2-Aryl-2*H*-benzotriazoles as Building Blocks for New Low-Bandgap Poly(arylene−ethynylene)s†

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Introduction. During the past decade considerable efforts have been put into the development of new conjugated polymers with reduced bandgaps (<2.0 eV).[1] Aim is the formation of organic photovoltaic devices (OPV) that absorb light with wavelengths longer than 600 nm and convert it efficiently into electric energy.[2] One way toward this goal is given by donor−acceptor systems in which the macromolecule contains both an electron donor and an electron acceptor group covalently linked together. The internal charge transfer complex lowers the excitation energy, thus shifting the absorption spectra into the red region of the spectrum when compared with the corresponding homopolymers. One of the most prominent electron acceptor groups in this context is benzothiadiazole (**1**) (Scheme 1). Copolymers of **1** with cyclopentadithiophene showing interesting power conversion efficiencies (PCE) were recently described.[3] Also, the modulation of the energy levels of the acceptor group by sulfur to oxygen exchange or carbon to nitrogen exchange is reported.[4]

Among numerous copolymers that contain benzothiadiazole in the main chain are also dialkoxyphenylene−ethynylene copolymers. As expected, their absorption spectra (λ_{max} = 498 nm in solution)[5] are red-shifted compared to the dialkoxyphenylene−ethynylene homopolymers.[6] A sulfur to nitrogen exchange in these copolymers would offer some additional benefits for the design of new low-bandgap polymers. For example, polymers with alkyl groups at the nitrogen in 2-position, as reported recently, increase the solubility of rigid polymers.[7] Our work focuses also on a sulfur to nitrogen exchange in the aforementioned system but concentrates on N-aryl derivatives, 2-aryl-2*H*-benzotriazoles (**2**). They offer the possibility to modulate the electronic properties of the acceptor by variation of the aryl substituents. In addition, flexible side chains that influence the solubility behavior of the polymer can also be attached and should affect the morphology in polymer/electron acceptor mixtures (e.g., with fullerenes).[8] Here we report a new route to electron-deficient heterocyclic monomers, 2-phenyl-2*H*-benzotriazole (**7a**) and 2-(3,4,5-trifluorophenyl)-2*H*-benzotriazole (**7b**), as well as the synthesis of the poly(arylene−ethynylene) (PAE) copolymers thereof, **11a** and **11b**, respectively.

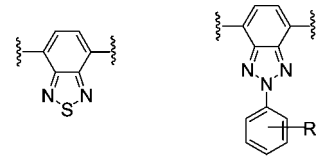
Results and Discussion. The synthesis of 2-aryl-2*H*-benzotriazoles can be accomplished either by oxidative cyclization of the respective 2-aminoazobenzenes[9] or by reductive cyclization of 2-nitroazobenzenes.[10] Preliminary experiments have shown that the latter approach is more general and allows a straightforward monomer synthesis (Scheme 2).

1-Nitro-2-nitrosobenzene (**4**)[11] is readily available by oxidation of 2-nitroaniline (**3**) with oxone in a dichloromethane−water mixture (70% yield).[12] Condensation of **4** with anilines **5a** and **5b** in acetic acid led to the formation of the azo-dyes **6a** and **6b** in yields of 77% and 97%, respectively. Reduction of dye **6a** with formamidinesulfinic acid in basic aqueous ethanol gave 2-phenyl-2*H*-benzotriazol (**7a**) in 78% yield. Reduction of dye **6b** under the same reaction conditions does not provide the desired 2-(3,4,5-trifluorophenyl)-2*H*-benzotriazole (**7b**); instead, 2-(3,5-difluorophenyl-4-ethoxy)-2*H*-benzotriazole is formed via nucleophilic aromatic substitution. Contrary, performing the reaction in *tert*-butanol as a non-nucleophilic solvent gave **7b** in 57% yield. During both reductive cyclizations a very typical color change from purple over black to light yellow occurs, which indicates that the reaction is finished and all intermediate *N*-oxide has vanished.[10] Treating solutions of **7a** and **7b** in HBr/acetic acid (45% w/v) with neat bromine formed 4,7-dibromo-2-phenyl-2*H*-benzotriazole (**8a**) and 4,7-dibromo-2-(3,4,5-trifluorophenyl)-2*H*-benzotriazole (**8b**) in 55% and 71% yield, respectively. This combination of modified literature methods for nitrosoarenes and phenyl-2*H*-benzotriazoles[10] provides an elegant and efficient access to substituted phenyl-2*H*-benzotriazole systems. Copolymerization of the dibromo compounds **8a** and **8b** with 1,4-diethynyl-2,5-bis(2-ethylhexyloxy)benzene (**9**), synthesized by slightly modified literature procedure,[13] under standard Sonogashira−Hagihara conditions, gave the corresponding copolymers **11a** and **11b** in good yields (**11a**: 88%; **11b**: 87%) (Scheme 3). Aqueous work-up and precipitation from THF/*n*-hexane removed low molecular weight impurities, resulting in high molecular weight copolymers with degrees of polymerization (P_n) of 2.1×10^2 for **11a** and 1.4×10^2 for **11b** and a polydispersity (M_w/M_n) of 4.1 for **11a** and 3.4 for **11b** according to GPC (THF, polystyrene).[14] Both polymers are well soluble in common organic solvents like chloroform and THF.

Thermogravimetric analysis shows an onset of weight loss at about 370 °C for both polymers. UV−vis absorption and fluorescence studies on the copolymers **11a** and **11b** in dichloromethane solution and in thin film are shown in Figure 1.

Both solutions appear orange (λ_{max} = 483 nm (**11a**), 493 nm (**11b**)) and show strong yellow fluorescence (λ_{max} = 527 nm (**11a**), 534 nm (**11b**)). Thin films of **11a** and **11b** are diaphanous red and show orange-red fluorescence with an emission maximum at 547 nm for **11a** and at 568 nm for **11b**. UV−vis absorption in thin films is red-shifted compared to the solutions with λ_{max} = 514 nm for **11a** and λ_{max} = 541 nm for **11b**. Optical spectra are in the range of the analogous benzothiadiazole copolymer, but spectral details depend on the aryl substituents of the aryltriazole. Cyclic voltammetry in 0.1 M $(Bu)_4NPF_6$ in dichloromethane shows two irreversible oxidation signals at 0.66 and 0.74 V vs Fc/Fc^+ (Fc: ferrocene) for **11a** and 0.64 and 0.76 V vs Fc/Fc^+ for **11b**. Reversible reduction signals can be detected at −1.81 V for **11a** and −1.72 V vs Fc/Fc^+ for **11b**.

Scheme 1. Electron Acceptor Groups



1 **2**

† Dedicated to Professor M. T. Reetz on the occasion of his 65th birthday.

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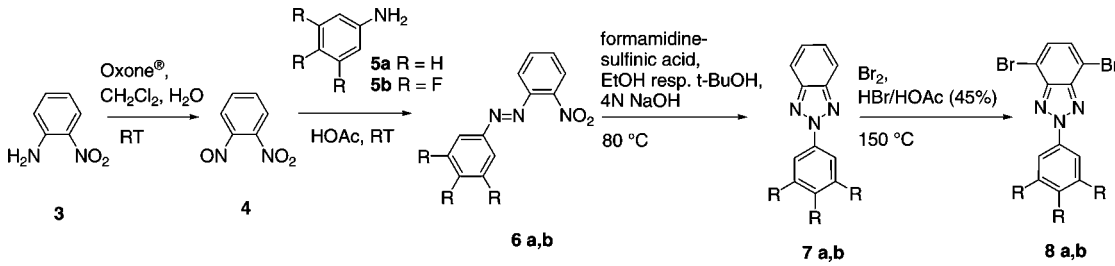
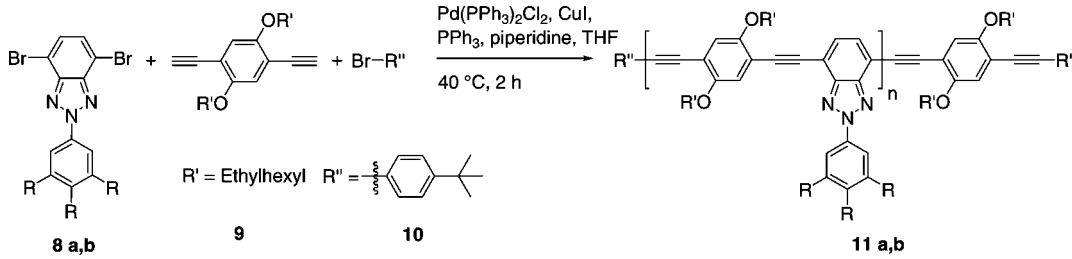
Scheme 2. Synthesis of Monomers



Scheme 3. Synthesis of Copolymers



The electrochemical bandgaps (2.47 eV for **11a** and 2.36 eV for **11b**) are in good agreement with the optically bandgaps determined (2.35 and 2.32 eV, respectively) from the onset of absorption in solution (dichloromethane). The optical bandgap decreases by 0.11 eV for **11a** and by 0.14 eV for **11b** when going from solution to thin films.

In conclusion, we have presented a straightforward and efficient synthesis of *N*-arylbenzotriazole monomers capable of undergoing Pd-catalyzed polymerization reactions to new low-bandgap polymers. The electronic behavior of these compounds can be fine-tuned by varying the substituents at the aryl position. Current investigations deal with the copolymerization of these new monomers with electron-rich building blocks and investigation of the photovoltaic properties thereof.

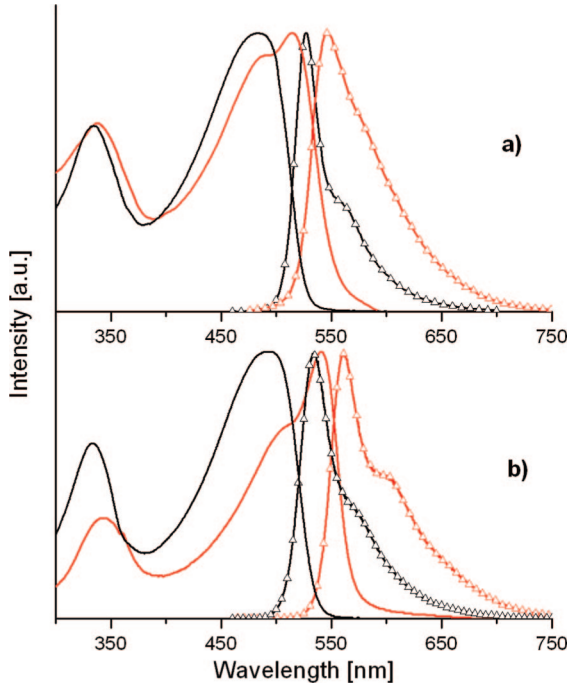


Figure 1. Absorption (—) and emission spectra (Δ, excitation at 450 nm) of polymers **11a** (a) and **11b** (b) in solution (CH_2Cl_2, black lines) and of thin films cast of CH_2Cl_2 solution (red lines). (a) Absorption: $\lambda_{max} = 483$ nm (sol.), $\lambda_{max} = 514$ nm (film); emission: $\lambda_{max} = 527$ nm (sol.), $\lambda_{max} = 547$ nm (film). (b) Absorption: $\lambda_{max} = 493$ nm (sol.), $\lambda_{max} = 541$ nm (film); emission: $\lambda_{max} = 534$ nm (sol.), $\lambda_{max} = 561$ nm (film).

Experimental Section. *General.* Solvents were dried, distilled, and stored under argon if necessary. Reagents were purchased at reagent grade from commercial sources and used without further purification. All air-sensitive reactions were carried out using standard Schlenk techniques under argon. Macherey-Nagel precoated TLC plates (Alugram SIL G/UV_{254}, 0.2 mm) were used for thin-layer chromatography (TLC) analysis. Silica gel 60 M (Macherey-Nagel, 0.04−0.063 mm, 230−400 mesh) was used as the stationary phase for column chromatography. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AM 300 (^1H, 300 MHz; ^{13}C, 75.5 MHz; ^{19}F, 282 MHz), AM 400 (^1H, 400 MHz; ^{13}C, 100.6 MHz), and AM 500 (^1H, 500 MHz; ^{13}C, 125.8 MHz; ^{19}F, 470 MHz) spectrometers, and chemical shifts are reported as δ values (ppm) and referenced to residual ^1H or ^{13}C signals in deuterated solvents. EI-MS analyses were performed on an AEI MS-50. EI-HRMS were recorded on a MAT 95 XL (Thermo Finnigan) and ESI-HRMS on an ESI micrOTOF-Q (Bruker Daltonics). UV−vis absorption spectra were obtained from a Shimadzu UV-2100, and fluorescence spectra were received from a Horiba Jobin Yvon Fluoromax 4. Gel permeation chromatography (GPC) measurements were carried out by using an Agilent Technologies instrument with a set of four columns (PSS, polystyrene, 8 mm × 300 mm, 10^2, 10^3, 10^5, and 10^6 Å) equipped with IsoPump G1310A, autosampler ALS G1329A, UV detector VWD G1314B, and refractive index (RI) detector RID G1362A, with THF (1 mL/min, HPLC grade, Fisher) as eluent. Universal calibration was performed with polystyrene standards (PSS Polymer Standards Service GmbH, Germany). Fourier transform infrared (FTIR) spectra were obtained using a Thermo Electron (Waltham, MA) Nicolet 380. Cyclic voltammetry was performed with a computer-controlled VA-Standard 663 and a μAutoLab type III potentiostat of Metrohm AG, Suisse, in dried and oxygen-free dichloromethane using 0.1 M tetrabutylammonium hexafluorophosphate (electrochemical grade, Fluka) as supporting electrolyte, a platinum disk ($\Phi = 5$ mm) as working electrode, a glassy carbon counter electrode, and an Ag/AgCl reference electrode. Redox potentials were referenced against ferrocene/ferrocenium (Fc/Fc^+). Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851^e.

*1-Nitro-2-nitrosobenzene (**4**).*[11] To a mixture of water (250 mL) and dichloromethane (700 mL) were added 2-nitroaniline (**3**) (12.5 g, 90.5 mmol) and oxone (93.7 g, 152 mmol). The solution was stirred at room temperature for 4 days. After separation of the organic layer the aqueous layer was extracted with dichloromethane (2 × 100 mL). The combined organic layers were washed with 1 N HCl (2 × 100 mL), water (100 mL), a saturated solution of $NaHSO_4$ in water (100 mL), and brine (50 mL). After drying over anhydrous Na_2SO_4 and removal of the solvent in vacuo, the resulting solid was purified by crystallization from ethanol to give a brownish solid (9.65 g, 70%) which was used without further purification. ^{1}H (400 MHz, $CDCl_3$): δ 8.09 (d, J = 7.98 Hz, 1 H), 7.97−7.91 (m, 1 H), 7.67 (t, J = 7.7 Hz, 1 H), 6.48 (d, J = 7.9 Hz, 1 H). EI MS m/z (M^+) calcd for $C_6H_4N_2O_3$: 152.0; found: 152.0.

*(E)-1-(2-Nitrophenyl)-2-(3,4,5-trifluorophenyl)diazene (**6b**).* A solution of 3,4,5-trifluoroaniline (**5b**) (5 g, 34.0 mmol) and 1-nitro-2-nitrosobenzene (**4**) (6.2 g, 44.0 mmol) was stirred in acetic acid (100 mL) for 14 h at room temperature. The solution was poured on ice/water, and the resulting solid was collected by filtration and purified by crystallization from ethanol (140 mL) to furnish a dark red crystalline solid (9.45 g, 97%). ^{1}H (300 MHz, $CDCl_3$): δ 7.97−7.94 (m, 1 H), 7.74−7.57 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.25, 149.90, 147.68, 147.11, 144.32, 140.67, 133.15, 131.44, 124.26, 118.21. ^{19}F NMR (282 MHz, $CDCl_3$): δ −132.35 (d, 2 F, J = 20.1 Hz), −153.82 (t, 1 F, J = 20.1 Hz). IR (cm^{-1}): ν 3088.6, 2356.6, 2331.8, 2004.7, 1990.2, 1954.1, 1621.4, 1597.2, 1581.1, 1538.1, 1517.9, 1484.2, 1443.7, 1344.6, 1230.1, 1206.7, 1189.4, 1029.5, 998.9, 889.9, 864.7, 850.3, 796.5, 749.8, 722.7, 703.1, 655.3, 642.6, 628.7, 570.7, 529.2, 472.2, 457.6, 404.8. ESI HRMS m/z (M^+) calcd for $C_{12}H_7F_3N_3O_2^+$: 282.0485; found: 282.0486.

*2-(3,4,5-Trifluorophenyl)-2H-benzotriazole (**7b**).* A mixture of dye **6b** (2 g, 7.11 mmol), ^{t}BuOH (50 mL), and 4 N aqueous NaOH (40 mL) was stirred at 80 °C when formamidinesulfinic acid (2.52 g, 23.4 mmol) was added in portions. After stirring for 10 h at 80 °C, while the color of the solution turns from deep red to pale yellow, the mixture was poured on ice. The resulting pale yellow solid was collected by filtration and purified by column chromatography on silica gel using dichloromethane−petrol ether (1:4) as eluent to yield the product as colorless needles (1.13 g, 57%). ^{1}H (300 MHz, $CDCl_3$): δ 8.07 (dd, J = 8.43 Hz, 2 H), 7.90 (dd, J = 6.70 Hz, 2 H) 7.44 (dd, J = 6.67 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.1, 149.8, 145.3, 138.4, 128.0, 118.4, 105.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ −131.52 (d, J = 20.4 Hz, 2 F), −159.46 (t, J = 20.6 Hz, 1 F). IR (cm^{-1}): ν 3106.9, 1635.4, 1614.1, 1568.2, 1521.9, 1503.9, 1463.4, 1452.4, 1420.7, 1345.4, 1255.4, 1185.5, 1150.7, 1132.1, 1065.8, 1042.7, 973.1, 904.2, 862.0, 847.9, 798.2, 740.3, 701.7, 664.1, 610.0, 568.5, 548.8, 480.4, 439.5. EI HRMS m/z (M^+) calcd for $C_{12}H_6F_3N_3^{\bullet+}$: 249.0508; found: 249.0510.

*4,7-Dibromo-2-(3,4,5-trifluorophenyl)-2H-benzotriazole (**8b**).* To a solution of **7b** (813 mg, 3.26 mmol) in HBr/acetic acid (45% w/v, 12 mL) at a temperature of 150 °C, bromine (8.3 mL, 163 mmol) was added dropwise over a period of 5 h. After stirring for another 2 h, the mixture was poured on a mixture of ice and 10% Na_2SO_3. The resulting colorless solid was collected by filtration and washed with water and methanol. Purification by crystallization from ethanol (80 mL) gave a colorless solid (940 mg, 71%). ^{1}H (300 MHz, $CDCl_3$): δ 8.15 (m, 2 H), 7.51 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.1, 149.8, 145.3, 138.4, 128.0, 118.4, 105.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ −130.8 (d, 2 F, J = 20.4 Hz), −157.50 (t, 1 F, J = 20.5 Hz). IR (cm^{-1}): ν 3070.5,.1630.9, 1612.0, 1542.2, 1521.4, 1504.2, 1465.1, 1442.0, 1335.1, 1320.0, 1257.8, 1237.7, 1196.6, 1189.6, 1054.9, 956.1, 925.4, 865.1, 819.5, 768.8, 677.3, 666.9, 633.1, 617.0, 556.0, 509.2. EI HRMS m/z (M^+) calcd for $C_{12}H_6Br_2F_3N_3^{\bullet+}$: 404.8719; found 404.8722.

*2-(3,4,5-Trifluorophenyl)-2H-benzotriazole-b-alkyne-b-2,5-bis(2-ethylhexyloxy)benzene Copolymer (**11b**).* Under inert conditions **8b** (182 mg, 0.428 mmol), **9** (174 mg, 0.476 mmol), $Pd(PPh_3)_2Cl_2$ (14.8 mg, 0.021 mmol), CuI (8 mg, 0.042 mmol), PPh_3 (14.4 mg, 0.055 mmol), and *tert*-butylphenyl bromide (**10**) (8.8 mg, 0.041 mmol) were stirred in a mixture of THF (10 mL) and piperidine (2 mL) at 40 °C for 2 h. The reaction mixture was diluted with dichloromethane, washed with water (2 × 50 mL) and brine (50 mL), and finally dried over Na_2SO_4. After removal of the solvent, the resulting solid was precipitated twice from THF/*n*-hexane, giving the desired polymer as a red solid with green metallic luster (255 mg, 87%). ^{1}H ($CDCl_3$, 500 MHz): δ 8.26 (bs, 2 H), 7.67 (bs, 2 H), 7.21 (bs, 2 H), 4.0−3.9 (bm, 4 H), 1.94−1.26 (bm, 16 H), 1.01−0.92 (bm, 6 H), 0.86−0.83 (bm, 6 H). ^{19}F NMR ($CDCl_3$, 470 MHz): δ −156. Two (bm, 2 F), −183.3 (bm, 1 F). IR (cm^{-1}): ν 2955.9, 2926.4, 2858.2, 1633.3, 1524.5, 1492.4, 1463.6, 1413.5, 1378.0, 1256.9, 1236.5, 1213.7, 1046.0, 982.6, 895.6, 857.0, 834.8, 773.7, 728.3, 704.8, 670.1, 633.0, 602.7, 586.7, 529.0, 495.9, 468.0, 457.2, 441.3, 434.3, 424.1, 411.3. GPC (THF, polystyrene): P_n = 137, M_w/M_n = 3.4.

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Supporting Information Available: Experimental procedures and characterization for **6a**, **7a**, **8a**, and **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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