Synthesis and Characterization of a 2,1,3-Benzothiadiazole-*b*-alkyne-*b*-1,4-bis(2-ethylhexyloxy)benzene Terpolymer, a Stable Low-Band-Gap Poly(heteroaryleneethynylene)

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Introduction. Poly(aryleneethynylene)s[1a] are an increasingly important class of stable, highly luminescent polymers with attractive optical,[1] electronic,[2] and sensory[3] properties. Until now, most of the attention has focused upon the dialkyl- and dialkoxy-PPEs, and only very few heteroaromatic poly(aryleneethynylene)s (PAE) have been reported, notably in the groups of Yamamoto, Schanze, Pang, and Klemm.[4−7] These polymers incorporated pyridine,[4] thiophene,[5] and bipyridine[6,7] units into PAEs. However, nothing is known about PAEs that contain larger and/or fused heterocyclic rings with two or more heteroatoms. We herein describe the synthesis and electrochemical characterization of a low-band-gap PAE **4** featuring 2,1,3-benzothiadiazole units. The electron-poor hetero-PAE **4** with its low-lying LUMO should be of interest as novel n-type semiconductor in which electron and not hole transport would be the predominant conduction process.

Results and Discussion. Coupling of 4,7-dibromo-2,1,3-benzothiadiazole to 1,4-diethynyl-2,5-bis(2-ethylhexyloxy)benzene under standard Pd catalysis at 80 °C in triethylamine was unsuccessful. The product was reddish in appearance and showed >20% diyne defects according to ^{13}C NMR. Attempts to improve this approach by optimizing the reaction conditions failed. We anticipated that 4,7-diethynyl-2,1,3-benzothiadiazole (**2**) and a suitably substituted diiodobenzene (**3**) would be better coupling partners in this polycondensation. For the successful synthesis of **2**, 4,7-diiodo-2,1,3-benzothiadiazole (**1**) was coupled to trimethylsilylacetylene, because the 4,7-dibromo-2,1,3-benzothiadiazole was quite unreactive under Heck−Sonogashira coupling conditions. Removal of the trimethylsilyl groups to furnish **2** was effected by potassium carbonate in methanol in an overall yield of 48% starting from **1** (Scheme 1).

Reaction of **2** with **3**[1f] was performed under standard Pd catalysis utilizing 5 mol % of $(Ph_3P)_2PdCl_2$ and CuI as catalyst at 85 °C for 48 h in a piperidine/toluene mixture. During the reaction the solution turned dark-red fluorescent and viscous. Aqueous workup, vacuum distillation of the solvents, and extraction of **4** with hexanes and methanol removed low-molecular-weight impurities and furnished **4** in a 58% yield with a degree of polymerization (P_n) of 18 repeating units and a polydispersity (M_w/M_n) of 2.78 according to GPC (polystyrene standard). The relatively low molecular weight of the polymer **4** and the low yield of the alkynylation of **1** suggests that the 2,1,3-benzothiadiazole ring may function as ligand for Pd(0). That would explain the moderate molecular weight and yield of **4**. The polymer was characterized by its NMR and IR data. As-obtained films show some degree of lamellar order, as evidenced by powder XRD (d = 1.54 nm). This d value represents the interlamellar distance between two polymer chains and corresponds approximately to the wingspan of the two extended (2-ethylhexyloxy) chains in **4**. In the range 0.3−0.4 nm there is a broad diffraction feature suggesting the presence of ample $\pi-\pi$ stacking, with the overall order in **4** being low.[1a]

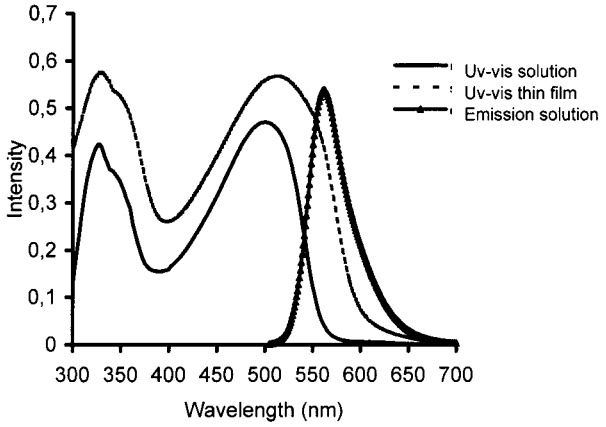

Figure 1. UV−vis spectrum of polymer **4** in chloroform (λ_{max} = 498 nm) and in the solid state (λ_{max} = 508 nm with a shoulder at λ = 553 nm (2.24 eV)). On the right side is shown the emission spectrum of **4** in chloroform solution with $\lambda_{emission}$ = 562 nm. In the solid, the polymer **4** is nonfluorescent.

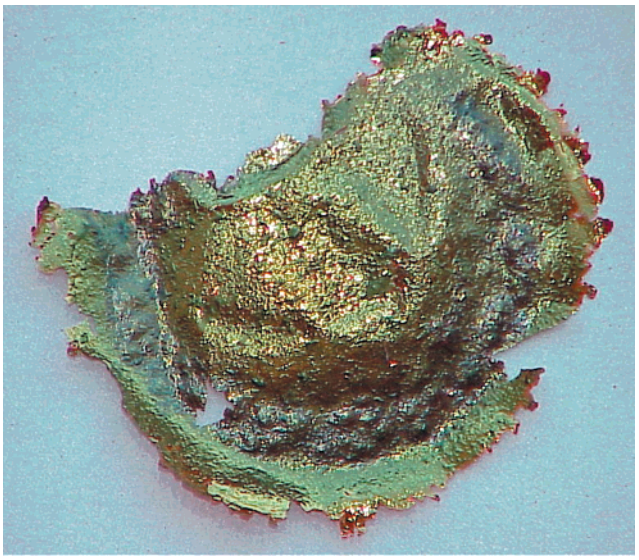

Figure 2. Thin drop-cast film of **4**. The material appears orange in solution, red in thin translucent films, and displays a golden-green luster in the solid state.

A solution of **4** in chloroform appears orange and displays orange-red fluorescence with a maximum emission at 562 nm (Figure 1). In the solid state **4** is nonfluorescent. Very thin films appear translucent-red (λ_{max} = 508, 553 nm; 2.24 eV; comparison dialkyl-PPE 439 nm, 2.92 eV).[1b,e] The most eye-catching property of any thick film of **4** is its golden-green metallic luster, visible in Figure 2. The appearance of **4** is unusual for a PAE. Normally these materials are powdery-yellow and nonlustrous. To explain this unusual behavior at

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Scheme 1

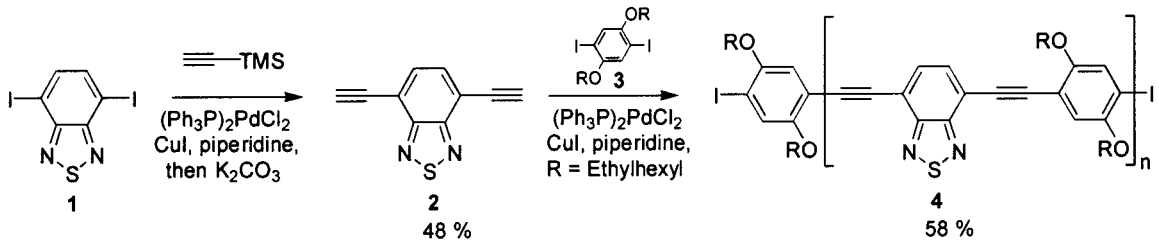
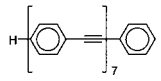
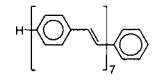
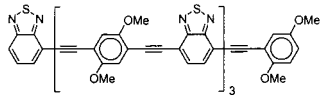


Table 1. Comparison of PM3 Band-Gap Calculations of Several Conjugated Oligomers

Structure	HOMO PM3 [eV]	LUMO PM3[eV]	Band Gap Calc. [eV]
 5_8	-8.46	-1.18	7.28
 6_8	-8.08	-1.21	6.87
 4_8	-8.42	-2.10	6.32

least qualitatively, we performed a series of PM3 semiempirical calculations on oligomers **4**−**6** (Table 1). In comparison to $\mathbf{5}_8$ (calculated band gap 7.3 eV), the HOMO of $\mathbf{4}_8$ is almost unchanged, but the LUMO is decreased by approximately 1 eV to give a calculated HOMO−LUMO gap of 6.32 eV. In $\mathbf{6}_8$, the decrease of the band gap (6.9 eV) in comparison to $\mathbf{5}_8$ is due to a rise in the HOMO. These values (PM3) are meaningful in comparison of the different oligomers and greatly overestimate the absolute band gap due to the omission of interchain, solid-state, and configuration interactions. We further extract from the PM3 calculations that the HOMO of **4** is delocalized, while its LUMO, LUMO+1, and LUMO+2 are *localized* on the heteroaromatic rings.

We know that from the optical data of the polymers in thin films the band gap decreases by 0.58 eV when going from PPEs to **4**. The (optical) band gap of **4** is almost as low as that of the poly(alkylthiophene)s (1.9−2.0 eV), making it an n-dopable low-band-gap polymer. Cyclic voltammetry displayed a *reversible* reduction of **4** with an $E_{1/2}$ of −1.42 V vs Ag/Ag^+. The reduction is accompanied by a color change from red to green. A second, irreversible reduction peak was observed at −2.45 V vs Ag/Ag^+. Oxidation of the polymer was irreversible with a small peak at 0.92 V vs Ag/Ag^+ and a larger peak at 1.34 V vs Ag/Ag^+. It is accompanied by a color change from red to black. The electrochemical band gap for **4** is 2.34 eV. Both optical *and* electrochemical band gaps are in excellent agreement, with the electrochemical band gap being slightly larger.

In conclusion, we have synthesized a low-band-gap heterocyclic poly(aryleneethynylene) that shows both a low-lying LUMO and a low-lying HOMO. This polymer is reversibly reduced and has a greenish-golden luster in the solid state. It may be interesting as n-semiconductor in organic device applications.

Experimental Section. a. 4,7-Bis(trimethylsilyl)-ethynyl-2,1,3-benzothiadiazole. Under inert conditions, **1**[11−13] (4.46 g, 11.5 mmol), $Pd(PPh_3)_2Cl_2$ (554 mg, 0.575 mmol), CuI (100 mg, 0.529 mmol), toluene (5 mL), and piperidine (20 mL) were combined. Trimethylsilylacetylene (2.45 g, 24.9 mmol) was added dropwise to the stirred solution. After 16 h at ambient temperature the reaction mixture was poured into dichloromethane (50 mL) and water. The organic layer was washed twice with water (75 mL), 25% NH_4OH (100 mL), and water (100 mL), dried over magnesium sulfate, and stripped of solvent. Purification by crystallization from methanol at −78 °C gives green-yellow crystals (2.12 g, 55%). ^{1}H NMR ($CDCl_3$): δ 6.80 (s, 2H), 0.00 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 154.19, 133.12, 117.24, 103.61, 99.96, 0.13. IR (cm^{-1}): ν 3306.7, 3051.1, 2962.3, 2900.5, 2853.5, 2247.0, 2152.9, 1944.6, 1875.7, 1683.6, 1559.8, 1537.8, 1490.1, 1411.1, 1357.0, 1338.9, 1248.6, 1027.6, 909.7, 888.9, 759.7.

b. 4,7-Diethynyl-2,1,3-benzothiadiazole (2). To a 250 mL round-bottom flask, 4,7-bis(trimethylsilyl)ethynyl-2,1,3-benzothiadiazole (2.00 g, 6.08 mmol), potassium carbonate (approximately 2.5 g), methanol (125 mL), and water (1 mL) were added and stirred overnight at room temperature. The solution was poured into dichloromethane (50 mL) and water (100 mL). Aqueous workup and crystallization from methanol at −78 °C furnished a green-yellow crystalline material (0.971 g, 86%). ^{1}H NMR ($CDCl_3$): δ 7.74 (s, 2H), 3.66 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 154.63, 132.67, 117.45, 102.24, 100.25. IR (cm^{-1}): ν 2943.0, 2890.7, 2864.4, 2724.8, 2249.1, 2152.7, 1882.8, 1641.8, 1559.3, 1488.7, 1462.0, 1383.5, 1365.3, 1338.0, 1261.2, 1169.0, 1072.3, 995.8, 916.5, 845.6.

c. Preparation of 2,1,3-Benzothiadiazole-*b*-alkyne-*b*-2,5-bis(2-ethylhexyloxy)benzene Copolymer (4). Under inert conditions, **2** (0.310 g, 1.68 mmol), **3**[1f] (0.908 g, 1.54 mmol), $Pd(PPh_3)_2Cl_2$ (74.0 mg, 0.077 mmol), CuI (15.0 mg, 0.077 mmol), dichloromethane (5 mL), and piperidine (15 mL) were added and heated to 85 °C for 48 h. Dilution with chloroform (100 mL), washing with water (2 × 100 mL), 25% NH_4OH (100 mL), and water (100 mL), and drying with $MgSO_4$ are followed by removal of solvent under vacuum. The resulting solid was thoroughly washed with hexanes (until clear) followed by extensive washings with methanol (until clear) to furnish a red-flaky solid with green-metallic luster that was well-soluble in chloroform and dichloromethane (0.412 g, 58%). ^{1}H NMR ($CDCl_3$): δ 7.77 (bs, 2H), 7.16 (bs, 2H), 3.97 (bs, 2H), 1.80−0.78 (bm, 15H). ^{13}C NMR ($CDCl_3$): δ 154.31, 154.23, 132.37, 117.35, 116.55, 114.00, 94.47, 91.28, 72.14, 39.69, 30.65, 29.26, 24.38, 23.99, 23.19, 14.19, 11.40. IR (cm^{-1}): ν 3009.7, 2958.7, 2929.2, 2872.6, 2858.3, 2361.0, 2339.8, 2204.6, 1683.7, 1616.2, 1506.9, 1464.7, 1416.7, 1381.0, 1342.9, 1277.0, 1215.5, 1157.4, 1115.6, 1032.6, 893.0, 844.8, 756.1. GPC (polystyrene): P_n 19, M_w/M_n = 2.78.

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Supporting Information Available: ^{13}C NMR spectrum of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (b) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655. (c) Pschirer, N. G.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 3961. (d) Pschirer, N. G.; Vaughn, M. E.; Dong, Y. B.; zur Loye, H.-C.; Bunz, U. H. F. *Chem. Commun.* **2000**, 85. (e) Evans, U.; Soyemi, O.; Doescher, M. S.; Bunz, U. H. F.; Kloppenburg, L.; Myrick, M. L. *Analyst* **2001**, 508. (f) Diiodide **3** was prepared as described: Kloppenburg, L.; Jones, D.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4194.

(2) (a) Montali, A.; Smith, P.; Weder, C. *Synth. Met.* **1998**, *97*, 123. (b) Schmitz, C.; Pösch, P.; Thelakkat, M.; Schmidt, H. W.; Montali, A.; Feldman, K.; Smith, P.; Weder, C. *Adv. Funct. Mater.* **2001**, *11*, 41. (c) Weder, C.; Sarwa, C.; Montali, A.; Bastiaansen, G.; Smith, P. *Science* **1998**, *279*, 835.

(3) (a) Yang, J.-S.; Swager, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 11864. (b) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593. (c) Swager, T. M. *Acc. Chem. Res.* **1988**, *21*, 201.

(4) (a) Li, Y. T.; Whittle, C. E.; Walters, K. A.; Ley, K. D.; Schanze, K. S. *Pure Appl. Chem.* **2001**, *73*, 497. (b) Ley, K. D.; Li, Y. T.; Johnson, J. V.; Powell, D. H.; Schanze, K. S. *Chem. Commun.* **1999**, 1749. (c) Ley, K. D.; Schanze, K. S. *Coord. Chem. Rev.* **1998**, *171*, 287. (d) Ley, K. D.; Whittle, C. E.; Bartberger, M. D.; Schanze, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3423.

(5) (a) Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 621. (b) Hayashi, H.; Yamamoto, T. *Macromolecules* **1998**, *31*, 6063.

(6) Li, J.; Pang, Y. *Macromolecules* **1998**, *31*, 5740.

(7) (a) Egbe, D. A. M.; Klemm, E. *Macromol. Chem. Phys.* **1998**, *199*, 2683. (b) Grummt, U. W.; Birckner, E.; Klemm, E.; Egbe, D. A. M.; Heise, B. *J. Phys. Org. Chem.* **2000**, *13*, 112.

(8) For synthesis of other interesting heterocyclic polymers: (a) Politis, J. K.; Curtis, M. D.; Gonzalez-Ronda, L.; Martin, D. C. *Chem. Mater.* **2000**, *12*, 2798. (b) Zhang, C. Y.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 8783. (c) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 7422.

(9) For an interesting low-band-gap polymer, see: Meng, H.; Wudl, F. *Macromolecules* **2001**, *34*, 1810.

(10) (a) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183. (b) Schopf, G.; Kossmehl, G. *Adv. Polym. Sci.* **1997**, *129*, 3. (c) Reddinger, J. L.; Reynolds, J. R. *Adv. Polym. Sci.* **1997**, *145*, 57.

(11) Pesin, V. G.; Khaletskii, A. M.; Chzi-chzhun, C. *J. Gen. Chem.* **1957**, *27*, 1643.

(12) Khaletskii, A. M.; Pesin, V. G.; Chzi-chzhun, C. *Acad. Sci. (USSR)* **1956**, *106*, 31.

(13) (a) Pilgram, K.; Zupan, M.; Skiles, R. *J. Heterocycl. Chem.* **1970**, *7*, 629. (b) Tsuba, Y.; Suzuki, T.; Miyashi, T. *J. Org. Chem.* **1992**, *57*, 6749.

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