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Thiophene-2-aryl-2*H*-benzotriazole-thiophene Oligomers with Adjustable Electronic Properties

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ABSTRACT

The synthesis and the optical and electrochemical properties of 2-aryl-2*H*-benzotriazole based thiophene oligomers with chemical modifications either on the phenyl side group or on the backbone are presented. All data, supported by DFT calculations, show that modification on the backbone has a major impact on the electronic properties while the side groups can fine-tune the electronic properties. In addition, one compound exhibits a thermotropic mesophase.

Thiophene based linear oligomers and polymers have been among the most attractive materials in various fields of organic electronics such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), or organic photovoltaics (OPVs).[1] With regard to device fabrication, organic materials are cheap and particularly simple to deposit (either from vacuum or solution). Defined oligomers sometimes have advantages over the corresponding polymers because they can, as a matter of principle, be obtained in higher purity with respect to defects/polymerization faults. Moreover, oligomers can act as model systems allowing estimation of the pure polymer properties by extrapolation of the oligomer properties to infinite molecular weight.[2] Compounds containing electron-poor moieties surrounded by electron-rich parts, so-called donor–acceptor–donor (DAD) compounds, offer the possibility to reduce the HOMO–LUMO gap, thereby shifting the absorption edge toward lower energies. This is of special importance, as there still is a need for new materials absorbing the longer wavelength region (> 600 nm) of the sunlight spectrum in OPVs[3] or giving stable

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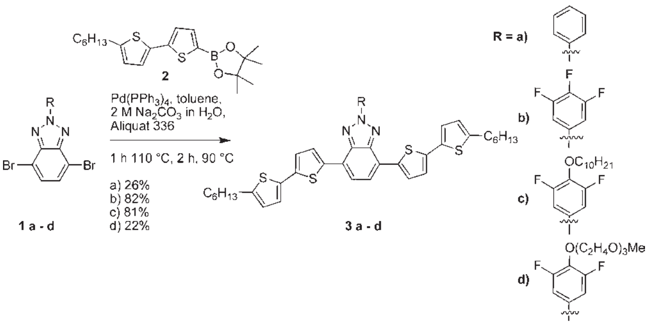
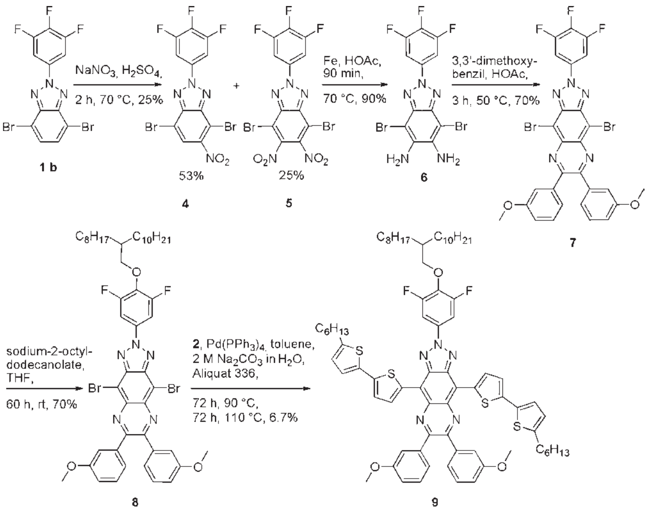
ambipolar OFETs.[4] For example, in the field of fused *N*- and *S*-heterocycles, benzothiadiazole thiophene hybrids have already found applications in OFETs and OPVs.[5] In addition, thiophene based DAD oligomers[6] and polymers[7] with stronger acceptors like [1,2,5]thiadiazolo[3,4-*g*]quinoxaline or diketopyrrolopyrrol exhibit even reduced optical gaps and have entered various fields of organic electronics. Recently, we introduced 2-aryl-2*H*-benzotriazoles as electron-accepting units in conjugated polymers and could show that copolymers thereof have optical properties similar to those of their benzothiadiazole analogues.[8]

Scheme 1. Synthesis of **3a**−**d**



In the present study we report the synthesis and the optical and electrochemical characterization of a series of defined benzotriazole and thiophene hybrids. Specifically we describe DAD compounds with terminal dithiophene units and a central electron-poor 2-aryl-2*H*-benzotriazole unit that is systematically varied at its aryl- (Scheme 1) and benzo-position (Scheme 2). The 2-phenyl-2*H*-benzotriazoles **1a** and **1b** were prepared as described before[8] while **1c** and **1d** were prepared by nucleophilic aromatic substitution of the *para*-fluoride of the 3,4,5-trifluorophenyl group with the respective alcoholate at characteristic points of the reaction pathway (Supporting Information). Future investigations will include both more electron-rich and more electron-poor substituents on the 2-aryl group. Suzuki−Miyaura reaction with 2-(5′-hexyl-2,2′-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) yielded the DAD oligomers **3a**−**d** (Scheme 1). Scheme 2 shows the synthesis of the triazolo[4,5-*g*]quinoxaline oligothiophene **9**. **1b** was nitrated with sodium nitrate in sulfuric acid to give a mixture of the mononitro compound **4** and the dinitro compound **5**.[9] We assume that the rather low yield of **5** is a result of the restricted solubility of **4** that precipitated during the course of the reaction. Nevertheless, pure **5** could be isolated in sufficient quantities to continue the multistep synthesis. Reduction with iron powder in acetic acid and subsequent condensation with 3,3′-dimethoxybenzil gave the triazoloquinoxaline **7** in good yields.

Scheme 2. Synthesis of **9**



The branched, solubilizing 2-octyldodecyl chain was introduced by nucleophilic *ipso* substitution of the fluorine atom in *para* position to the benzotriazole group with sodium-2-octyldodecanolate in THF. A trace amount of *meta* substituted byproduct could be removed via recycling gel permeation chromatography (rec-GPC) after the Suzuki−Miyaura coupling reaction of **8** with **2** and yielded pure **9**. Figure 1 shows the UV/vis absorption spectra of **3a**−**d** and **9** and the emission spectra of **3a**−**d** (**9** does not show any measurable emission). Both the absorption and emission spectra follow the same trend.

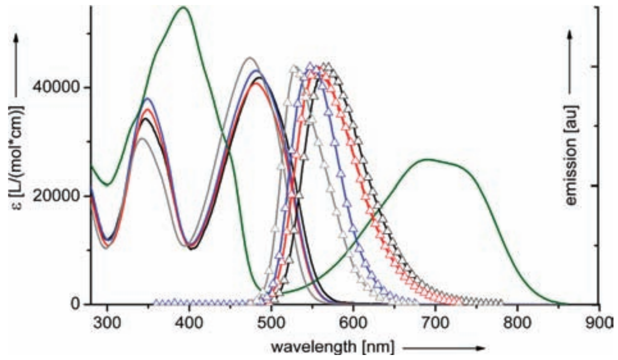


Figure 1. UV/vis absorption spectra (CH_2Cl_2, 1×10^{-5} M, —) and emission spectra (CH_2Cl_2, -Δ-) of **3a** (gray), **3b** (black), **3c** (red), **3d** (blue), and **9** (green).

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(9) **5** could also be crystallized from CH_2Cl_2/pentane. Details on the structure of **5** are given in the Supporting Information.

Table 1. UV/Vis Absorption (λ_{max}^{abs}, ε) and Emission Data (λ_{max}^{em}) As Well As the Optical Band Gap[a] (E_g^{opt}); Redox Potentials of the Reversible Oxidations and Reductions ($E_{1/2}^{ox1}$, $E_{1/2}^{ox2}$, and $E_{1/2}^{red1}$), the Potential Onset of the Second Reduction (E_{ons}^{red2}) vs Fc/Fc$^+$ and the Electrochemical Gap (E_g^{CV})

	λ_{max}^{abs} [nm]/ ε [L mol^{-1} cm^{-1}]	λ_{max}^{em} [nm]	E_g^{opt} [eV]	$E_{1/2}^{ox1}$ [V]	$E_{1/2}^{ox2}$ [V]	$E_{1/2}^{red1}$ [V]	E_{ons}^{red2} [V]	E_g^{CV} [eV]
3a	474/45500	550	2.29	0.32	0.64	−1.96	−2.21	2.28
3b	485/41800	588	2.22	0.40	0.65	−1.86	−2.12	2.26
3c	480/40800	577	2.25	0.37	0.67	−1.90	−2.15	2.27
3d	482/43100	569	2.25	0.37	0.66	−1.89	−2.14	2.26
9	692/26600	–	1.52	0.21	0.52	−1.28	−1.70[b]	1.49

[a] Determined by absorption onset. [b] The second reduction potential of **9** is reversible; therefore the half wave potential was used.

With increasing electron affinity of the benzotriazole moiety a slight but measurable bathochromic shift of the absorption maxima can be observed (Table 1), thus allowing a fine-tuning of the optical properties. Most notably, introduction of the alkoxy or oligoethyleneoxy chain in **3a** and **3b**, respectively, does not affect this behavior. This shows that the benzotriazole acceptor unit bears the possibility to alter the solubility and wettability as well as the morphological behavior of the hybrid compounds without dramatically influencing their optical properties.

When comparing the absorption characteristics of **9** with **3c** a remarkable bathochromic shift is observed (815 vs 550 nm for the absorption onset). Both, the low energy and the higher energy absorptions of **9** are much broader than those for **3c** and indicate the presence of two or more overlapping absorption bands.

A detailed theoretical analysis of the optical transitions will be studied in the near future. Nevertheless, all hybrids reported here can be viewed as DAD structures with a reduced optical gap when compared to their constituents. Cyclic voltammetry (CV) of **3a**−**d** in CH_2Cl_2 shows for all four compounds two reversible oxidations, one reversible and one irreversible reduction signal (Figure 2, irreversible reduction omitted for clarity). The electronic gap was calculated as $E_g^{CV} = E_{1/2}^{ox1} - E_{1/2}^{red1}$ and is only marginally influenced by the substitution pattern (e.g., the values of **3a** and **3b** differ by 0.02 eV; Table 1).

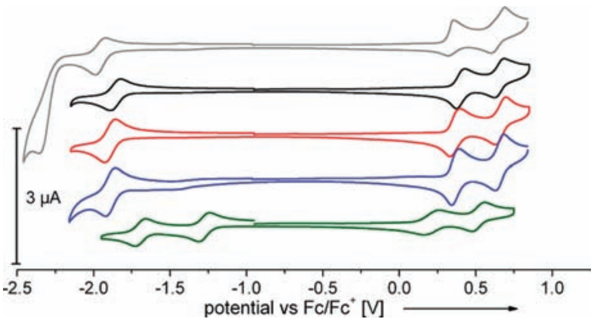

Figure 2. Cyclic voltammograms of **3a** (gray), **3b** (black), **3c** (red), **3d** (blue), and **9** (green) in CH_2Cl_2 ($c \approx 2 \times 10^{-4}$ M) at a sweep rate of 100 mV s^{-1}.

The absolute energy levels, on the other hand, show the expected trends as both the first oxidation and the first reduction potentials shift upon substitution. **3a** is easiest to oxidize and hardest to reduce; **3b** on the other hand shows a higher electron affinity and thereby a less pronounced tendency of being oxidized. Despite similar HOMO−LUMO gaps, the absolute frontier orbital levels can be adjusted by the substitution pattern. Interestingly, quinoxaline **9** shows both an increased electron affinity and a slightly increased tendency of being oxidized. The reversible second reduction of the highly electron-poor aza heterocycle **9** is even lower than the first reductions of **3a**−**d**. In order to gain better insight into the electronic structure of these DAD hybrids, theoretical calculations based on the density-functional theory (DFT) were performed.

The ground state geometries, the frontier orbitals for **3c** and **9** (displayed in Figure 3a), and their respective energies were calculated with the B3LYP functional using a def2-TZVP basis set (Figure 3b and Supporting Information) using the quantum-chemical program package ORCA.[10] The HOMOs are delocalized over the thiophene and benzo units while there is only limited contribution on the triazole subunit. In contrast, the LUMOs are delocalized over the whole molecules with larger coefficients at the electron-poor parts of the molecule. This difference in the HOMO/LUMO localization is especially pronounced for **9**, in accordance with the assumption of the stronger electron-accepting behavior of the quinoxaline moiety. Under the assumption that the long wavelength transitions are predominantly determined by the HOMO−LUMO transition, the excitation leads to an intramolecular charge-transfer (CT) from the thiophenes to the benzotriazole or benzotriazole-quinoxaline units, respectively. These calculations verify our initial assumption that the electron-rich thiophene units act as electron donors and the electron-poor benzotriazole units as electron acceptors in these intramolecular CT complexes. Notably, there is an almost linear relationship between the experimentally determined (CV) and the theoretically calculated energy levels for the

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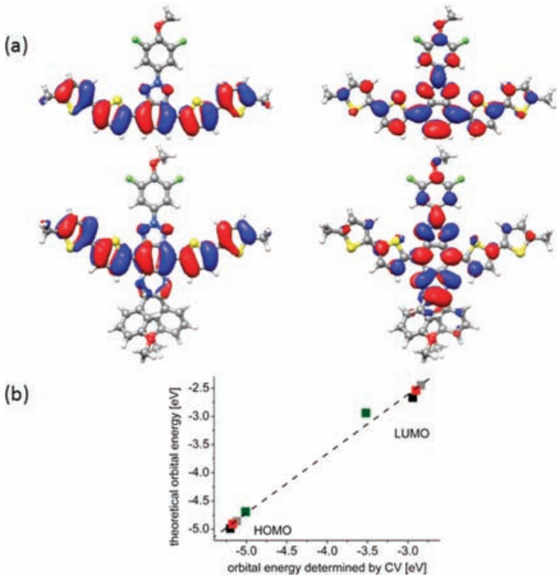

Figure 3. (a) HOMO (left) and LUMO (right) of **3c** (top) and **9** (bottom) calculated with B3LYP/def2-TZVP. (b) Energy level correlation between cyclic voltammetric and computational data Y-axis: **3a** (gray), **3b** (black), **3c** (red), and **9** (green).

HOMOs and LUMOs of these benzotriazole thiophene hybrids (Figure 3b). This relationship shows that, despite the error in the calculated absolute values, theoretical calculations can serve as a valuable tool to guide the synthesis of future DAD materials.

Additionally, **9** exhibits a thermotropic mesophase which was characterized by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) (Figure 4), and that was not observed for the hybrids **3**. The DSC traces show two major transitions during heating which can be assigned to the melting temperature (T_m = 68.6 °C, ΔH = 17.0 kJ/mol) and the isotropization temperature (T_i = 230.8 °C, ΔH = 3.02 kJ/mol) of the compound. The cooling curve shows that recrystallization of the sample from the liquid crystalline phase is slow and the original heating curve could be only reproduced after keeping the sample at room temperature for at least 20 h. A detailed analysis of the phase behavior of **9** is in progress and will be reported elsewhere.

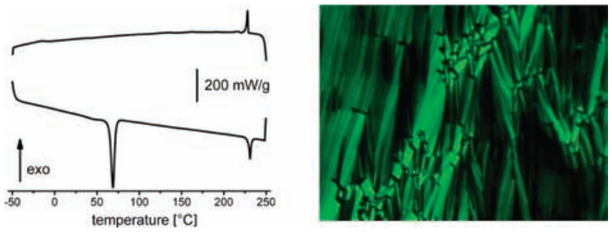

Figure 4. DSC signal of heating and cooling **9** with 10 K min^{-1} and texture of **9** at 150 °C (100 μm × 74 μm).

In summary, we have synthesized a series of benzotriazole-thiophene hybrids with different acceptor units and studied the impact of these substitutions on the optical and electronic properties of the compounds. The UV/vis spectroscopic data support the assumption that the electron-rich thiophene parts act as donors and the electron-poor benzotriazole parts as acceptors. This was further supported by quantum mechanical calculations. CV data show that the absolute levels of the frontier orbitals are more sensitive to the substituents than the optical gap. In addition, a triazoloquinoxaline has been prepared that has an optical gap of 1.5 eV and which exhibits a liquid crystalline phase as indicated by DSC and POM measurements. In addition to tunable electronic properties, benzotriazoles allow the advantageous introduction of solubilizing side groups.

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Supporting Information Available. Synthesis and characterization of all new compounds. Crystallographic data for **4** and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.