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Organoborane Acceptor-Substituted Polythiophene via Side-Group Borylation

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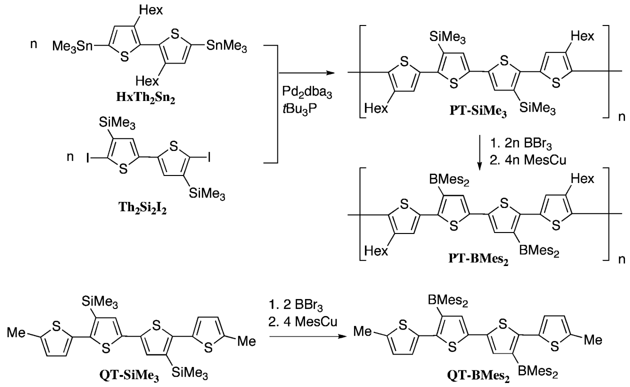
Conjugated organic polymers have emerged as an important class of new materials with applications, for example, in organic light emitting devices, photovoltaics, organic field-effect transistors, and sensor materials.[1] An intriguing aspect is their modification with inorganic or organometallic functionalities, which provides a means to impart new characteristics and different properties.[2] The functionalization with organoborane groups is particularly attractive due to their electron-deficient nature,[3] which can be exploited in the sensing of nucleophiles and may lead to unusual electronic properties. For instance, the use of tri-coordinate organoboranes as small molecule organic device materials has been successfully implemented by Shirota and since further pursued by several other groups.[4] Various examples of conjugated boron-modified polymers with the boron sites embedded into the conjugated polymer main chain have also been reported.[5] While this approach leads to facile preparation of electronically interesting polymers, and in one case *n*-type semiconductivity has been demonstrated,[5c] the tunability is limited since two valencies of boron are tied up in the polymer backbone. Side-chain modification of conjugated polymers with boronate moieties has been studied for use as electrochemical sensors,[6] but the boron centers are electronically stabilized by π-interaction with alkoxy substituents and the polymer films are in many cases insoluble. We describe here a new modular approach to soluble polythiophenes that are functionalized with highly electron-deficient boryl groups.

The silylated polymer **PT-SiMe$_3$** ($M_w = 9107$, PDI = 1.35) was prepared in 66% yield by Stille-type polycondensation (Scheme 1). The NMR spectra of this new soluble polythiophene are consistent with the proposed structure, and MALDI-TOF analysis showed peak patterns corresponding to linear polymers with the expected repeating unit and dihexylbithiophene or Me end groups (Me transfer from SnMe$_3$ groups). The feasibility of the B/Si exchange was confirmed for the model **QT-SiMe$_3$**, where treatment with BBr$_3$ resulted in selective borylation within 6 h.[7] Analogous reaction of the silylated polymer **PT-SiMe$_3$** with a slight excess of BBr$_3$ in CH$_2$Cl$_2$ at room temperature led to quantitative cleavage of the Si−C(sp^2) bonds over a period of 24 h. The ^{11}B NMR resonance of the resulting polymer **PT-BBr$_2$** at $\delta = 50$ compares favorably with that of the model **QT-BBr$_2$** at $\delta = 51$. As expected for the attachment of electron-withdrawing boryl groups, the protons adjacent to the functional groups experience a pronounced downfield shift from $\delta(^1H) = 7.02$ in **PT-SiMe$_3$** to $\delta(^1H) = 7.66$ for **PT-BBr$_2$**.

The soluble borylated polymer **PT-BBr$_2$** was used in situ for exchange of the bromide substituents with nucleophilic reagents. The dimesitylboryl-substituted polythiophene **PT-BMes$_2$** was obtained as a red solid in ca. 68% yield upon treatment of **PT-BBr$_2$** with the arylcopper reagent mesitylcopper, (MesCu)$_n$ (n = 4, 5),[8] at elevated temperature and subsequent precipitation into cold hexanes. **PT-BMes$_2$** is stable in air for several weeks as a solid or in solution. The polymer was fully characterized by multinuclear NMR spectroscopy. The large downfield shift in the ^{11}B NMR to $\delta = 62$ for **PT-BMes$_2$** in comparison to $\delta = 50$ for **PT-BBr$_2$** is consistent with conversion to triarylborane moieties. However, the chemical shift is slightly upfield relative to the quaterthiophene model **QT-BMes$_2$** ($\delta = 69$), which likely is due to greater shielding effects in the polymer. GPC analysis coupled with light scattering in THF gave $M_w = 20650$ (PDI = 1.88, DP = 11, ca. 44 thiophene rings) for **PT-BMes$_2$**. The peak patterns in the MALDI-TOF spectrum are consistent with the expected repeating units and H, Me, and BMes$_2$ end groups (see Supporting Information).[9]

Scheme 1. Synthesis of Boron-Modified Polythiophenes and Quaterthiophene Model Compounds (Mes = 2,4,6-trimethylphenyl)



To examine the ability of the thiophene groups to adopt a coplanar conformation that promotes extended conjugation, single-crystal X-ray structures of the models were obtained. The thiophene rings of two independent molecules in the unit cell of **QT-SiMe$_3$** adopt an all-*trans* arrangement, where the central thiophene rings are coplanar or nearly so (5.87(8)°); however, they are strongly twisted (45.13(5)°/47.30(5)°) relative to the terminal thiophene rings (see Figure S1 of Supporting Information). In contrast, upon substitution with electron-withdrawing Mes$_2$B groups in **QT-BMes$_2$**, an almost coplanar conformation with small dihedral angles of 15.16(9)° is realized despite the steric bulk of the substituents (Figure 1). Similar conformations are likely also encountered for the polymer, providing for favorable electronic communication.[10] DFT calculations on **QT-BMes$_2$** revealed that the HOMO level is situated on the quaterthiophene chain, while the LUMO level shows additional strong contributions from the empty p-orbitals on B that effectively overlap with the quaterthiophene π-system (Figure 1). DFT further indicates that the LUMO level of **QT-BMes$_2$** is lowered by 0.326 eV relative to that of **QT-SiMe$_3$**, and the HOMO−LUMO gap decreases by 0.408 eV.

The absorption spectra of **QT-SiMe$_3$** and **QT-BMes$_2$** in CH$_2$Cl$_2$ display maxima at 357 and 412 nm, respectively, which are well reproduced by TD-DFT calculations, and correspond to excitation from the HOMO to the LUMO levels. For **QT-BMes$_2$**, an additional band is observed at 340 nm, which is primarily due to excitation to a cross-conjugated state (LUMO+2) with orbital contributions from the central bithiophene moiety and two BMes fragments (see Figure S5 of Supporting Information).[11] The polymers display very similar absorptions that are red shifted by about 25 to 30 nm,

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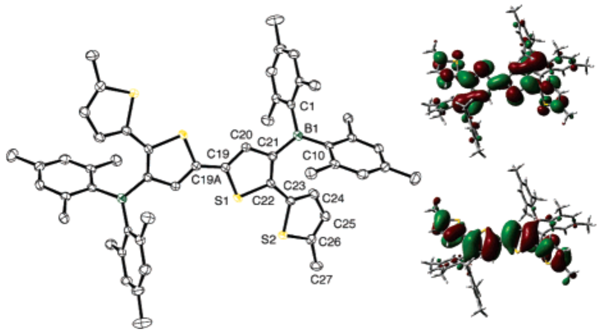

Figure 1. ORTEP plot (50% thermal ellipsoids; hydrogen atoms and a disordered $CHCl_3$ molecule are omitted) and HOMO and LUMO orbital plots from DFT calculations (contour value 0.02) of **QT-BMes$_2$**.

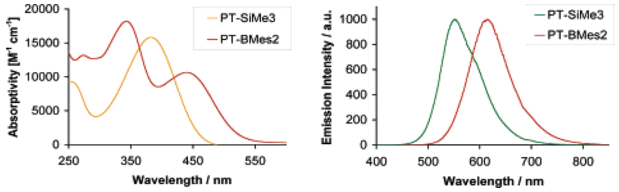

Figure 2. UV−vis absorption and emission spectra of **PT-SiMe$_3$** and **PT-BMes$_2$** in CH_2Cl_2 solution.

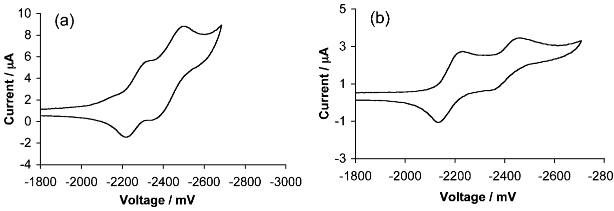

Figure 3. Cyclic voltammograms of (a) **QT-BMes$_2$** and (b) **PT-BMes$_2$** (THF/0.1 M $Bu_4N[PF_6]$, 100 mV/s, referenced vs Fc/Fc$^+$ couple).

indicative of moderately extended conjugation.[10] The strong bathochromic shift (ca. 60 nm) of the absorption of **PT-BMes$_2$** relative to that of **PT-SiMe$_3$** demonstrates that the presence of electron-withdrawing boryl side groups leads to narrowing of the optical gap from ca. 2.70 to 2.36 eV (Figure 2). Likewise, the red emission of **PT-BMes$_2$** (617 nm, $\Phi = 3\%$) is strongly shifted relative to the orange emission of **PT-SiMe$_3$** (554 nm, $\Phi = 10\%$), thereby further confirming the presence of significantly lower LUMO energy levels upon boryl substitution. The absence of a shift in absorption and emission of thin films of **PT-BMes$_2$** suggests that the bulky side groups prevent interchain aggregation.[12]

The electron-accepting ability was studied by cyclic voltammetry in THF. Both **PT-BMes$_2$** and the model **QT-BMes$_2$** show two separate quasi-reversible reduction events that occur at considerably lower potential than for the silylated species. The redox potentials for the boron polymer at $E_{1/2}(1) = -2.18$ V and $E_{1/2}(2) = -2.41$ V are slightly less negative in comparison to those of **QT-BMes$_2$** with $E_{1/2}(1) = -2.27$ V and $E_{1/2}(2) = -2.44$ V relative to the Fc/Fc$^+$ couple (Figure 3).[13] They are similar to those reported by Shirota for the electron transport material 5,5′-bis(dimesitylboryl)-2,2′-bithiophene,[4a] and the first reduction is considerably less cathodic than those of the silylated species **QT-SiMe$_3$** ($E_{1/2}(1) = -2.53$ V) and **PT-SiMe$_3$** ($E_{1/2}(1) = -2.35$ V).

In conclusion, we have prepared the first polythiophene that is substituted with organoborane acceptor moieties and established the strong influence of the boryl groups on the electronic and photophysical properties. Thus, the modification of conjugated polymers with electron-deficient boryl groups as a new design principle for the preparation of electronically interesting materials is demonstrated. The new synthetic route to borylated polythiophenes will likely also open up opportunities in the area of sensor materials and the preparation of other polythiophenes through Suzuki-type coupling chemistry.[14]

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Supporting Information Available: Additional details of experimental and theoretical studies for all polymers and models; full ref 4g. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Mes_2B end groups result from borylation at the α-position of the terminal bithiophene group. Consistently, reaction of 3,3′-dihexyl-2,2′-bithiophene with BBr_3 leads to borylation at the 5,5′-positions.

(10) The head-to-head connection of the dihexylbithiophene moieties in the polymers limits extensive delocalization; thus, the quaterthiophene model systems quite accurately reflect the electronic structures of the polymers.

(11) Despite the charge-transfer character involving states with strong contributions from the boron p-orbitals, **PT-BMes$_2$** shows almost no solvatochromism.

(12) The absorption and emission spectra are essentially independent of the temperature (+50 to −30 °C).

(13) The oxidation potentials for **PT-BMes$_2$** and **QT-BMes$_2$** are similar to those of the silylated species, consistent with comparable energy of the HOMO levels for **QT-BMes$_2$** and **QT-SiMes$_3$** from DFT calculations.

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