Organic LETTERS

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Acceptor−Donor−Acceptor Oligomers Containing Dithieno[3,2-*b*:2′,3′-*d*]pyrrole and Thieno[2,3-*c*]pyrrole-4,6-dione Units for Solution-Processed Organic Solar Cells

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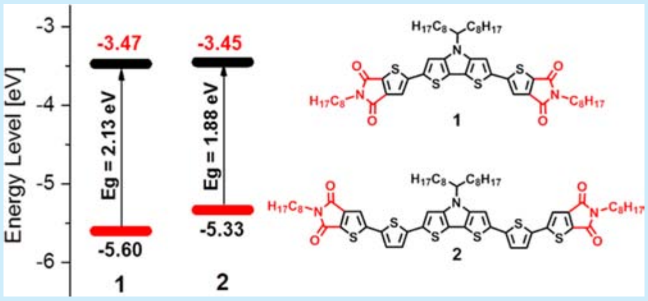
Supporting Information

ABSTRACT: New acceptor−donor−acceptor (A−D−A) oligomers (**1** and **2**) containing a central dithieno[3,2-*b*:2′,3′-*d*]pyrrole unit and end-capping thieno[2,3-*c*]pyrrole-4,6-dione groups have been synthesized and characterized. Bulk heterojunction solar cells were prepared together with $PC_{61}BM$ and $PC_{71}BM$, and the best results were obtained for the latter acceptor using 1,8-diiodooctane as an additive. Photovoltaic devices containing these oligomers achieved high external quantum efficiencies up to 50%.



In recent years, large efforts have been made in the development of novel oligomers, typically referred to as “small molecules”, used as p-type donor materials in bulk heterojunction organic solar cells (BHJ OSCs).[1−5] Currently, power conversion efficiencies (PCEs) of 8−9%[6−9] have been achieved in solution-processed single junction cells using the fullerene derivative [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as the n-type acceptor material. The molecular architecture of donor oligomers typically involves alternating π-electron donor and acceptor units (D−A) since this gives strong absorptions at long wavelengths owing to charge transfer character. We have recently shown that dithieno[3,2-*b*:2′,3′-*d*]pyrroles (DTP)[10] are suitable π-electron donor units in dicyanovinyl (DCV)-end-capped A−D−A oligothiophenes for OSCs (Figure 1, **I**).[11] PCEs of up to 4.8% were achieved for **I** using [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) as the acceptor.[11] In order to blue-shift the absorption spectra of these types of oligomers, we have utilized a thieno[2,3-*c*]pyrrole-4,6-dione (TPD) as the weaker π-accepting end group. This end group has been previously incorporated into A−D−A oligomers with bithiophenes (**II**)[12,13] and bis(1-octyl)dithieno[3,2-*b*;2′,3′-*d*]silole] (**III**)[14] as the donor groups (Figure 1). Ambipolar behavior in organic field effect transistors (OFETs) was observed for **II**,[12,13] with hole mobilities of 6.4×10^{-5} $cm^2/(V\ s)$ and electron mobilities reaching 5.3×10^{-2} $cm^2/(V\ s)$.[12,13] Dithienosilole-containing oligomer **III** (E_g = 1.92 eV) was employed as the donor material in OSCs using $PC_{61}BM$ as the acceptor, and the highest measured PCE was 1.2% with a V_{OC} of 0.97 V.[14]

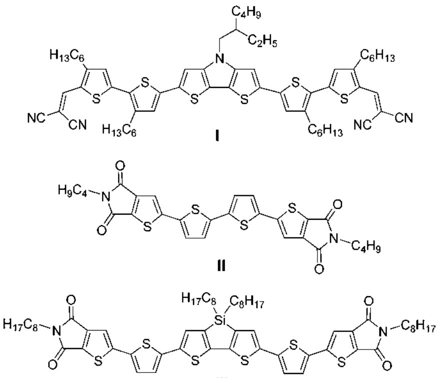


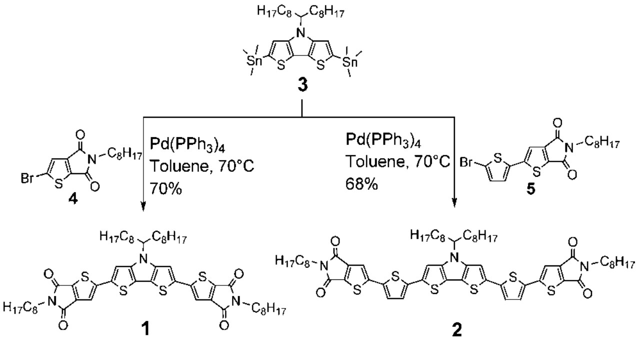
Figure 1. Representative donor−acceptor oligomers constructed from the donor or acceptor units used in this study.

We herein report the synthesis and characterization of two new A−D−A oligomers, **1** and **2**, and their implementation as donor materials in oligomer OSCs. Our molecular design employed DTP and TPD components as the π-electron donor and acceptor groups, respectively. We also incorporated a thiophene spacer unit in order to decrease the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO−LUMO) gap by extending the conjugation length of the oligomer.

The synthetic pathway to oligomers **1** and **2** began with 2,6-bis(trimethylstannyl)dithieno[3,2-*b*:2′,3′-*d*]pyrrole[15] **3** and brominated TPDs[14] **4** and **5**, which were prepared according to known procedures (Scheme 1). Branched (1-octylnonyl) and long *n*-octyl alkyl chains were used in order to increase the solubility of the incipient oligomers. Stille coupling reactions rendered **1** and **2** in 80% and 82% yield, respectively, after column chromatography and preparative size exclusion

Received: March 18, 2014
Published: May 5, 2014

Scheme 1. Synthesis of Oligomers 1 and 2



chromatography (SEC). Differential scanning calorimetry measurements (Figure S1) gave melting points of 127 and 162 °C without decomposition, which is typically observed for DCV-substituted oligomers.[16]

Characterization details of oligomers **1** and **2** are shown in Table 1. Both oligomers were soluble in common organic solvents such as chloroform, dichloromethane, and toluene. UV–vis absorption spectroscopy was measured for chloroform solutions (Figure 2a) and thin films (Figure 2b). In solution, **1** and **2** exhibited absorption maxima of 505 nm (ε = 42 300 M^{-1} cm^{-1}) and 519 nm (ε = 59 400 M^{-1} cm^{-1}), respectively, which were slightly red-shifted in thin films to 530 and 532 nm, respectively. No vibronic fine structure was observed for the broad absorption peaks in solution; however a slight low-energy shoulder around 570 nm appeared in the thin film spectrum of **2**, most likely due to ordering in the solid state. Large optical band gaps (E_g^{opt}) of 2.04 and 1.92 eV in the films were measured for **1** and **2**, respectively, which are about 0.10 and 0.17 eV lower compared to the HOMO–LUMO energy gaps determined from solution spectra.

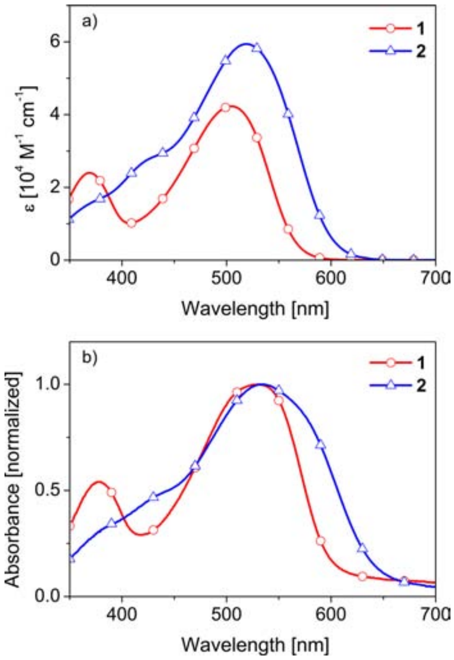


Figure 2. UV–vis absorption spectra of oligomers **1** and **2** in (a) chloroform solution and (b) thin films.

Compared to the A–D–A oligomer **II** ($\lambda_{\max}$ = 450 nm) containing bithiophene as the π-bridge, oligomer **1** displayed a red-shifted absorption maximum ($\lambda_{\max}$ = 505 nm) in solution and, therefore, a smaller HOMO–LUMO gap (2.53 eV for **II** vs 2.13 eV for **1**), due to the rise in the HOMO energy level of **1** resulting from the strong electron-donating ability of the DTP unit.[13] Oligomer **2** can be likened to its dithieno[3,2-*b*;2′,3′-*d*]silole analogue **III** prepared by Chen and co-workers,[13] which also had comparatively blue-shifted absorption maxima (519 vs 501 nm). In both cases discussed above, red shifts in absorption were observed for **1** and **2** as a result of the superior electron-donating strength of the central DTP unit in comparison to bithiophene and dithieno[3,2-*b*;2′,3′-*d*]silole.[17] However, the TPD end group is a weaker acceptor unit compared to DCV, which is seen when comparing **2** with oligomer **I** (*vide infra*). The latter has a bathochromically shifted absorption maxima of 593 nm (E_g^{opt} = 1.80 eV) and 698 nm (E_g^{opt} = 1.61 eV) in the solution and film, respectively.[11]

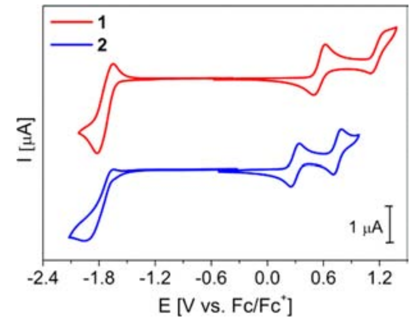


Figure 3. Cyclic voltammograms of oligomers **1** and **2** measured in dry dichloromethane–[TBA][PF_6] (0.1 M) solution with a scan speed of 100 mV/s referenced to Fc/Fc^+.

Cyclic voltammetry measurements in dichloromethane showed two reversible oxidation and one quasi-reversible reduction waves (Figure 3, Table 1). Similar behavior has been seen for the DCV end-capped DTP **I**,[11] where stepwise oxidations were delegated to the electron-rich oligomeric backbone and the reduction was assigned to the electron-deficient DCV end groups. The first oxidation of **2** was similar

Table 1. Summary of Optical and Electrochemical Properties of Oligomers 1 and 2

	λ_{abs} [nm]^a sol	ε [M^{-1} cm^{-1}]	λ_{abs} [nm] film	E_g^{opt} [eV]^b sol	E_g^{opt} [eV]^b film	E°_{ox1} [V]^c	E°_{ox2} [V]^c	E°_{red} [V]^c	HOMO [eV]^d	LUMO [eV]^d	E_g^{CV} [eV]^e
1	505	42 300	514	2.18	2.04	0.56	1.17	−1.74	−5.60	−3.47	2.13
2	519	59 400	532	2.06	1.92	0.29	0.75	−1.80	−5.33	−3.45	1.88

[a]Measured in CHCl_3. [b]Estimated using the onset of the UV–vis spectrum ($E_g^{\mathrm{opt}} = 1240/\lambda_{\mathrm{onset}}$). [c]Measurements made in $\mathrm{CH}_2\mathrm{Cl}_2$ using [TBA][PF_6] (0.1 M) as the electrolyte. The redox potentials (E°_{ox} and E°_{red}) were calculated by the mean of the cathodic and anodic peak potentials of a reversible or quasi-reversible wave: $E^\circ = (E_{\mathrm{pa}} + E_{\mathrm{pc}})/2$. [d]Estimated from the onset of the respective redox waves with the Fc/Fc^+ value set to −5.1 eV vs vacuum.[18] [e]Calculated from $E_g = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$.

Table 2. Characteristic Photovoltaic Parameters of Oligomers 1 and 2 as Donor[a]

oligomer	acceptor	D:A ratio	additive	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	PCE [%]
1	$PC_{61}BM$	1:2	–	1.3	1.10	0.25	0.3
2	$PC_{61}BM$	1:2	–	3.6	0.95	0.37	1.3
1	$PC_{71}BM$	2:3	–	1.5	1.12	0.24	0.4
2	$PC_{71}BM$	2:3	–	5.8	0.95	0.40	2.2
1	$PC_{71}BM$	2:3	DIO[b]	3.2	1.10	0.35	1.2
2	$PC_{71}BM$	2:3	DIO[b]	5.8	0.95	0.47	2.6

[a] Device structure: ITO|PEDOT:PSS|D:A|LiF|Al using chlorobenzene as the solvent for donor:acceptor blend. [b] 4 mg/mL.

to that of **I** (0.25 and 0.27 V, respectively)[11] and, therefore, most likely corresponded to oxidations of the DTP-thiophene backbone. Also, the reduction of **2** (−1.80 V) occurred at a more negative potential than **I** (−1.49 V) suggesting that the TPD unit is less electron deficient than the DCV group.[11] As expected, the reduction potentials ($E°_{red}$) of **1** and **2** were only marginally different ($\Delta E°_{red}$ = 0.06 V). Strong cathodic shifts of the oxidation potentials ($\Delta E°_{ox1}$ = 0.27 V and $\Delta E°_{ox2}$ = 0.47 V) were observed due to elongation of the conjugated backbone from **1** to **2**. The onsets of the first redox potentials were used to calculate the HOMO and LUMO orbital energies and gave values of −5.60 and −3.47 eV for **1** and −5.33 and −3.45 eV for **2** (Fc/Fc^+ referenced to −5.1 eV vs vacuum[18]). Addition of thiophene spacers decreased the HOMO−LUMO energy gap primarily by raising the HOMO energy resulting from the increased donor strength of the *π*-conjugated backbone. The HOMO energy of **I** was slightly higher compared to **2** (Δ_{HOMO} = 0.05 eV), while the LUMO energy was significantly lowered (Δ_{LUMO} = 0.23 eV), suggesting that the TPD group is a weaker electron acceptor compared to the DCV unit.[11]

Oligomers **1** and **2** were employed as donor materials in BHJ organic solar cells with a standard device architecture ITO/PEDOT:PSS/D:A/LiF/Al using blends of both $PC_{61}BM$ and $PC_{71}BM$ acceptors. The results are outlined in Table 2 and the *J*−*V* and EQE curves for blends prepared with $PC_{61}BM$ are shown in Figures S2, while those measured for $PC_{71}BM$ are shown in Figure 4a and 4b, respectively. Spin-casting from chlorobenzene solutions with excess acceptor (D:A = 2:3 or 1:2) gave the best results for both fullerene acceptors. With $PC_{61}BM$, power conversion efficiencies (PCEs) of only 0.3% for **1** and 1.3% for **2** could be achieved due to a low short circuit current density (J_{SC}) and fill factor (FF). Oligomer **1** exhibited a higher open circuit voltage (V_{OC}) of 1.1 V compared to 0.95 V measured for **2**, owing to its lower lying HOMO energy level. The obtained V_{OC} is one of the highest values ever reported for oligomer-based solution-processed BHJ solar cells.[19−23] In order to further improve efficiencies, we employed $PC_{71}BM$ as the acceptor material since it is known to increase J_{SC} due to stronger, red-shifted absorption compared to $PC_{61}BM$. However, only a small increase in J_{SC} was observed for **1** with a PCE of 0.4%. Much larger improvements were observed for **2** (1.3% to 2.2%) due to an increased J_{SC} value; the V_{OC} and FF remained relatively constant. We further optimized solar cells containing $PC_{71}BM$ by the addition of 1,8-diiodoctane (DIO), which is known to selectively dissolve $PC_{71}BM$ giving smaller domains, therefore larger donor−acceptor interfaces, in polymeric BHJ-OSCs.[24] Power conversion efficiencies of **1** were increased from 0.4% to 1.2% when 4 mg/mL of DIO was added to the blend due to an elevation of J_{SC} (1.5 to 3.2 mA cm^{-2}) and FF (0.24 to 0.35). For **2**, only a small enhancement of the efficiency was measured (2.6%) owing to the elevation of FF to 0.47 from 0.40. Overall, **2** exhibited superior PCEs compared to **1** due to a higher J_{SC} and FF, which most likely resulted from strong absorption and better charge transport. The PCE obtained is among the best values reported for oligomers with a similar band gap.[19−23]

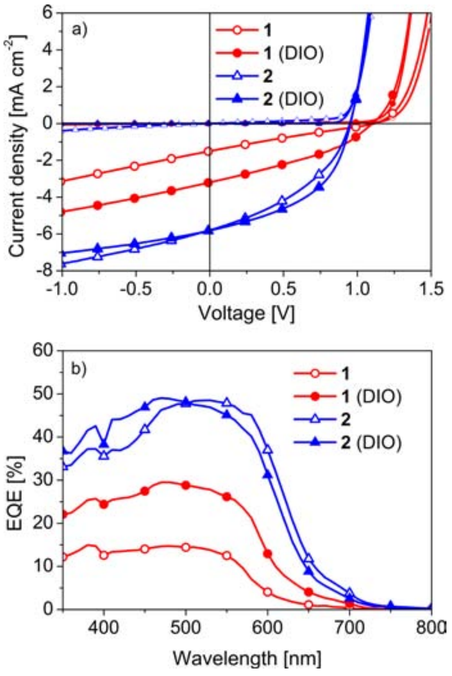


Figure 4. (a) *J*−*V* curves and (b) EQE curves of photovoltaic devices containing oligomers **1** and **2** as the donor and $PC_{71}BM$ as the acceptor, with and without DIO (4 mg/mL) as the additive.

The EQE spectra of **1**:$PC_{71}BM$ and **2**:$PC_{71}BM$ with and without DIO are shown in Figure 4b. Both blends displayed broad curves with a maxima ranging from ~420 to ~550 nm for **1** and ~580 nm for **2**. Based on the differences in J_{SC}, overall higher EQEs were measured for **2** (49%@530 nm) than for **1** (30%@480 nm), with little change by the addition of DIO seen for the former.

In conclusion, we have synthesized two new A−D−A donor oligomers that incorporate a dithieno[3,2-*b*:2′,3′-*d*]pyrrole and thieno[2,3-*c*]pyrrole-4,6-dione units by traditional Stille coupling methods. By incorporating a weaker electron-accepting terminal TPD unit, the absorption profiles were shifted to higher energy yielding band gaps of 1.92−2.04 eV. Upon extension of the electron-rich core by additional thiophenes in **2**, the HOMO−LUMO gap was diminished by an increase in the HOMO orbital energy. Solution-processed BHJ solar cells using the $PC_{71}BM$ acceptor and DIO as an additive gave PCEs of 1.2% and 2.6% for **1** and **2**, respectively. Although a large band gap limits the J_{SC} value, high V_{OC} values up to 1.1 V were obtained. Furthermore, a higher EQE close to 50% could be measured for **2**:$PC_{71}BM$ blends. We are currently pursuing further structural variations in these DTP-based oligomers in order to improve the optical absorption as well as device performance.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Syntheses, NMR, MS, analysis details. 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.

■ ACKNOWLEDGMENTS

We would like to thank the German Ministry of Education and Research (BMBF) for financial support in the frame of joint project LOTsE, Alexander von Humboldt Foundation for a Postdoctoral Research Fellowship for L.G.M., and the Japan Society for the Promotion of Science (JSPS) for a grant to Y.I.

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