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High-Performance Electron-Transporting Polymers Derived from a Heteroaryl Bis(trifluoroborate)

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S Supporting Information

ABSTRACT: In this communication, we report that dipotassium aryl bis(trifluoroborate)s make stable and easy-to-purify yet reactive monomers under Suzuki polycondensation reactions. A bis(trifluoroborate) of 2-alkylbenzotriazole was prepared successfully and copolymerized with dibromobenzothiadiazole in the presence of a Pd catalyst and LiOH, yielding high molecular weight conjugated polymers. This polymer (**P1**) composed of all electron-accepting units shows excellent electron-transport properties ($\mu_e = 0.02$ cm^2 V^{-1} s^{-1}), which proves the value of the aryl bis(trifluoroborate) monomers and suggests that many other types of semiconducting polymers that could not be accessed previously can be synthesized using this approach.

Palladium-mediated carbon−carbon coupling reactions are extraordinarily powerful methods which enable the synthesis of diverse compounds from biologically active molecules to π-conjugated polymers.[1−3] The Nobel Prize in Chemistry in 2010 awarded to Heck, Negishi, and Suzuki highlights the status of these protocols in modern chemical science. In particular, the Suzuki polycondensation reactions employing dihaloarenes and aryl diboronic acids (or esters) have made significant contributions to the progress of organic electronics by supplying it with high-performance organic semiconductors.[4−6] Syntheses of the majority of these polymers are achieved through alternating copolymerizations of all electron-donating comonomers or one electron-donating and one electron-accepting comonomer,[5] either of which make hole-transporting materials for organic light-emitting devices, photovoltaics, and field-effect transistors (OFETs).

However, conjugated polymers composed of all electron-accepting monomers are scarce,[7−10] and actually there are none by Suzuki polycondensation reactions as far as we know. Considering the high electron affinity of these units, the resulting polymers are expected to yield interesting electron-transporting materials for optoelectronic devices.[11−13] One of the issues of synthesizing this material class is the difficulty in recovering high-purity diboronic acids of electron-accepting heteroarenes, a key factor for successful Suzuki polycondensation reactions. Boronic acids are, in general, present together with considerable amounts of anhydrides and cyclic trimers rendering purifications and determination of stoichiometry difficult.[14,15] In addition, electron-deficient heteroaryl boronic acids are vulnerable to protodeboronation reactions.[16,17] Although hindered cyclic boronic esters show improved stability, as demonstrated with the isolation of a benzothiadiazole diboronic ester,[18,19] facile syntheses and purifications of these electron-accepting boronic esters are still far from routine.

To overcome the hurdles in monomer preparation and to realize such new electron-accepting semiconducting polymers, we have thus looked at other types of organoboron derivatives which are stable and easy-to-purify by recrystallization yet reactive under a Suzuki polycondensation protocol. Research by Genet and Molander led us to consider that potassium organotrifluoroborates are likely to satisfy the aforementioned requirements.[14,15] The electron-donating nature of the trifluoroborate moiety is compatible with electron-accepting heteroarenes,[20] which enables the synthesis of comonomers not accessible with trivalent boron functionalities. Grisorio et al. have prepared poly(phenylenevinylene)s with potassium vinyltrifluoroborate through Suzuki−Heck cascade reactions.[21−23] These developments encouraged us to attempt the synthesis of aryl bis(trifluoroborate)s employing electron-accepting heteroarenes.

In this communication, we report the successful synthesis of a dipotassium bis(trifluoroborate) of 2-alkylbenzotriazole and its Suzuki polycondensation reaction with dibromobenzothiadiazole (Scheme 1). Since one of our objectives is to identify a versatile heteroaromatic unit which is electron-accepting, modified with alkyl chains and copolymerized with any dibromo heteroarenes, benzotriazole is thought to be the appropriate choice.[24] We also present the electron-transport characteristics of the resulting solution-processable copolymers in high-performance OFETs demonstrating the significant potential of semiconducting polymers composed of electron-accepting monomers.

Syntheses of the bis(trifluoroborate) **4** of 1,2,3-benzotriazole begin with the bromination of 2,1,3-benzothiadiazole.[8,25] Following desulfurization of the brominated product in the presence of $NaBH_4$ and ring closure with a $NaNO_2$ and AcOH mixture, the dibromobenzotriazole **1** is recovered as a crystalline solid. It is subsequently alkylated with heptadecan-9-ol[26] **2** providing the

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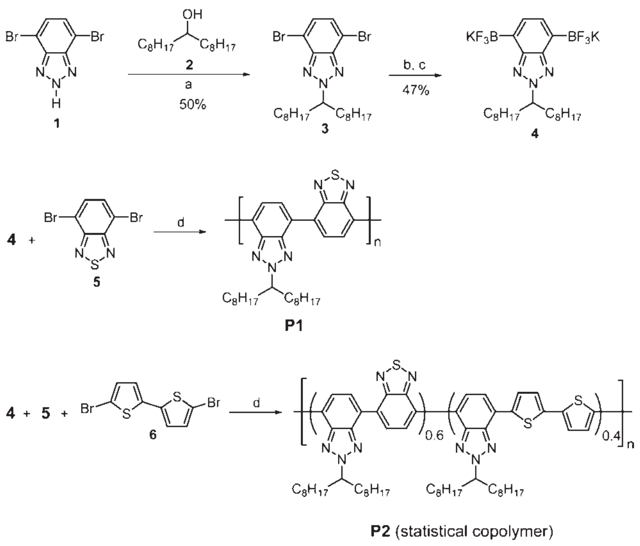
Scheme 1. Synthesis of Copolymers P1 and P2[a]



[a] Reagent and conditions: (a) diisopropyl azodicarboxylate, PPh_3, 0 °C → rt, THF, 3 h; (b) ^{t}BuLi, 2-isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxaborolane, THF, −78 °C → rt, 1 h; (c) KHF_2, MeOH + water, rt, 0.5 h; (d) $Pd(PPh_3)_4$, $LiOH \cdot H_2O$, Et_4NOH, toluene + water, 90 °C, 2 h, end-capping with $PhB(OH)_2$ and PhBr.

Table 1. Summary of the physical properties of P1 and P2

Polymer	M_n (M_w/M_n) (g mol^{-1})[a]	$T_{decomp.}$ (°C)[b]	E_{gap} (eV)[c]	HOMO (eV)[d]	LUMO (eV)[e]
P1	120 000 (1.5)	404	2.0	−5.4	−3.4
P2	29 000 (1.8)	403	1.85	−5.0	−3.15

[a] GPC using 1,2,4-trichlorobenzene at 140 °C with respect to the polystyrene standard (Supporting Information). [b] Onset temperature on TGA thermogram. [c] Band gap energy was extracted from the UV−vis spectra of polymers in thin film state. [d] Measured by ultraviolet photoelectron spectroscopy. [e] Estimated from the HOMO energy level and E_{gap}.

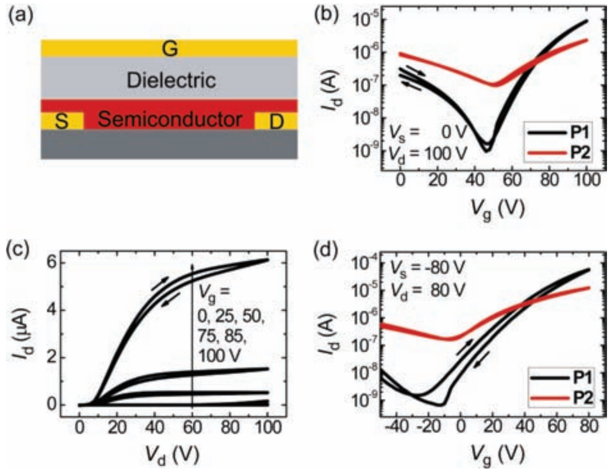


Figure 1. (a) Schematic of top gate/bottom contact OFETs. (b) Transfer characteristics of **P1** and **P2** OFETs using Au electrodes and 550 nm PMMA dielectric (L = 20 μm, W = 2 cm). (c) Electron output characteristics of a **P1** OFET. (d) Transfer characteristics of **P1** and **P2** OFETs analogous to the devices in (b) with 550 nm PS dielectric.

dibromide **3** as colorless crystals in 50% yield. We note that the alkylation reaction can be accomplished conveniently under Mitsunobu reaction conditions employing diisopropyl azodicarboxylate and PPh_3,[27] an interesting feature of benzotriazole. It is, however, not avoidable to obtain an 1-alkylated isomer as a side product which is isolated in 38% yield as a viscous liquid (Supporting Information).[8] The dipotassium bis(trifluoroborate) **4** is then obtained through a diboronic ester as an intermediate. The dibromide **3** is converted into a pinacolyl diboronate by lithiation using ^{t}BuLi and a substitution reaction with isopropoxydioxaborolane. The crude product mixture is treated with a KHF_2 aqueous solution in MeOH.[28,29] It is probable that the pinacolyl diboronate and its hydrolyzed boronic acid are all transformed into the bis(trifluoroborate) **4**, as these compounds are feedstock in this reaction.[30] Without chromatographic purifications, the bis(trifluoroborate) **4** can be recovered as colorless crystals in 47% yield after double recrystallizations from an acetone/Et_2O/water mixture. ^{1}F NMR spectroscopy and elemental analysis proved the high purity of the isolated compound, and X-ray crystallography confirmed the chemical identity of the final monomer **4** (Supporting Information). Heating the dipotassium bis(trifluoroborate) **4** up to 300 °C in air does not induce any appreciable phase change, demonstrating the stability of this compound.

With all the monomers ready, Suzuki polycondensation reactions (Scheme 1) were attempted in toluene, employing an Et_4NOH aqueous solution.[25,31] Interestingly, the molecular weight (M_n) of **P1** was 4.6k. When a portion of LiOH aqueous solution was added to the reaction, the polymerization mixture became much more viscous resulting in an M_n value of 120k (Table 1). The success with LiOH may be related to its superior capability in hydrolyzing the trifluoroborate to the boronic acid, as was suggested by Yuen and Hutton.[29] Along with **P1**, another copolymer **P2** containing a small fraction of a bithiophene unit (20 mol %) was prepared under the same polymerization conditions for comparison.

Differential scanning calorimetry did not provide information on glass transition temperatures of the polymers **P1** and **P2**. Thermogravimetric analysis showed that both polymers have high decomposition temperatures (onset >400 °C, Supporting Information). In the case of **P1**, the thermogram showed a slight weight loss starting at around 230 °C, which is attributed to the release of captured solvent molecules activated by the polymer chains' thermal movement. Solubility tests confirmed that both polymers are soluble in chlorinated aromatic solvents to enable spin coating from solution. Using ultraviolet photoemission spectroscopy (UPS) the HOMO levels of **P1** and **P2** were measured to be about 5.4 and 5.0 eV, respectively. By extracting the optical band gap (2.0 eV for **P1** and 1.85 eV for **P2**) from the UV−vis absorption spectra, respective LUMO levels of about 3.4 and 3.15 eV can be estimated for **P1** and **P2** (Supporting Information).

In order to quantify their electrical performance, **P1** and **P2** were integrated into a top gate/bottom contact OFET architecture with Au electrodes and a poly(methyl methacrylate) (PMMA) dielectric (Figure 1a and Supporting Information). Both polymers allow observation of ambipolar transport without the need for low workfunction metals. For **P1**, an electron mobility of $\mu_e = 3 \times 10^{-3}$ cm^2 V^{-1} s^{-1} and a hole mobility of $\mu_h = 4 \times 10^{-5}$ cm^2 V^{-1} s^{-1}, with respective threshold voltages of

$V_{th,e} = 67$ V and $V_{th,h} = -57$ V, are extracted when using air-stable Au electrodes without further optimization.[32,33] The respective mobilities of $\mu_e = 3 \times 10^{-4}$ cm^2 V^{-1} s^{-1} and $\mu_h = 7 \times 10^{-5}$ cm^2 V^{-1} s^{-1}for **P2** lead to a more balanced transport behavior due to the additional bithiophene units and higher ambipolar currents with lower thresholds ($V_{th,e} = 46$ V, $V_{th,h} = -34$ V). The corresponding output characteristics of the electron transport in **P1** OFETs are shown in Figure 1c. The superlinear increase for low drain voltages is attributed to contact resistance effects, mainly due to the injection barrier from using Au electrodes. Nevertheless, clean electron transport with little hysteresis is achieved.

To further enhance the electron mobilities, OFETs with a polystyrene (PS) dielectric have been fabricated. PS exhibits a lower dielectric constant and thus reduces dipolar disorder.[34] Using an increased voltage range, electron mobilities of $\mu_e = 2 \times 10^{-2}$ and 8×10^{-4} cm^2 V^{-1} s^{-1} can be achieved for **P1** and **P2**, respectively. The transfer characteristics are shown in Figure 1d and demonstrate the capability of particularly **P1** as a high mobility n-type polymer.

In summary, we have shown that dipotassium heteroaryl bis(trifluoroborate)s are stable and easy-to-purify yet reactive monomers under Suzuki polycondensation reaction conditions. With the help of LiOH, bis(trifluoroborate) of benzotriazole copolymerizes successfully with dibromobenzothiadiazole resulting in high molecular weight polymers. These polymers composed of all electron-accepting units show excellent electron-transport properties, which demonstrates the value of bis(trifluoroborate) monomers and indicates that many other types of semiconducting polymers that could not be accessed previously can be synthesized using this approach.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, synthetic procedure, spectroscopic, crystallographic, and thermal analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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