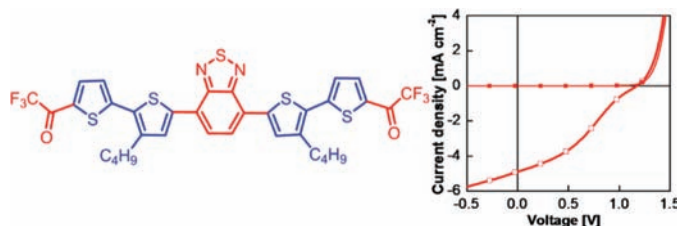


A-D-A-D-A-Type Oligothiophenes for
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ABSTRACT



Novel A-D-A-D-A-type oligothiophenes incorporating electron-withdrawing benzo[*c*][1,2,5]thiadiazole (BTDA) as core and trifluoroacetyl (TFA) as terminal acceptor groups have been developed. Vacuum-processed planar heterojunction organic solar cells incorporating these new oligomers as donor and C₆₀ as acceptor showed very high open circuit voltages up to 1.17 V, resulting in power conversion efficiencies of 1.56% under AM1.5G conditions.

Organic solar cells (OSC) have attracted a great deal of interest in recent years for their ability to convert solar light to electricity at low cost. They can be fabricated at low temperatures and on flexible substrates.¹ Since the pioneering work on bilayer organic solar cells² based on small molecules, encouraging breakthroughs in efficiencies have been achieved over the past decade. The success was mainly due to the synthetic progress in multifunctional organic semiconductors.^{3,4} In contrast to most inorganic semiconductors, the main advantage of organic materials is their high absorption coefficient, enabling the fabrication of very thin photovoltaic devices with low material consumption. Currently, for small molecule tandem solar cells prepared by vacuum processing, a certified power conversion efficiency

(PCE) of 8.3% has been released.⁵ The latest improvement was achieved by the use of a dicyanovinyl-substituted oligothiophene (DCVnT) as donor and C₆₀ as acceptor, which facilitated a simultaneous increase in both the open circuit

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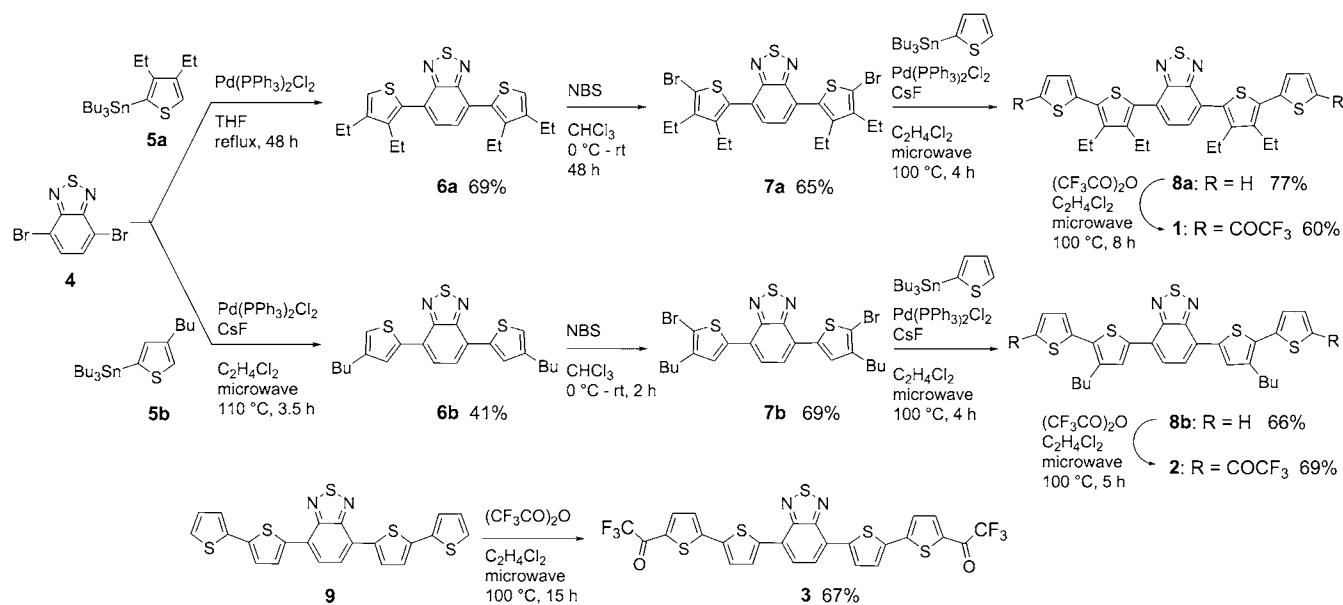
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Scheme 1. Synthesis of Oligomers 1–3



voltage (V_{OC}) and short circuit current density (J_{SC}). By using similar DCVnT derivatives, photovoltages as high as 1.0 V and PCEs of up to 4.9% have been reported.^{3b,f} Bulk heterojunction solar cells based on the same class of compounds showed even improved PCEs of 5.2%.^{3g}

Today, benzo[*c*][1,2,5]thiadiazole (BTDA) is one of the most widely used acceptor moieties in low band gap materials for organic electronic applications, such as organic solar cells (OSC).⁶ For this purpose, the BTDA unit has been combined with carbazoles, fluorines, pyrroles, thiophenes, and other electron-rich building blocks.⁷ Motivation for the incorporation of the heterocyclic BTDA unit into π -conjugated systems is its excellent thermal stability, high absorption coefficient, suitable HOMO and LUMO energy levels, and strong intermolecular π - π interactions, leading to ordered morphologies in the solid state.

In this study, we report the synthesis, characterization, and application of novel A-D-A-D-A-type oligothiophene-based pentamers, comprising the electron-deficient BTDA unit as core and trifluoroacetyl (TFA) as terminal acceptor moiety.

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The application of these materials as donor in m-i-p-type planar heterojunction solar cells prepared by vacuum sublimation technique is described.

The new A-D-A-D-A oligomers were synthesized according to Scheme 1. 3,4-Diethylthiophene was synthesized according to literature.⁸ Lithiation of 3,4-diethylthiophene followed by quenching with tributyltin chloride afforded tributyl(3,4-diethylthien-2-yl)stannane **5a** in 87% yield. Terthiophene **6a** was prepared by Pd⁰-catalyzed Stille-type cross-coupling reaction of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole **4**⁹ and **5a** in a yield of 69%. Bis-bromination of **6a** with NBS in chloroform gave terthiophene **7a** as yellow-orange crystals in 65% yield. Subsequent microwave-assisted Stille-type coupling of **7a** with tributyl(thien-2-yl)stannane afforded pentamer **8a** in a yield of 77%. By reacting **8a** with trifluoroacetic anhydride under microwave irradiation, title compound **1** was obtained as an orange powder in 60% yield. Derivative **2** was prepared following the procedure of title compound **1**. Therefore, tributyl(4-butylthien-2-yl)stannane **5b** was synthesized in analogy to literature.¹⁰ A Stille-type coupling reaction of **4** and **5b** gave trimer **6b** in a yield of 41%. The subsequent dibromination of **6b** with NBS followed by a Stille-type coupling reaction with tributyl(thien-2-yl)stannane gave **8b** in a yield of 66%. Reaction of **8b** with trifluoroacetic anhydride under microwave irradiation afforded title compound **2** in a yield of 69%. Pentamer **9** was synthesized via microwave-assisted Stille-type cross coupling of dibromobenzo[*c*][1,2,5]-thiadiazole⁹ and monostannylated bi thiophene¹¹ in analogy to literature.^{7a} By adding

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cesium fluoride and applying microwave irradiation yields for the synthesis of **9** were improved from 14% to nearly 60%. Reaction of **9** with trifluoroacetic anhydride under microwave conditions gave title compound **3** as a dark red powder in 67% yield.

Thermal stability of the BTDA derivatives was investigated by thermogravimetric analysis (TGA). The onset of decomposition temperature (T_d) was about 355 °C for **1** and 367 °C for **2** and **3**, respectively (Figure S1, Supporting Information). This indicates that they have good thermal stability, which is an important parameter in device fabrication.

Electronic absorption spectra of BTDA-oligomers **1**, **2**, and **3** in dichloromethane are displayed in Figure 1a and corresponding data are summarized in Table 1.

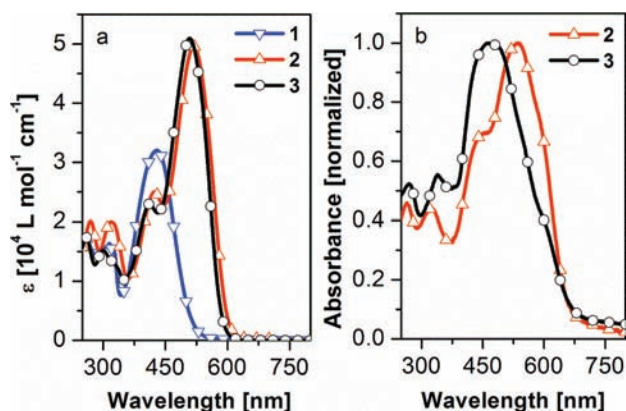


Figure 1. Absorption spectra of BTDA-oligomers **1–3** in (a) solution and (b) thin film (30 nm).

The UV–vis spectrum of ethyl-substituted derivative **1** showed a longest wavelength absorption maximum at 430 nm, which is blue-shifted by about 80 nm when compared to pentamers **2** and **3**. The hypsochromic shift indicates a twist of the aromatic system, due to strong sterical hindrance in **1**, caused by the BTDA moiety and its adjacent ethyl-substituted thiophene rings. By attaching the terminal acceptor groups, the molar extinction coefficients of the resulting target oligomers were increased by almost a factor of 2 (e.g., **3**: $\lambda_{\text{max}} = 509 \text{ nm}$, $\epsilon = 50\,300 \text{ L mol}^{-1} \text{ cm}^{-1}$; **9**: $\lambda_{\text{max}} = 505 \text{ nm}$, $\epsilon = 25\,400 \text{ L mol}^{-1} \text{ cm}^{-1}$) in comparison to the parent oligomers. This effect can be assigned to (1) the extension of the conjugated π -system and (2) the enforced

quinoidal character of the conjugated system, due to the terminal electron-withdrawing TFA groups. The alkyl side chains in BTDA-oligomer **2** increase the donor character of the thiophene rings by hyperconjugation, resulting in a more distinct alternation of electron-rich and electron-deficient moieties in the conjugated system. Thus, derivative **2** showed a longest wavelength absorption at 518 nm, which is red-shifted by 9 nm when compared to the nonalkylated counterpart **3**.

Figure 1b depicts the normalized solid-state UV–vis absorption spectra of **2** and **3** deposited by vacuum evaporation as 30 nm thin films on a quartz plate. Due to the strong hypsochromic shift in solution, no thin films or OSCs were prepared of compound **1**. In the solid state, derivative **3** showed a broad longest wavelength absorption with a maximum at 466 nm, which is 43 nm blue-shifted when compared to the absorption in solution. The hypsochromic shift in the film is presumably caused by the formation of H-type aggregates.¹² The solid state spectrum of **2** showed a broad absorption band and a bathochromic shift of 15 nm, when compared to the absorption in solution, which is probably caused by π -stacking of the molecules in the film.

In cyclic voltammetry measurements, the studied compounds **1–3** each showed two reversible one electron oxidation waves (Figure 2, Table 1). Due to the twist of the

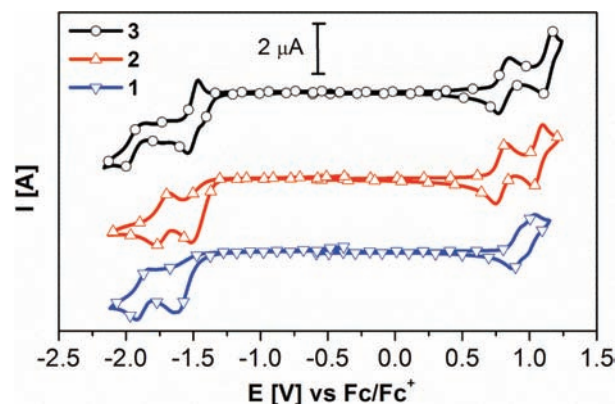


Figure 2. Electrochemical characterization of BTDA-oligomers **1–3** in dichloromethane-TBAPF₆ (0.1 M), scan speed 100 mV/s. Fc/Fc^+ was used as external reference.

thiophene rings adjacent to the BTDA moiety and the resulting weakened conjugation, the electronic influence of the BTDA acceptor on the neighboring bithiophene units in

Table 1. Optical and Electrochemical Data of BTDA Derivatives **1–3**

oligomer	λ_{abs} (nm) soln (ϵ , $\text{L mol}^{-1} \text{ cm}^{-1}$)	λ_{abs} (nm) film	ΔE^{opt} (eV) soln	ΔE^{opt} (eV) film	E^{ox1} (V)	E^{ox2} (V)	E^{red1} (V)	E^{red2} (V)	HOMO (eV)	LUMO (eV)	ΔE^{CV} (eV)
1	430 (32 000)		2.44		0.91	1.00	-1.57	-1.88	-5.94	-3.64	2.30
2	518 (49 500)	533	2.08	1.89	0.79	1.06	-1.46	-1.73	-5.82	-3.74	2.08
3	509 (50 300)	466	2.10	1.83	0.81	1.14	-1.50	-1.93	-5.84	-3.73	2.11

compound **1** is strongly reduced. Thus, in contrast to BTDA derivatives **2** and **3**, the first oxidation wave in **1** is shifted to higher potential and is therefore observed very close to the second oxidation wave. In the cathodic potential regime, compounds **1** and **2** showed each one irreversible and a reversible reduction wave, corresponding to the reduction of the central BTDA and the terminal TFA moieties, respectively. BTDA-derivative **9** showed a quasireversible reduction wave at -1.62 V (Figure S2, Supporting Information). Compound **3** displayed a reversible wave corresponding to the reduction of the BTDA unit and one quasireversible reduction wave for the terminal acceptor groups. The HOMO and LUMO energy values of these dyes, determined from electrochemical measurements, are suitable for the application in OSCs (Table 1).

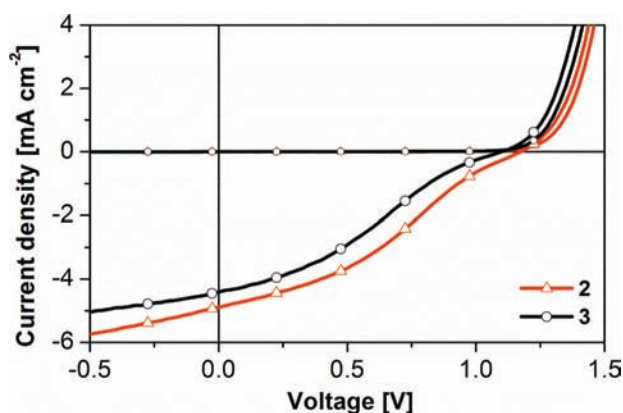


Figure 3. J - V characteristics of PHJ solar cells with BTDA **2** and **3** as donors under AM 1.5G white light illumination.

Figure 3 shows the current density–voltage (J - V) characteristics of m-i-p-type planar heterojunction (PHJ) solar cells comprising the layer structure: ITO/ C_{60} (15 nm)/BTDA-oligomer **2** or **3** (6 nm)/BPAPF (5 nm)/BPAPF:NDP9 (30 nm 9 wt %)/BPAPF:NDP9 (10 nm 18 wt %)/p-ZnPc (10 nm 4 wt %)/Au (50 nm). The corresponding solar cell data are summarized in Table 2. The cells showed clear rectifica-

Table 2. Characteristic Solar Cell Data of Oligomers **2** and **3**

oligomer	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF	η (%)	cell area (mm^2)
2	1.17	4.04	0.33	1.56	2.76
3	1.10	4.38	0.30	1.45	2.76

^a Values measured with shadow mask and using a linear correction to an illumination level of 100 mW cm^{-2} . ^b Measured with an aperture mask.

tion behavior in the dark. The devices based on compound **2** gave an excellent open circuit voltage (V_{OC}) of 1.17 V and a shortcut current density (J_{SC}) of 4.04 mA cm^{-2} . In combination with a fill factor (FF) value of 0.33, the devices led to overall power conversion efficiencies (PCE) of 1.56%

under simulated solar illumination under AM 1.5G conditions. With compound **3** as donor and a similar layer sequence, we observed an equally high V_{OC} of 1.10 V, a J_{SC} of 4.38 mA cm^{-2} , and a FF value of 0.30, leading to an overall PCE of 1.45%.

Due to the low-lying HOMO energy level of the donors the obtained V_{OC} values of up to 1.17 V are among the highest values reported for OSCs.¹³ The V_{OC} is generally governed by the energy difference between the HOMO of the donor and the LUMO of the acceptor. However, the S-shape of the J - V curve results in a modest FF of about 30%. The reason for this S-shape is that the HOMO of the BTDA derivatives (ca. -5.8 eV) lies deeper than the HOMO of the hole transporter (BPAPF/NDP9). As pointed out in more detail by Uhrich et al.¹⁴ such an energetic situation in combination with a planar photoactive heterojunction has two consequences: First, hole injection from the hole transport layer (HTL) into the donor faces an energetic barrier, resulting in a low slope of the J - V curve for positive currents slightly above V_{OC} . Second, the V_{OC} tends to exceed the built-in potential of the cell so that the (negative) photocurrent for applied voltages slightly below V_{OC} is only driven by diffusion against the electric field. However, the S-shape caused by the HOMO misalignment is not the only reason for the low FF. We also observe a lack of saturation of photocurrent with reverse bias that indicates significant recombination losses around 0 V. Such behavior may have two reasons: it is connected either with low carrier mobilities (slow escape of the hole from the Coulomb attraction of the electron on C_{60}) or with an insufficient HOMO and/or LUMO offset between the donor and C_{60} .

In summary, we have successfully synthesized novel oligothiophenes **1**, **2**, and **3** comprising BTDA as core and TFA as terminal acceptor units, and obtained materials with interesting optical and electrochemical properties. Vacuum-processed planar “small molecule” organic solar cells have been assembled and PCEs as high as 1.56% were obtained. Very high V_{OC} up to 1.17 V shown here represents one of the highest values reported for organic solar cells. Further improvement of the FF and the device efficiency should be possible by using suitable hole-transporting materials.

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Supporting Information Available: Detailed experimental procedures, synthesis, and characterization of all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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