followed. 2,6-Bis(trimethylstannyl)-4-[3,4,5-tris-(dodecyloxy)phenyl]-4H-dithieno[3,2-b:2',3'-d]pyrrole was used. Polymer DTBDPD-DTPy was obtained as a black solid with a yield of 85.9%. Anal. Calcd for ( $C_{80}H_{113}N_3O_5S_4$ )<sub>n</sub>: C, 72.52; H, 8.60; N, 3.17. Found: C, 72.15; H, 8.06; N, 3.20.

Suzuki Polymerization. PDTBDPD-F. A mixture of 7 (0.150 g, 0.221 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-diethylhexylfluorene (0.149 g, 0232 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5.0 mg), (*o*-tol)<sub>3</sub>P (3.0 mg), K<sub>3</sub>PO<sub>4</sub> (0.187 g), and toluene/H<sub>2</sub>O (20 mL/1 mL) was heated at reflux for 24 h. 2-Bromothiophene (0.035 g, 0.22 mmol) in toluene (1 mL) was added, and the resulting mixture was stirred for another 12 h. Then after cooling to room temperature, the mixture was dropped into methanol to precipitate. After being filtered and dried, the precipitation was Soxhlet extracted with methanol, acetone, hexane, dichloromethane, and chloroform in succession. The chloroform solution was concentrated and reprecipitated in methanol. The solid was filtered and dried to yield polymer (0.165 g, 82.5%) as a blue-green solid. Anal. Calcd for (C<sub>59</sub>H<sub>74</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>)<sub>n</sub>: C, 78.10; H, 8.22; N, 3.09. Found: C, 78.20; H, 8.05; N, 3.22.

PDTBDPD–DF. The same procedure as preparing DTBDPD-F was followed. Polymer DTBDPD-DF was obtained as a green solid with a yield of 85%. Anal. Calcd for  $(C_{88}H_{114}N_2O_2S_2)_n$ : C, 81.56; H, 8.87; N, 2.16. Found: C, 81.30; H, 8.50; N, 2.35.

#### 3. RESULTS AND DISCUSSION

**Synthesis.** For preparation of DTBDPD, attempts following the same procedures as the phenyl analogues turned out to be unsuccessful.<sup>24</sup> The condensation reaction of *p*-phenylenediamine with  $\alpha$ -hydroxy-2-thiopheneacetic acid gave an insoluble, dark solid complex mixture whose structure was not possible to determine. We therefore developed another method to prepare dibromobenzodipyrrolidone first and then synthesize dithie-nylbenzodipyrrolidone by means of coupling reaction. Scheme 1 shows the synthetic route for the preparation of dibromobenzodipyrrolidone. Condensation of 1,4-cyclohexane-dione with hexylamine in the presence of air afforded *N*,*N*'-

dihexylbenzene-1,4-diamine (1). Acetamide 2 was synthesized by treating 1 with chloroacetyl chloride. The ring-closure reaction was performed in molten  $AlCl_3$  at 190 °C to afford dioxindole 3. The most important intermediate, dibromobenzodipyrrolidone (5), was obtained by bromination with NBS in the presence of AIBN in  $CCl_4$ , followed by reductive debromination with sodium iodide in acetonitrile.

The structures of these compounds were determined by means of <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS elemental analysis, and single crystal X-ray diffraction. To our knowledge, due to the symmetry of compounds 3, 4, and 5, proton a (Scheme 1) should be a single peak in the <sup>1</sup>H NMR spectrum. But two peaks were observed at 6.775 and 6.756 ppm (ratio 1:0.5) in the spectrum of 3, 7.068 and 7.048 ppm (ratio 1:0.5) in 4, and 5.896 and 5.885 ppm (ratio 1:0.5) in 5, respectively. In the  $^{13}$ C NMR spectra, at each position, there is also more than one peak with very small difference in chemical shift (about 0.1 ppm). The complex NMR spectra indicated that there should be some other component with very similar structure to the target molecules, and the mass spectra and elemental analyses showed the desired exact molecular weight and C, H content. A possible explanation could be the formation of linear and bent isomers during the ring-closure reaction that were similar to the isomers obtained from a two-directional Pummerer-type cyclization.<sup>22,25</sup> However, this is not a plausible rationalization because the X-ray structure analysis shows only one isomer. Though the R factor was 10% (due to side chain disorder), $^{26}$  it is certainly good enough to have detected a "bent" isomer. The crystal structure afforded bond lengths from C1 to C2 to C3 to C4 to C5 to be 1.356, 1.441, 1.366, and 1.485 Å, respectively. The alternating bond length pattern firmly verified the quinodimethane structure of the benzodipyrrolidone core.

With two active bromine atoms in 5, any units that can react with them can be easily introduced, in principle. Dithienylbenzodipyrrolidone (6) can be readily synthesized by means of a Stille coupling reaction with 2-(tributylstannyl)thiophene. Bromination of 6 with NBS afforded dibromodithienylbenzodipyrrolidone (7).

DTBDPD copolymers were synthesized by means of palladium-catalyzed Suzuki (fluorene and difluorene) and Stille (dithienosilole and dithienopyrrole) polymerization. Diboronic ester derivatives of fluorene<sup>27</sup> and difluorene<sup>28</sup> and distannyl reagent of dithienosilole<sup>29</sup> and dithienopyrrole<sup>7a</sup> were prepared by literature procedures. Suzuki coupling reactions were

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performed using tris(dibenzylideneacetone)dipalladium as catalyst, potassium phosphate as base, and triphenylphosphine as ligand in toluene/water. Stille cross-coupling polymerizations were performed in the presence of tris(dibenzylideneacetone)dipalladium in toluene. The reaction time of Suzuki and Stille coupling was 24 h. The polymers were easily soluble in common solvents such as chloroform and chlorobenzene and were characterized by <sup>1</sup>H NMR ( $d_4$ -ODCB, 100 °C) and gel permeation chromatography (GPC) with PS (polystyrene) as standard and chloroform as eluent. Polymers showed strong aggregation as featured by rather broad and featureless signals. PDTBDPD-F and PDTBDPD-DF signals can be detected at room temperature. But those of PDTBDPD-DTSi and PDTBDPD-DTPy can only been observed after being heated to 100 °C. The number-average molecular weight and (PDI) were found to be 7 kDa (2.42) of PDTBDPD-F, 12 kDa (2.86) of PDTBDPD-DF, 38 kDa (2.80) of PDTBDPD-DTSi (3.00), and 20 kDa (3.20) of PDTBDPD-DTPy, respectively.

**Solid State Structure of DTBDPP.** A single crystal of dithienylbenzodipyrrolidone (6) was prepared from chloroform solution (Figure 1). The dihedral angle between the thiophene and benzodipyrrolidone core was decreased to  $12.7^{\circ}$  compared to  $38.0^{\circ}$  of the phenyl analogue.<sup>24</sup> The packing structure of BDPD molecules can be modified by linking with different units. The solid state structure was found to be monoclinic for dibromobenzodipyrrolidone, orthorhombic for diphenylbenzo-dipyrrolidone, and triclinic for dithienylbenzodipyrrolidone. Moreover, the nearest distance in DTBDPD is 3.29 Å between thiophene and the middle six-member ring, a distance that is much smaller than the 3.56 Å observed in the DPBDPD, indicating much stronger  $\pi - \pi$  interactions in the thiophene analogue.

**Thermal Properties.** The thermal behavior of the polymers was evaluated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As depicted in



Figure 1. Single crystal structure of DTBDPD.

Figure 2, all the polymers showed good thermal stability. The 5% weight loss of the polymers happened at 395.2 °C for PDTBDPD-F, 399.0 °C for PDTBDPD-DF, 405.6 °C for PDTBDPD-DTSi, and 396.9 °C for PDTBDPD-DTPy. No transition was detected from the DSC characterization, during the scan from 30 to 350 °C at a rate of 10 °C/min under nitrogen flow.

**Optical Properties.** The UV–vis absorption spectra of DTBDPD monomer and D–A polymers were recorded in chloroform at a concentration of  $10^{-5}$  M and in spin-coated thin film. The maximum absorption wavelength of DTBDPD in solution was 559 nm (Figure S2, top), which was 101 nm red-shifted relative to DPBDPD (458 nm). The overwhelming red-shift of absorption can be ascribed to the more electron-rich



Figure 2. TGA curves of DTBDPD polymers (10  $^{\circ}C/min$  under nitrogen flow).

thiophene and the increased conjugation between thiophene and BDPD. Moreover, due to the extended conjugation of the central six-membered ring, the absorption of DTBDPD was also at longer wavelength than DPP (548 nm). In the solid state, the absorption spectrum of DTBDPD became broadened and red-shifted (593 nm) and exhibited a distinguishable structure. All these observations indicated a strong intermolecular interaction of DTBDPD in the solid state, usually associated with possible improved charge transport.

All the DTBDPD polymers absorbed in the NIR or even the IR range. The fluorene and difluorene polymers showed two absorptions: from 300 to 500 nm and from 500 nm to around 900 nm. The maximum absorption wavelengths were 706 nm of PDTBDPD-F and 687 nm for PDTBDPD-DF. The slightly (19 nm) blue-shifted absorption of PDTBDPD-DF, compared to fluorene, could be ascribed to the twist between the fluorene units. Polymers PDTBDPD-DTSi and PDTBDPD-DTPy showed a main absorption band at long wavelength. The maxima were 849 nm for PDTBDPD-DTSi and 1021 nm for PDTBDPD-DTPy. In the solid state, absorption edges at long wavelength for all the polymers were red-shifted (Table 1).

Comparing all the DTBDPD polymers together, we can see red-shifted absorption wavelengths with increasing electron donating capability of the donor moiety (Figure 1 and Table 1). The absorption and band gaps of the DTBDPD polymers can be tailored easily by choosing different donor strength.

**Electrochemical Properties.** The electrochemical properties of the monomer (Figure S3) and polymers (Figure 4) were investigated by CV in DCM or ODCB. The dithienylbenzodipyrrolidone monomer showed three reversible redox processes during negative scan and no reversible redox under positive potential. The energy levels were estimated to be -3.76 eV for the LUMO and -5.43 eV for the HOMO. The LUMO level was deeper than that of DPBDPD (-3.53 eV) and DPP (-3.25 eV). Because of the more electron-rich thiophene units, the HOMO level of DTBDPD increased compared to



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Figure 3. Absorption spectra of the DTBDPD copolymers in chloroform solution (top) and film (bottom).





that of DPBDPD. As to DTBDPD copolymers, the oxidation and reduction behavior varied with different donor unit. PDTBDPD-F showed *quasi*-reversible reduction and oxidation during negative and positive scans, while two couples of reversible redox processes were observed for PDTBDPD-DF. For PDTBDPD-DTSi and PDTBPD-DTPy, no obvious *quasi*-

#### Table 1. Photophysical and Electrochemical Data of DTBDPD Polymers

polymer	$M_{\rm n}~({\rm kDa})/{\rm PDI}$	$\lambda_{\max}^{ m sol}/\lambda_{ m onset}$ (nm)	$\lambda_{\mathrm{max}}^{\mathrm{film}}/\lambda_{\mathrm{onset}}$ (nm)	$\Delta E_{\mathrm{opt}}^{a}$ (eV)	HOMO (eV)	LUMO (eV)	$\Delta E_{\rm g}~({\rm eV})$
PDTBDPD-F	7.0/2.42	706/954	682/973	1.27	-5.13	-3.78	1.35
PDTBDPD-DF	12.0/2.86	687/947	640/1008	1.20	-5.11	-3.81	1.30
PDTBDPD-DTSi	38/3.00	849/1118	878/1200	1.03	$-4.78^{b}$	-3.75	
PDTBDPD-DTPy	20/3.20	1021/1508	1006/1562	0.79	$-4.57^{b}$	-3.78	

<sup>a</sup>Calculated from  $\Delta E_{opt}$  (eV) = 1240/ $\lambda_{onset}^{film}$  <sup>b</sup>Calculated from the difference of LUMO level and optical band gap  $\Delta E_{opt}$ .

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reversible or reversible redox was observed during positive scans. Only two reversible redox processes were detected during catholic scans. The LUMO levels of the polymers, estimated from the reduction onset, were -3.78 eV for PDTBDPD-F, -3.81 eV for PDTBDPD-DF, -3.75 eV for PDTBDPD-DTSi, and -3.78 eV for PDTBDPD-DTPy. The LUMO levels of the polymers did not show a substantial difference with variation of the electron donating ability of the donor units. They remained essentially constant and similar to that of acceptor unit (DTBDPD) itself. The HOMO levels of the polymers increased with the donor strength, which caused a decrease in band gap (Table 1 and Figure 3).

#### 4. CONCLUSIONS

In summary, an analogue of DPP, dithienylbenzodipyrrolidone (DTBDPD), was successfully synthesized. Comparing with DPP, a longer wavelength absorption and even deeper LUMO level were observed. A LUMO level as low as -3.75 eV makes these molecules behave as strong electron withdrawing units. Several D-A copolymers with different electron donating units (fluorene, difluorene, dithienosilole, and dithienopyrrole) as donors and DTBDPD as acceptor were prepared by means of Suzuki or Stille coupling. Optical and electrochemical properties were demonstrated through UV-vis-NIR absorption and CV. All polymers showed near-infrared or even infrared absorption, directly related to the electron donating ability of the donor units. A broad and long wavelength absorption suggested good light harvesting, auguring well for the application to organic photovoltaics. The LUMO levels were estimated to be as low as -3.80 eV. Such low LUMO level indicates a strong electron withdrawing capability of the polymers, making them useful as polymer acceptors in organic photovoltaics or other electron transporting applications. Device performance evaluation by using DTBDPD copolymers as donor, acceptor in solar cells, and n-type or ambipolar transistors is on the way.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Information regarding single crystal X-ray diffraction data of 5 (image and CIF) and 6 (CIF), absorption and CV spectra of 6, and NMR spectra of compounds 2, 3, 4, 5, 6, 7, polymer PDTBDPD-F, PDTBDPD-DF, PDTBDPD-DTSi, and PDTBDPD-DTPy. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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(26) Because the geometry of the bent structure is *so dramatically different* and according to the NMR results, the "other isomer" is at least 30% of the signal. An X-ray structure with a 10% R factor, while

high, should have shown the other isomer. We thought there could be an enol-carbonyl equilibrium related to the enol form of the lactam, but temperature- and pH-dependent NMR spectroscopy did not support this hypothesis. Closer examination of the alkyl region in the NMR spectra as well as in the X-ray results indicated a deep-seated rearrangement of the alkyl group with the possible migration of a methyl group. We therefore examined simulated NMR spectra of lactam N-alkylindolin-2-one with R varying *n*-hexyl and 3-methylpentyl (Figure S20).



#### 1-Alkylindolin-2-one

The simulation containing *N*-*n*-hexylindolin-2-one with 3pentylindolin-2-one came closest in appearance to the alkyl region of the NMR spectra of compounds 3-7; however, the aromatic region did not show the additional peaks. Hence, this part of the magnetic resonance spectroscopy still remains a mystery.

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