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Tetrahedron Letters 45 (2004) 5637–5641

Tetrahedron
Letters

Synthesis of bis[(3,4-ethylenedioxy)thien-2-yl]-substituted benzenes

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Received 27 November 2003; revised 21 May 2004; accepted 24 May 2004
Available online 11 June 2004

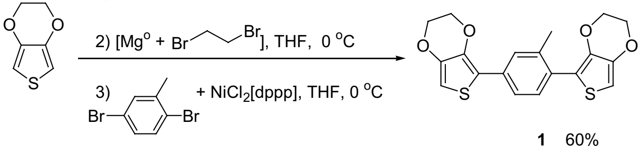
Abstract—A series of bis-EDOT-aryl monomers have been synthesized, which have blue emission characteristics with quantum yields ranging from 0.01% to 10.3%. Polymers were obtained by electrochemical synthesis. Cyclic voltammetry was employed to characterize the electrochemical behavior of these systems.

The past decade has seen a rapid growth in the application of semiconducting conjugated polymers such as poly(*p*-phenylenevinylene) (PPV), polyfluorenes, poly(thiophene), and their derivatives, for use as photonic/electronic materials for LED, thin-film organic transistor and NLO applications, fluorescence sensors for chemical and biological applications, etc.[1] Co-polymers of these systems have been used as the emissive layer in polymeric LEDs (PLEDs).[2] This has led to a renewed focus on π-conjugated oligomers based on thiophenes with a specifically tuned molecular property, because their chemical structures can be well defined and their physical properties can be molecularly tuned with a relative ease.[3] Extensive research has been done on poly(3,4-ethylenedioxythiophene) (PEDOT),[4] however, in contrast to other thiophene based systems, 3,4-ethylenedioxythiophene (EDOT) systems have received less attention.[5]

EDOT-aryl based monomers have been synthesized and polymerized to yield electrochromic polymers.[6] Dialkoxyaryl substituted materials were synthesized by Negishi cross couplings, followed by chemical or electrochemical methods to obtain low-oxidation potential conductive EDOT-dialkoxyaryl systems.[7] Linear and star branched EDOT-dialkoxyaryl based systems obtained from Stille and Grignard metathesis couplings[8] afforded electro- and thermochromic polymers.[9] Polyoxadiazoles based on EDOT-aryl systems prepared by the polyhydrazide precursor route allowed both p- and n-dopable polymers, which also exhibit photoluminescent behavior.[5a] EDOT has also been used as a building block for push–pull nonlinear optic chromophores.[10] Recently, the synthesis of two EDOT analogues, its unsymmetrical sulfur,[11] and selenophene[12] derivatives have been developed as building blocks for linear π-conjugated systems.

Herein we report the synthesis and photoluminescent properties of EDOT-benzene based materials, containing alkyl, alkoxy, nitro, fluoro, methyl ester, and carboxylic acid substituents on the aryl ring as potential materials for opto-electronic devices including the emissive layer of LEDs and microring organic lasers.

Scheme 1 depicts the synthesis of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-toluene **1** (BEDOT-TOL) by a Kumada cross-coupling reaction, using an entrainment



1 60%

Scheme 1. Kumada coupling.

Keywords: EDOT; Optical properties; Cross-coupling; Electrochemistry.

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doi:10.1016/j.tetlet.2004.05.114

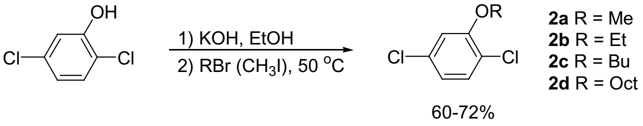
procedure and 2,5-dibromotoulene to afford BEDOT-TOL in 60% yield and was previously reported by our group and included in this discussion.[13]

The formation of the alkoxy precursors, previously reported by Chen and Chao,[14] was obtained by a Williamson ether synthesis by reacting commercially available 2,5-dichlorophenol in the presence of ethanolic KOH followed by the addition of the corresponding alkylhalides to afford compounds **2a–d** in good yields after purification by Kugelrohr distillation (Scheme 2).[15]

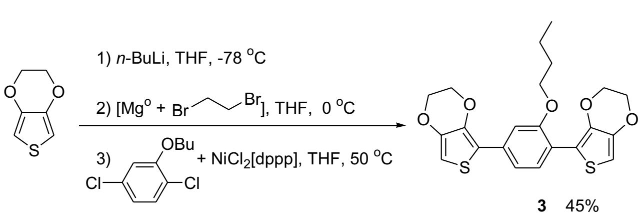
The resulting 2-alkoxy-1,4-dichlorobenzenes were then cross-coupled with EDOT by a Kumada coupling similar to the formation of **1**, but more vigorous reaction conditions were used to promote reaction of the sluggish dichlorobenzenes. Scheme 3 shows the formation of 1,4-bis[(3,4-ethylenedioxy)thien-2-yl]-2-butoxybenzene **3** (BEDOT-BOB).

Initial attempts at the synthesis of 1,4-bis[(3,4-ethylenedioxy)thien-2-yl]-2-nitrobenzene **4** (BEDOT-NITRO) by a Negishi cross-coupling with EDOT and 2,5-dibromonitrobenzene using commercially available $Pd(Ph_3P)_4$ failed to give the cross coupled product under a variety of reaction conditions, but formation of the mono-coupled derivative was obtained after column chromatography. However, formation of the Pd(0) species in-situ from $Pd(OAc)_2$ and $(o\text{-Tol})_3P$ afforded **4** in 55% yield.

Negishi protocol were also employed for the synthesis of 1,4-bis[(3,4-ethylenedioxy)thien-2-yl]-2-fluorobenzene **5** (BEDOT-FB), 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-benzoic acid methyl ester **6** (BEDOT-MEB) (Scheme 4).[16] Methyl ester **6** was hydrolyzed to yield 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-benzoic acid **7** (BEDOT-BA).



Scheme 2. Formation of 2-alkoxy-1,4-dichlorobenzenes.



3 45%

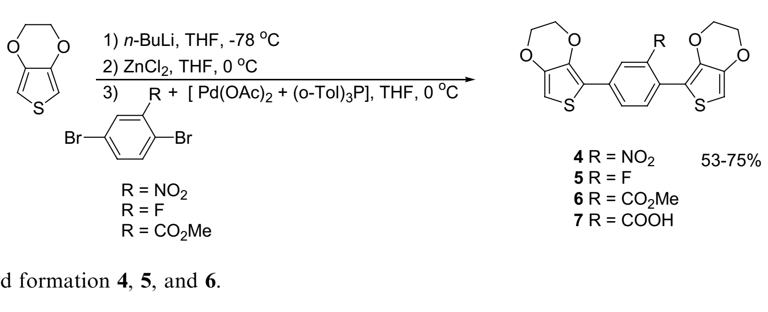
Scheme 3. Kumada coupling of EDOT and **2c**.

Figure 1 shows the absorbance and emission spectra of the substituted benzene derivatives. Corrected emission spectra were obtained in dilute chloroform solution and quantum yields were calculated using quinine sulfate as a standard.[17] All monomers have blue emission with λ_{max} ranging from 397 to 440 nm, with quantum yields ranging from 0.001 to 0.103. As expected, the nitro derivative **4** exhibited a very low quantum yield, as it is known for this group to quench the emission.

The electrochemical behavior of these materials was studied by cyclic voltammetry (CV) using glassy carbon electrode (GCE) as the working electrode. Figure 2 is the cyclic voltammagram of BEDOT-BOB (**3**), which is generally representative (i.e., two irreversible oxidation peaks) of the materials reported in this study. Table 1 summarizes the oxidation potentials measured for these monomers. Using the oxidation potential of BEDOT-benzene (650 mV as reported by Sotzing et al.[6]) as a basis for comparison, the first oxidation peak potential is clearly related to the electron donating or withdrawing character of the substituents (decreases or increases, respectively).

Application of recurrent potential scans of each monomer solution with a positive limit set at the lower oxidation potential ($E_{pa,1}$) of the monomer, a new redox process develops at a lower potential, −220 mV for BEDOT-BOB and −130 mV for BEDOT-TOL. The current of this new redox process continues to increase in intensity upon additional cycling consistent with the deposition of an electroactive polymer onto the surface of the working electrode, as shown in Figure 3 for BEDOT-BOB. Further evidence for the formation of the polymer is the observation of a bronze film on the surface of the working electrode. In contrast to BEDOT-TOL, -BOB, and -FB, during cyclic potential scanning of BEDOT-NITRO and -MEB, only very thin films could be obtained on glassy carbon due to electrode passivation upon continued potential cycling. However, films of doped poly(BEDOT-NITRO) and poly(BEDOT-MEB) were obtained electrochemically on indium-tin-oxide (ITO) coated glass slides using constant current methods.

The electrochemically prepared polymer films were subsequently thoroughly washed with MeCN to remove



Scheme 4. Negishi protocol and formation **4**, **5**, and **6**.

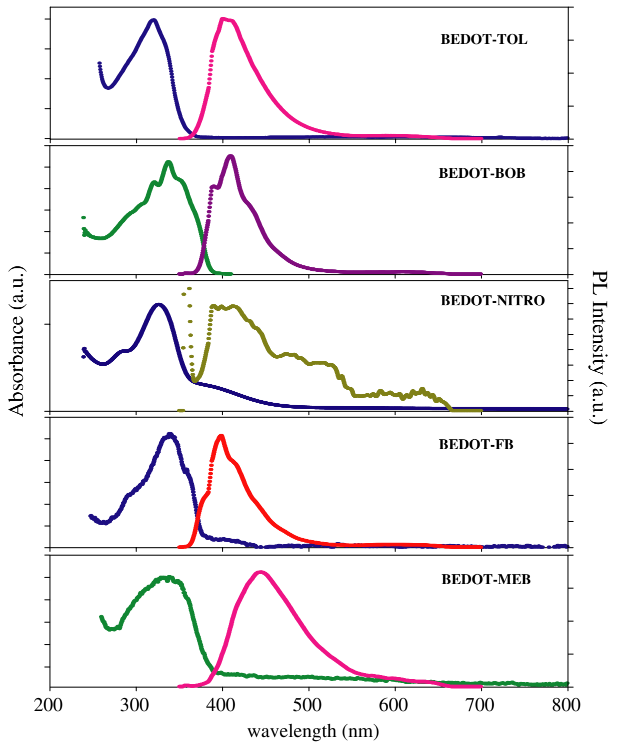


Figure 1. Absorbance and corrected emission of spectra of **1**, **3**–**6** in $CHCl_3$.

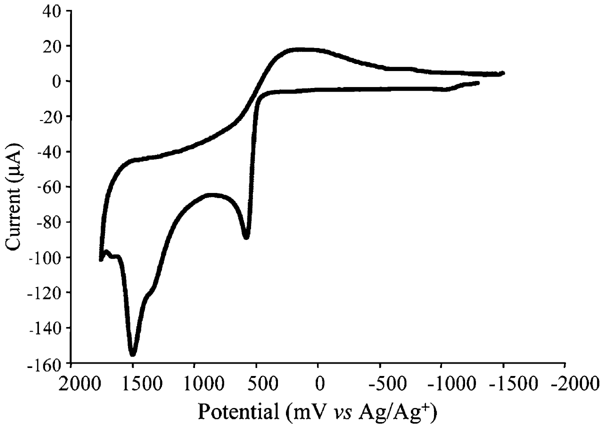


Figure 2. Cyclic voltammetry of BEDOT-BOB.

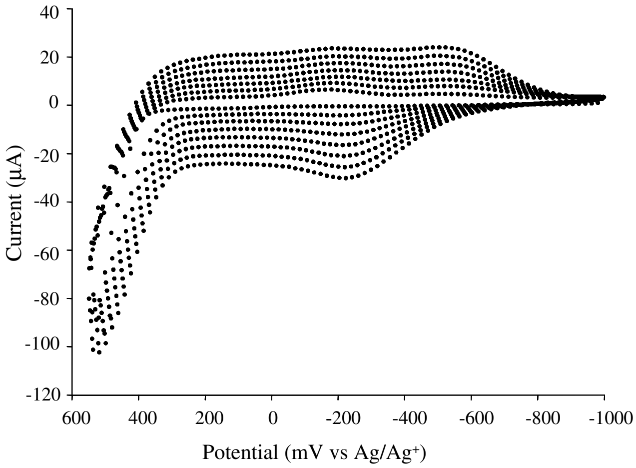


Figure 3. Cyclic voltammetric scanning electropolymerization of BEDOT-BOB in 0.1 M $TBAPF_6$/MeCN cycled at 100 mV s^{-1}.

excess monomer and their electrochemical behavior was performed in contact with monomer-free electrolyte solution. Cyclic voltammetry at various scan rates shows the general shape of the voltammagrams to be similar for poly(**1**); (**3**); (**5**), which exhibit a low anodic wave peak at 60 mV (TOL), 100 mV (BOB), and −287 mV(FB). For these three polymers, the peak current varies linearly with scan rate as expected for electroactive species that are surface bound. This indicates that the electroactive polymer is well adhered to the electrode surface (Fig. 4).

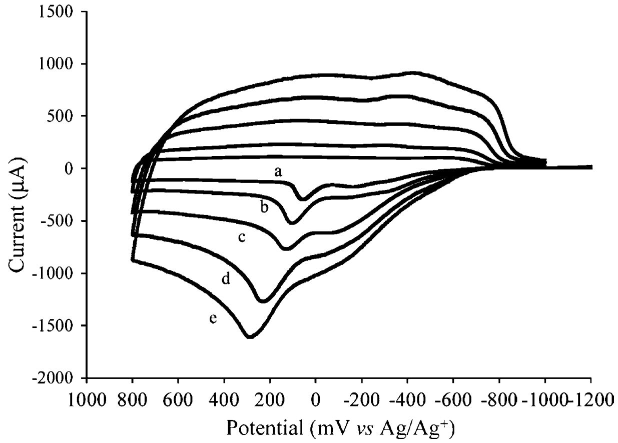


Figure 4. Cyclic voltammagram of poly(BEDOT-BOB) thin film in 0.1 M $TBAPF_6$/MeCN. Scan rate: (a) 50, (b) 100, (c) 200, (d) 300, (e) 400 mV s^{-1}.

Table 1. Optical and electrochemical data for monomers (polymers)

Monomer	$E_{pa,1}$[a] (mV)	$E_{pa,2}$[a] (mV)	Absorbance[b] λ_{max} (nm)	Emission[b] λ_{max} (nm)	ϕ_f[c]
1 (TOL)	528 (60)	1373	318 (542)	401 (610)	0.071
3 (BOB)	523 (100)	1440	336 (514)	410 (630)	0.103
4 (NITRO)	970	1447	326 (492)	413 (610)	0.001
5 (FB)	403 (−287)	730	339 (476)	397 (612)	0.096
6 (MEB)	848	1338	338 (480)	440	0.025

[a] Versus Ag/Ag^+ in 0.1 M $TBAPF_6$/MeCN, GCE working electrode, 100 mV s^{-1}.

[b] In $CHCl_3$.

[c] Quinine sulfate as standard.

Optical measurements of poly(**1**); (**3**); (**4**); (**5**) were obtained from electrochemically polymerized films of **1**, **3**, **4**, and **5**. Those films were deposited on ITO coated glass substrates using similar conditions as on GCE at a scan rate of $50\,\mathrm{mV\,s^{-1}}$. Reduction of the films by immersion in hydrazine hydrate for at least 24 h followed by washing with DI H_2O, MeOH, and drying under a stream of N_2. UV–vis–NIR spectra of the as prepared oxidized films show the characteristic charge carrier tail. The reduced poly(**1**); (**3**); (**4**); (**5**) show the disappearance of the charge carrier tail and have Abs λ_{max} ranging from 476 to 542 nm. Photoluminescence (PL) spectra of the reduced films were obtained at a 30° angle of incidence and a 430 nm excitation wavelength, all polymers show similar PL spectra with λ_{max} values from 610 to 630 nm. Results are summarized in Table 1.

To summarize, a series of bis-EDOT-benzene monomers have been synthesized by Kumada and Negishi cross couplings in moderate to good yields. These monomers have blue emission characteristics, with quantum yields up to 10.3%, and exhibited lower oxidation potentials than that of EDOT. Preliminary results show that polymerization can be achieved by electrochemical methods, yielding PL active polymers. The power of molecular architecture—property relationship concepts has been demonstrated in the design of these materials for organic emitting devices, in which a shift in the oxidation potential of up to 500 mV was obtained by modifying only a single substituent.

Acknowledgements

This work was supported by a grant from the National Science Foundation (ERC-9731680). We thank Bayer AG Corporation for the donation of EDOT.

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15. Selected data for **1**: Light green solid, ^1H NMR: δ 7.55 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 6.37 (s, 1H), 6.29 (s, 1H), 6.26 (s, 1H), 4.31 (m, 2H), 4.23 (m, 2H), 4.21 (m, 4H), 2.38, (s, 3H). ^{13}C NMR: δ 142.15, 141.30, 138.22, 137.79, 137.51, 132.77, 131.15, 129.89, 127.65, 123.34, 117.13, 116.40, 98.29, 97.63, 64.66, 64.52, 64.45, 64.37, 20.67. Anal. Cacld: $C_{19}H_{16}O_4S_2$. C 61.27; H 4.33; O 17.18; S 17.22. Found: C 61.22; H 4.35; O 17.11; S 17.30. Compound **2a**: (92°/2 mm) ^1H NMR: δ 7.24 (d, $J = 8.2$ Hz, 1H), 6.88 (d, $J = 2.2$ Hz, 1H), 6.84 (dd, $J = 8.2, 2.2$ Hz, 1H), 3.86 (s, 3H). ^{13}C NMR: δ 155.37, 133.03, 130.57, 121.09, 120.85, 112.60, 56.15. Compound **2b**: (102°/2 mm) ^1H NMR: δ 7.24 (d, $J = 8.2$ Hz, 1H), 6.88 (d, $J = 2.2$ Hz, 1H), 6.84 (dd, $J = 8.2, 2.3$ Hz, 1H), 4.05 (q, $J = 7.0$ Hz, 2H), 1.47 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR: δ 154.88, 132.94, 130.63, 121.20, 121.01, 113.67, 64.92, 14.51. Compound **2c**: (125°/2 mm) ^1H NMR: δ 7.24 (d, $J = 8.0$ Hz, 1H), 6.88 (d, $J = 2.3$ Hz, 1H), 6.84 (dd, $J = 8.0, 2.3$ Hz, 1H), 3.98 (t, $J = 6.5$ Hz, 2H), 1.85–1.76 (m, 2H), 1.57–1.48 (m, 2H), 0.98 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR: δ 155.04, 132.90, 130.56, 121.28, 120.88, 113.62, 68.98, 30.96, 19.11, 13.74. Compound **2d**: (172°/2 mm) ^1H NMR: δ 7.25 (d, $J = 8.3$ Hz, 1H), 6.88 (d, $J = 2.3$ Hz, 1H), 6.84 (dd, $J = 8.3, 2.3$ Hz, 1H), 3.97 (t, $J = 6.5$ Hz, 2H), 1.87–1.78 (m, 2H), 1.49–1.44 (m, 2H), 1.30 (br s, 8H), 0.89 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR: δ 155.06, 132.92, 130.57, 121.29, 120.89, 113.63, 69.31, 31.78, 29.24, 29.19, 28.92, 25.88, 22.64, 14.07.
16. General Negishi protocol: To a Schlenk flask under Argon atmosphere equipped with a Teflon stir bar and septum was added 1.00 g (7.04 mmol) of EDOT and 25 mL of THF. The flask was cooled to −78 °C and 7.05 mmol of *n*-BuLi was added drop wise via syringe, reacted at −78 °C for 1 h, and the contents were cannulated into a similarly equipped Schlenk flask at 0 °C, equipped with an addition funnel, containing 1.44 g (10.56 mmol) of $ZnCl_2$, 30 mL of THF, and stirred for 1 h at 0 °C. The organozincate was transferred to the addition funnel and the funnel was connected to a Schlenk flask, containing 3.52 mmol of the dibromobenzene, 0.032 g [(0.148 mmol), 0.02 equiv] of $[Pd(OAc)_2]$, 0.171 g [(0.563 mmol), 0.08 equiv] of $[(o\text{-}Tol)_3P]$, and 30 mL of THF. The organozincate was added drop wise at 0 °C. After complete addition, the funnel was rinsed with 5 mL of THF, and the flask was warmed to rt and reacted 48 h. The reaction mixture was then poured into crushed ice containing NH_4Cl and the layers were separated, the aqueous layer was extracted with 3×25 mL of Et_2O, the organics were combined, washed with 5×100 mL of H_2O, 30 mL of brine, dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Compound **4**: Column chromatography [$CHCl_3$–pet. ether (2:1 v/v)] afforded 0.753 g (53%) as an orange solid. ^1H NMR: δ 8.24 (d, $J = 1.8$ Hz, 1H), 7.79 (dd, $J = 6.5, 1.8$ Hz, 1H), 7.42 (d, $J = 8.2$ Hz, 1H), 6.43 (s, 1H),

6.37 (s, 1H), 4.35–4.32 (m, 2H), 4.26–4.23 (m, 2H), 4.19–4.15 (m, 4H). ^{13}C NMR: δ 149.00, 142.31, 141.49, 139.69, 139.09, 133.40, 131.95, 128.75, 123.66, 121.56, 114.50, 111.70, 100.01, 99.30, 64.88, 64.45, 64.44, 64.30. Anal. Cacd: $C_{18}H_{13}NO_6S_2$: C 53.59; H 3.25; N 3.47; O 23.80; S 15.90. Found: C 53.64; H 3.20, N 3.38, O 23.85, S 15.68. Compound **5**: Column chromatography [$CHCl_3$] afforded 1.00 g (75%) as a yellow solid. ^{1}H NMR: δ 7.88 (t, $J = 8.3$ Hz, 1H), 7.54 (dd, $J = 11.3$, 1.8 Hz, 1H), 7.44 (dd, $J = 6.6$, 1.8 Hz, 1H), 6.42 (s, 1H), 6.32 (s, 1H), 4.33–4.29 (m, 4H), 4.26–4.22 (m, 4H). Compound **6**: Column chromatography [$CHCl_3$–pet. ether (2:1 v/v)] afforded 0.953 g (60%) as a light green solid. ^{1}H NMR: δ 8.09 (d, $J = 1.8$ Hz, 1H), 7.79 (dd, $J = 6.3$, 1.8 Hz, 1H), 7.39 (d, $J = 8.2$ Hz, 1H), 6.35 (s, 1H), 6.30 (s, 1H), 4.26–4.24 (m, 2H), 4.19–4.17 (m, 2H), 4.13 (s, 4H), 3.79 (s, 3H). ^{13}C NMR: δ 168.68, 142.12, 141.22, 138.82, 137.78, 132.25, 131.36, 130.97, 129.22, 128.12, 126.90, 115.69, 115.55, 98.61, 98.20, 64.62, 64.48, 64.26, 64.18, 51.99.

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