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Synthesis and Characterization of Photoluminescent 3,4-Ethylenedioxythiophene Derivatives

Michael F. Pepitone, Stephen S. Hardaker, and Richard V. Gregory*

School of Materials Science and Engineering, Clemson University,
Clemson, South Carolina 29634-0971

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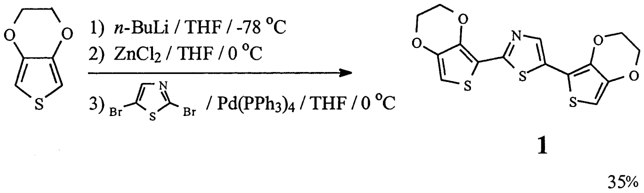
We report the synthesis of novel 3,4-ethylenedioxythiophene (EDOT) derivatives and the investigation of their photoluminescent properties. Lithiation of EDOT followed by the conversion to the 2-substituted zinc chloride or Grignard derivatives (useful for subsequent coupling reactions using organopalladium and organonickel chemistry) led to the formation of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-thiazole (**1**), 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-alkylthiophene (**2**, **3**), and 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-toluene (**4**). The lithiated EDOT provided a route for the formylated species followed by a Knoevenagel condensation which led to the cyanovinylene derivatives 1,4-bis[1-cyano-2-{(3,4-(ethylenedioxy)thien-2-yl}vinyl]benzene (**5**), 1,4-bis[1-cyano-2-{(3,4-(ethylenedioxy)thien-2-yl}vinyl]-2,5-dimethoxybenzene (**6**). The lithated EDOT also provided a convenient method for preparation of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole (**12**) by the hydrazide method. These materials exhibit blue to red emission characteristics with quantum yields ranging from 3.2 to 9.0%. Cyclic voltammetry shows oxidation potentials ranging from 422 to 617 mV. The prepared monomers may be used as optical building blocks in other unique polymer systems.

Introduction

Recently, much attention has focused on thiophene-based linear π-conjugated oligomers for their potential applications as active materials in organic electronic and photonic devices.[1] 3,4-Ethylenedioxythiophene (EDOT) has been used as a building block in several conjugated systems that incorporate unique properties such as electrochromic behavior[2] and low band gap polymers.[3] The 3-alkylthiophene class of oligomers and polymers has shown enhanced solubility, processibilty, and environmental stability relative to other linear π-conjugated systems.[4] Thiazole-based systems exhibit semiconductor properties[5] while the 1,3,4-oxadiazole class of oligomers and polymers are well-known to manifest luminescent activity.[6] The cyanovinylene-based donor−acceptor systems have yielded polymers with low band gap[7] polymers and materials having nonlinear optical properties.[8]

Scheme 1. Synthesis of BEDOT-TZ



Herein, we report the synthesis and photoluminescent properties of five novel classes of EDOT-based materials containing thiazole, 3-alkythiophene, toluene, cyanoterephthalylidene, and 1,3,4-oxadiazole moieties. These unique materials may have applications to a wide range of optical devices including microring organic lasers and photoemissive devices we have previously reported.[9] In addition, they may form the optical building blocks in other unique polymer systems.

Scheme 1 depicts the synthesis of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-thiazole (**1**) (BEDOT-TZ) by a Negishi cross-coupling reaction with 3,4-ethylenedioxythiophene and 2,5-dibromothiazole in 35% yield. ^{1}H, ^{13}C NMR, and elemental analysis characterized BEDOT-TZ.

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* To whom correspondence should be addressed. E-mail: richar6@clemson.edu.

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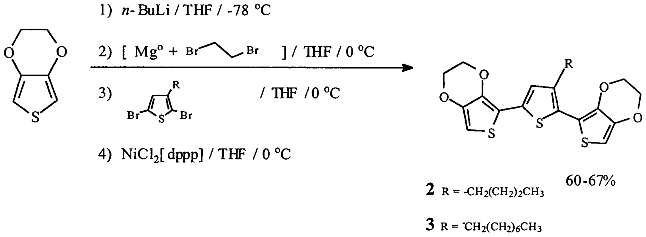
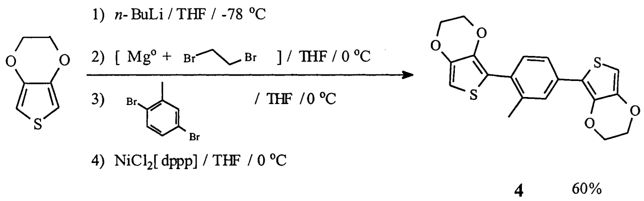
Scheme 2. Synthesis of BEDOT-3BT, −3OT



Scheme 3. Synthesis of BEDOT-TOL

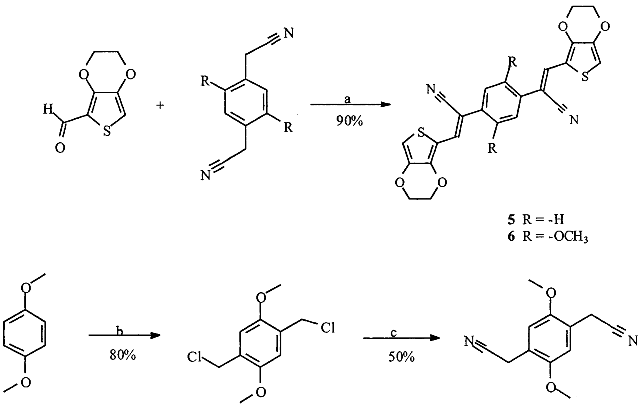


Scheme 2 depicts the synthesis of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-butylthiophene (**2**) (BEDOT-3BT) and 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-octylthiophene (**3**) (BEDOT-3OT) by a nickel(II) chloride catalyzed Grignard cross-coupling reaction, using an entrainment procedure and the corresponding 2,5-dibromo-3-alkylthiophenes to afford BEDOT-3BT or BEDOT-3OT in yields of 67% or 60%, respectively. The 2,5-dibromo-3-alkythiophenes were synthesized by literature procedures starting from thiophene, 2,3,5-tribromthiophene,[10] 3-bromothiophene,[11] 3-alkylthiophene,[12] and 2,5-dibromothiophene-3-alkylthiophene.[13] ^{1}H, ^{13}C NMR, and elemental analysis characterized both BEDOT-3BT and BEDOT-3OT.

Scheme 3 depicts the synthesis of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-toluene (**4**) (BEDOT-TOL) by a nickel(II) chloride catalyzed Grignard cross-coupling reaction, using an entrainment procedure with 3,4-ethylenedioxythiophene and 2,5-dibromotoluene in 60% yield. ^{1}H, ^{13}C NMR, and elemental analysis characterized BEDOT-TOL.

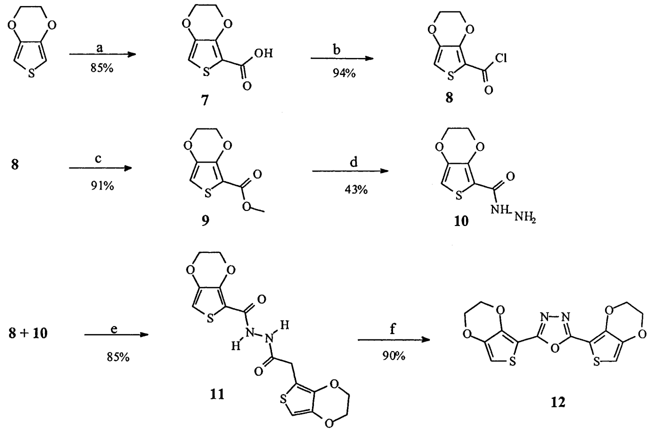
Scheme 4 depicts the synthesis of 1,4-bis[1-cyano-2-{(3,4-(ethylenedioxy)thien-2-yl}vinyl]benzene (**5**) (BEDOT-CNVB) and 1,4-bis[1-cyano-2-{(3,4-(ethylenedioxy)thien-2-yl}vinyl]-2,5-dimethoxybenzene (**6**) (BEDOT-CNVMOB). The first step entailed the formation of 3,4-ethylenedioxythiophene-2-carboxaldehyde[14] by literature procedures. A Knoevenagel condensation of 3,4-ethylenedioxythiophene-2-carboxaldehyde with benzene-1,4-diacetonitrile or 2,5-bis(methoxy)benzene-1,4-diacetonitrile, which was prepared by a chloromethylation reaction and then a substitution reaction using potassium cyanide, afforded either (**5**) or (**6**) in yields of 92% and 88%, respectively. Both BEDOT-CNVB and BEDOT-CNVMOB were characterized by FTIR, ^{13}C solid-state NMR, and elemental analysis.

Scheme 4[a]



[a] (a) KO^{t}BU, THF/EtOH (1:4), 60 °C. (b) (CH$_2$O)*n*, ZnCl$_2$, HCl, 1,4-dioxane, 55 °C. (c) KCN, EtOH/H$_2$O (3:1), 80 °C.

Scheme 5[a]



[a] (a) *n*-BuLi, THF, −78 °C, CO$_2$, H+. (b) SOCl$_2$, △. (c) MeOH, △. (d) N$_2$H$_2$·H$_2$O, MeOH, △. (e) Pyr., NMP, LiCl, 80 °C. (f) POCl$_3$, 80 °C.

Synthesis of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole (**12**) (BEDOT-OXA) is shown in Scheme 5. BEDOT-OXA was synthesized by functional group interconversion of 3,4-ethylenedioxythiophene, starting with the formation of 3,4-ethylenedioxythiophene-2-carboxylic acid (**7**) via the 2-lithio adduct with dry ice and an acidic workup. 3,4-Ethylenedioxythiophene-2-carbonyl chloride (**8**) was obtained by reaction of the carboxylic acid (**7**) with thionyl chloride. 3,4-Ethylenedioxythiophene-2-methylcarboxylate (**9**) was obtained by reacting the carbonyl chloride (**8**) with methanol. Reacting (**9**) with hydrazine monohydrate obtained 3,4-ethylenedioxythiophene-2-carboxylic hydrazide (**10**). Reaction of the carboxylic hydrazide (**10**) with the carbonyl chloride (**8**) in NMP with LiCl and pyridine resulted in the precursor 1,2-bis[(3,4-ethylenedioxy)thiophene-2-carbonyl]-hydrazine (**11**). Cyclodehydration of the precursor (**11**) with POCl$_3$ afforded (**12**) in an overall yield of 25%; ^{1}H NMR, FTIR, and elemental analysis confirmed its structure. The FTIR spectra clearly indicate the disappearance of the carbonyl stretching and N−H stretching at 1622 and 3366 cm^{-1}, respectively, for the precursor (**11**), and the addition of peaks at 1585 and 1040 cm^{-1} of the 1,3,4-oxadiazole ring stretching.[15]

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Experimental Section

All chemicals were purchased from Aldrich, except for 3,4-ethylendioxythiophene, which was donated by Bayer AG. Reactions were carried out on a Schlenk line under an argon atmosphere using inert air atmosphere techniques. 3,4-Ethylenedioxythiophene was degassed with argon and then vacuum-distilled from CaH_2. THF was distilled from sodium benzophenone ketyl. 2,5-Dibromothiazole was dried in vacuo. 2,5-Dibromotoluene was degassed with argon and vacuum-distilled. Thionyl chloride was distilled. *n*-Butyllithium (2.5 M in hexanes) was titrated prior to use by the method of Watson and Eastham.[16] [1,3-Bis(diphenylphosphino)propane]-dichloronickel(II) and tetrakis(triphenylphosphine)palladium-(0) were opened, manipulated, and stored in an MBraun glovebox. Magnesium turnings were dried by heating under vacuum. Zinc chloride was fused under vacuum. 1,2-Dibromoethane was dried over $CaCl_2$ and distilled. ^1H and ^{13}C NMR were conducted on a Bruker AC-300 FT-NMR using $CDCl_3$ as a solvent unless otherwise stated. All chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm. Microanalyses were performed by Galbraith Laboratories.

2,5-Bis[(3,4-ethylenedioxy)thien-2-yl]-thiazole (1). To a 100-mL Schlenk flask equipped with a Teflon stir bar and septum were added 1.00 g (7.04 mmol) of 3,4-ethylenedioxythiophene and 25 mL of THF. The flask was cooled to −78 °C via a dry ice/2-propanol slush and 2.82 mL (7.05 mmol) of *n*-BuLi was added dropwise via a syringe, reacted at −78 °C for 1 h, warmed to 0 °C, and reacted for 1 h. To a 100-mL Schlenk flask equipped with a Teflon stir bar, rubber septum, and a 100-mL dropping funnel were added 0.959 g (3.52 mmol) of $ZnCl_2$ and 30 mL of THF. The flask containing the zinc chloride solution was cooled to 0 °C via an ice bath and the 2-lithio adduct was transferred dropwise via a cannula; transfer was completed with 3 × 3 mL of THF and the solution was stirred for 1 h at 0 °C. The organozincate was transferred to the dropping funnel and the funnel was connected to a 200-mL Schlenk flask equipped with a Teflon stir bar, 0.855 g (3.52 mmol) of 2,5-dibromothiazole, 0.163 g [0.148 mmol) 0.02 equiv] of $Pd(PPh_3)_4$, and 30 mL of THF. The organozincate was added dropwise over a period of 1 h at 0 °C. After complete addition, the flask was rinsed with 5 mL of THF, warmed to RT, and reacted for 96 h at RT. 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 3 × 100 mL of H_2O, 30 mL of $NaHCO_3$, and 2 × 100 mL of H_2O, dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. Column chomatography (silica gel 230−400 mesh) of the brown/red residue eluting with petroleum ether: CH_2Cl_2 (1:1 v/v) and then dissolving in DMF, precipitating with water, and drying in vacuo afforded 0.451 g (35%) of the title compound as a yellow solid. ^1H NMR: δ 7.83 (s, 1H), 6.41 (s, 1H), 6.26 (s, 1H), 4.40 (m, 2H), 4.33 (m, 2H), 4.23 (m, 4H). ^{13}C NMR: δ 156.40, 141.78, 141.54, 140.10, 138.14, 137.24, 128.81, 112.75, 108.57, 101.09, 97.82, 65.36, 65.01, 64.48. Anal. Calcd for $C_{15}H_{11}NO_4S_3$: C, 49.30; H, 3.03; N, 3.83; O, 17.51; S, 26.32. Found: C, 49.25; H, 3.09; N, 3.78; O, 17.53; S, 26.24.

2,5-Bis[(3,4-ethylenedioxy)thien-2-yl]-3-butylthiophene (2). To a Schlenk flask were added 1.00 g (7.04 mmol) of 3,4-ethylenedioxythiophene and 25 mL of THF. The flask was cooled to −78 °C and 2.85 mL (7.11 mmol) of *n*-BuLi was added dropwise and reacted at −78 °C for 1 h, warmed to 0 °C, and reacted for 1 h. The $MgBr_2{\cdot}THF$ suspension [from 0.256 g (10.61 mmol) of magnesium turnings, 1.323 g (7.04 mmol) of 1,2-dibromoethane, and 30 mL of THF] was transferred to the 2-lithio adduct though a frit, transfer was completed with 3 × 15 mL of THF washings, and the solution was reacted at 0 °C for 1 h. This was then transferred dropwise to a Schlenk flask at 0 °C containing 1.049 g (3.52 mmol) of 2,5-dibromo-3-butylthiophene, 0.0725 g (0.134 mmol, 1.9 mol %) of [1,3-bis(diphenylphosphino)propane]dichloronickel(II), 30 mL of THF and was reacted for 36 h at RT. It was then poured into crushed ice acidified with 2 N HCl and the layers were separated. The aqueous layer was extracted with 3 × 25 mL of Et_2O, the organics were combined, washed with 3 × 100 mL of H_2O, 30 mL of $NaHCO_3$, and 2 × 100 mL of H_2O, dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. Column chomatography (silica gel 230−400 mesh) of the brown residue eluting with pentane:$CHCl_3$ (1:1 v/v) afforded 1.00 g (67%) of the title compound as a tan solid. ^1H NMR: δ 7.04 (s, 1H), 6.34 (s, 1H), 6.20 (s, 1H), 4.31 (m, 2H), 4.27 (m, 2H), 4.23 (m, 4H), 2.67, (t, 2H), 1.61 (m, 2H), 1.33 (m, 2H), 0.91 (t, 3H). ^{13}C NMR: δ 141.77, 141.41, 140.83, 138.04, 137.39, 133.64, 125.69, 125.01,112.23, 110.35, 98.67, 96.71, 64.91, 64.76, 64.52, 64.44, 32.62, 29.11, 22.63, 13.90. Anal. Calcd for $C_{20}H_{20}O_4S_3$: C, 57.12; H, 4.79; O, 15.22; S, 22.87. Found: C, 56.95; H, 4.83; O, 15.11; S, 23.03.

2,5-Bis[(3,4-ethylenedioxy)thien-2-yl]-3-octylthiophene (3). 3 was prepared as above and column chomatography (silica gel 230−400 mesh) of the brown residue eluting with pentane:$CHCl_3$ (1:1 v/v) afforded 1.00 g (60%) of the title compound as a tan viscous oil. ^1H NMR: δ 7.04 (s, 1H), 6.33 (s, 1H), 6.18 (s, 1H), 4.31 (m, 2H), 4.27 (m, 2H), 4.23 (m, 4H), 2.66, (t, 2H), 1.62 (m, 2H), 1.26 (bs, 10H), 0.85 (t, 3H). ^{13}C NMR: δ 141.76, 141.40, 140.85, 138.62, 137.38, 133.62, 125.67, 124.98, 112.20, 110.33, 98.65, 96.68, 64.88, 64.74, 64.49, 64.41, 31.82, 30.47, 29.54, 29.46, 29.37, 29.13, 22.61, 14.06. Anal. Calcd for $C_{24}H_{28}O_4S_3$: C, 60.48; H, 5.92; O, 13.43; S, 20.18. Found: C, 59.98; H, 6.05; O, 13.43; S, 20.03.

2,5-Bis[(3,4-ethylenedioxy)thien-2-yl]-toluene (4). To a 100-mL Schlenk flask equipped with a Teflon stir bar and septum were added 1.00 g (7.04 mmol) of 3,4-ethylenedioxythiophene and 25 mL of THF. The flask was cooled to −78 °C via a dry ice/2-propanol slush, then 2.82 mL (7.05 mmol) of *n*-BuLi was added dropwise via a syringe, and the solution was reacted at −78 °C for 1 h, warmed to 0 °C, and reacted for 1 h. The $MgBr_2{\cdot}THF$ suspension [from 0.256 g (10.61 mmol) of magnesium turnings, 1.323 g (7.04 mmol) of 1,2-dibromoethane, and 30 mL of THF] was transferred to the 2-lithio adduct though a frit, transfer was completed with 3 × 15 mL of THF washings, and the solution was reacted at 0 °C for 1 h. This was then transferred dropwise to a 200-mL Schlenk flask at 0 °C containing 0.879 g (3.52 mmol) of 2,5-dibromotoluene, and 0.0725 g (0.134 mmol, 1.9 mol %) of [1,3-bis(diphenylphosphino)propane]dichloronickel(II), in 30 mL of THF and the solution was reacted for 36 h at RT. The reaction mixture was then poured into crushed ice acidified with 2 N HCl and the layers were separated. The aqueous layer was extracted with 3 × 25 mL of Et_2O, the organics were combined, washed with 3 × 100 mL of H_2O, 30 mL of $NaHCO_3$, and 2 × 100 mL of H_2O, dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. Column chomatography (silica gel 230−400 mesh) of the brown residue eluting with petroleum ether:CH_2Cl_2 (1:1 v/v) afforded 0.786 g (60%) of the title compound as a light green solid. ^1H NMR: δ 7.57 (d, 1H), 7.33 (d, 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. Calcd for $C_{19}H_{16}O_4S_2$: 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.

1,4-Bis[1-cyano-2-{(3,4-(ethylenedioxy)thien-2-yl}vinyl]-benzene (5). To a 100-mL 3NRBF equipped with a condensor with a N_2 inlet, thermometer, rubber septum, and a Teflon stir bar were added 3,4-ethylenedioxythiophene-2-carboxaldehyde (0.200 g, 1.176 mmol), benzene-1,4-diacteonitrile (0.092 g, 0.588 mmol), and THF/MeOH (50 mL, 1:4 v/v), KO^tBU (1.17 mmol) was added dropwise via a syringe and the mixture was heated to 60 °C for 1 h and then cooled to RT. The brown precipitate was collected, washed with H_2O, EtOH, and cold $CHCl_3$, and dried in vacuo to yield 0.245 g (0.532 mmol) of the title compound in 90% yield. Solid-state ^{13}C NMR: 144.73, 139.89, 132.48, 125.64, 111.66, 106.93, 98.05, 64.85. Anal. Calcd for $C_{24}H_{16}N_2O_4S_2$: C, 62.60; H, 3.50; N, 6.08; O, 13.90;

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S, 13.92. Found: C, 62.76; H, 3.92; N, 6.08; O, 14.05; S, 14.21.

1,4-Bis[1-cyano-2-{(3,4-(ethylenedioxy)thien-2-yl}vinyl]-2,5-dimethoxybenzene (6). **6** was prepared as above using 3,4-ethylenedioxythiophene-2-carboxaldehyde (0.200 g, 1.176 mmol), 2,5-dimethoxybenzene-1,4-diacteonitrile (0.127 g, 0.588 mmol), and THF/MeOH (50 mL, 1:4 v/v), KO^{t}BU (1.17 mmol) to yield 0.268 g (0.515 mmol) of the title compound in 88% yield. Solid-state ^{13}C NMR: δ 156.60, 144.70, 139.65, 132.48, 125.66, 111.60, 106.80, 98.05, 64.85, 56.68. Anal. Calcd for $C_{24}H_{20}N_2O_6S_2$: C, 59.99; H, 3.87; N, 5.38; O, 18.44; S, 12.32. Found: C, 60.10; H, 3.89; N, 3.89; O, 18.51; S, 12.42.

3,4-Ethylenedioxythiophene-2-carboxylic Acid (7). To a 100-mL Schlenk flask equipped with a Teflon stir bar and rubber septum were added 2.00 g (14.08 mmol) of 3,4-ethylenedioxythiophene and 50 mL of THF. The flask was cooled to −78 °C via a dry ice/2-propanol bath and 5.69 mL (14.22 mmol) of *n*-BuLi was added dropwise via a syringe over a 5-min period. The resulting 2-lithio adduct was reacted at −78 °C for 1 h, warmed to 0 °C via an ice bath, and reacted for 1 h. The yellow solution was then cooled to −78 °C, poured into a beaker containing a slurry of dry ice/ether under a nitrogen atmosphere, and left overnight in a fume hood. The resulting white solid was dissolved in a 10% KOH solution and washed with ether. The ether washings were extracted with 3 × 30 mL 10% KOH and combined. The KOH solution was heated on a hot plate to remove residual ether and then cooled to 0 °C via an ice bath where it was acidified with dropwise addition of concentrated HCl. The resulting white precipitate was collected by vacuum filtration, washed with copious amounts of DI H_2O, and dried under vacuum (50 °C, 12 h) to afford 2.25 g (85%) of the title product as a white solid. ^{1}H NMR (DMSO-d_6, ppm): δ 12.69 (s, 1H), 6.95 (s, 1H), 4.30 (m, 2H), 4.21 (m, 2H). ^{13}C NMR (DMSO-d_6, ppm): δ 162.11, 145.51, 141.59, 107.701, 106.34, 64.77, 63.81. Anal. Calcd for $C_7H_6O_4S$: C, 45.16; H, 3.25; O, 34.37; S, 17.22. Found: C, 44.95; H, 3.24; O, 34.16; S, 17.10.

3,4-Ethylenedioxythiopene-2-carbonyl Chloride (8). To a 50-mL 1NRBF equipped with a Teflon stir bar and condenser with a $CaCl_2$ guard tube were added 2.30 g (12.36 mmol) of **7** and an excess of thionyl chloride (25 mL). After a 3-h reflux, the excess thionyl chloride was distilled off and a black residue remained in the flask. The residue was triturated with pentane and 2.40 g (95%) of the resulting black solid was used immediately without further purification. ^{1}H NMR: δ 6.87 (s, 1H), 4.43 (m, 2H), 4.27 (m, 2H). ^{13}C NMR: δ 155.56, 148.30, 141.96, 113.02, 111.89, 65.53, 63.86. Anal. Calcd for $C_7H_5Cl O_3S$: C, 41.09; H, 2.47; Cl, 17.33; O, 23.46; S, 15.67. Found: C, 41.60; H, 2.50; Cl, 17.40; O, 23.75; S, 15.67.

3,4-Ethylenedioxythiophene-2-methlycarboxylate (9). To a 50-mL 1NRBF equipped with a Teflon stir bar and condenser were added 2.00 g (10.39 mmol) of **8** and an excess of methanol (25 mL). After a 6-h reflux, the methanol was distilled off under reduced pressure. The yellow crystals were dissolved in 100 mL of $CHCl_3$ and 100 mL of DI H_2O was added. The layers were separated and the aqueous layer was extracted with 3 × 25 mL of $CHCl_3$. The extracts were combined, washed with 3 × 100 mL DI H_2O, dried over $MgSO_4$, and filtered and solvent was removed under reduced pressure. Recrystallization from ethanol afforded 1.89 g (91%) of the title product as light yellow crystals. ^{1}H NMR: δ 6.58 (s, 1H), 4.37 (m, 2H), 4.23 (m, 2H), 3.85 (s, 3H). ^{13}C NMR: δ 161.77, 145.79, 141.59, 107.54, 106.44, 65.23, 64.04, 51.77. Anal. Calcd for $C_8H_8O_4S$: C, 47.99; H, 4.03; O, 31.97; S, 16.01. Found: C, 47.43; H, 4.08; O, 32.11; S, 15.81.

3,4-Ethylenedioxythiophene-2-carboxylic Hydrazide (10). To a 100-mL 1NRBF equipped with a Teflon stir bar and condenser with a N_2 inlet was added 1.50 g (7.50 mmol) of **9** and 50 mL of methanol; 0.380 g (7.58 mmol) of hydrazine monohydrate was added and the mixture was refluxed for 3 h. After removal of the solvent at reduced pressure, the off-white crystals were dissolved in 100 mL of $CHCl_3$ and 100 mL of DI H_2O was added. The layers were separated and the aqueous layer was extracted with 3 × 25 mL of $CHCl_3$. The extracts were combined, washed with 3 × 100 mL of DI H_2O, dried over $MgSO_4$, and filtered, and solvent was removed under reduced pressure. Recrystallization from ethanol afforded 0.65 g (43%) of the title product as white crystals. ^{1}H NMR: δ 7.93 (s, 1H), 6.60 (s, 1H), 4.37 (m, 2H), 4.24 (m, 2H), 4.07 (s, 2H). ^{13}C NMR: δ 162.55, 141.13, 140.94, 111.94, 105.43, 65.52, 64.03. Anal. Calcd for $C_7H_8N_2O_3S$: C, 41.99; H, 4.03; N, 13.99; O, 23.97; S, 16.01. Found: C, 41.92; H, 4.16; N, 13.85; O, 23.81; S, 16.14.

1,2-Bis[(3,4-ethylenedioxy)thiophene-2-carbonyl]-hydrazine (11). To a 50-mL 1 NRBF equipped with a Teflon stir bar and condenser with a N_2 inlet were added 0.300 g (1.50 mmol) of **10** and 25 mL of NMP; 0.307 g (1.50 mmol) of **5** was added along with 0.100 g of LiCl and 0.5 mL of pyridine. The suspension was reacted at 80 °C for 6 h and then cooled to RT. Cooling in a freezer completes the precipitation. The precipitate was collected by vacuum filtration and washed with 300 mL of DI H_2O and 150 mL of ethanol. The solid was vacuum-dried and 0.471 g (85%) of white crystals was collected. Due to its limited solubility in common solvents, further purification and characterization were not attempted. Anal. Calcd for $C_{14}H_{12}N_2O_6S_2$: C, 45.65; H, 3.28; N, 7.60; O, 26.06; S, 17.41. Found: C, 45.55; H, 3.39; N, 7.59; O, 26.46; S, 17.39.

2,5-Bis[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole (12). To a 50-mL 1 NRBF equipped with a Teflon stir bar and condenser with a N_2 inlet was added 0.350 g (0.950 mmol) of **11** along with an excess of phosphorus oxychloride (20 mL). The suspension was heated to 80 °C and reacted for 12 h. The green suspension was cooled to RT and then poured into crushed ice. The green precipitate was collected by vacuum filtration, washed with 3 × 100 mL of DI H_2O, 50 mL of cold ethanol, and 50 mL of cold $CHCl_3$, and dried in a vacuum oven (14 h, RT). The title compound was obtained as 0.300 g (90%) of gray/green crystals. ^{1}H NMR (DMF-d_7, ppm): δ 7.05 (s, 1H), 4.50 (m, 2H), 4.38 (m, 2H). Anal. Calcd for $C_{14}H_{10}N_2O_5S_2$: C, 47.99; H, 2.88; N, 8.00; O, 22.83; S, 18.30. Found: C, 47.79; H, 2.82; N, 7.98; O, 22.85; S, 18.55.

Spectroscopy. Absorbance spectra were obtained on a Shimadzu UVPC-3101 spectrometer using a slow scanning speed and 1-nm slit width. Photoluminescence spectra were obtained on a Perkin-Elmer LS 50B. The excitation slit width was 15 nm, while the emission slit width was 5 nm. Emission spectra were corrected using standard spectra of quinine sulfate and *N,N′*-dimethyl-*m*-nitroaniline.[17] The quantum yield of the BEDOT derivatives was estimated by comparison with a quantum yield standard.[18] With this method, the fluorescence quantum yield, ϕ_f, of a material is calculated by eq 1 in

$$\phi_f = \phi_r \frac{I}{I_r} \frac{A_r}{A} \frac{n^2}{{n_r}^2} \qquad (1)$$

where *I* is the integrated emission intensity, *A* is the absorbance, and *n* is the refractive index.

The subscript “r” refers to the reference material, in this case quinine sulfate in 0.1 M H_2SO_4 ($\phi_r = 0.577$ at 22 °C for excitation at 350 nm).[19] Emission spectra for quantum yield measurements were obtained at the same temperature and excitation wavelength as the standard. To minimize reabsorption and inner filter effects, the solutions were diluted such that the absorbance was below 0.05 at the excitation wavelength. Quantum yield measurements were carried out in chloroform (*N,N′*-dimethylformamide for BEDOT-OXA **12**). The solvents were purged with nitrogen to minimize the influence of O_2 quenching. The sodium D-line (589 nm) refractive index of the solutions was measured with a Thermospectronic Abbé 3L refractometer at 23 °C. Excitation and emission spectra of the insoluble cyanovinylene derivatives were obtained with a 30°-incidence front face cell.

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(19) Eastman, J. W. *Photochem. Photobiol.* **1967**, *6*, 55.

Electrochemistry. Cyclic voltammetry was conducted with a Bioanalytical Systems BAS-100B/W electrochemical analyzer equipped with the C2 cell stand. A nonaqueous cell was used for the electrochemical analysis consisting of acetonitrile (distilled over CaH_2) as the solvent and tetrabutylammonium hexafluorophosphate (recrystallized from ethanol) as the electrolyte (0.1 M). The three electrodes used were a Pt auxiliary electrode, a glassy carbon working electrode, and a Ag/Ag^+ reference electrode. The reference electrode solution was 0.01 M $AgNO_3$ in the 0.1 M electrolyte solution. Monomer solutions of BEDOT-TZ **1**, BEDOT-3BT **2**, BEDOT-3OT **3**, and BEDOT-TOL **4** were prepared at concentrations between 1.0 and 10.0 mM. A solution of BEDOT-OXA was prepared to 1.0 mM, though the actual concentration was much lower due to poor solubility. Cyclic voltammagrams were obtained over a broad potential range at a scan rate of 100 mV/s (50 mV/s for BEDOT-3OT **3**).

Discussion

The synthesis of BEDOT-3BT, BEDOT-3OT, and BEDOT-TOL was achieved via a nickel(II) chloride catalyzed Grignard cross-coupling using an entrainment procedure with Mg^0 turnings and 1,2-dibromoethane in THF to form $MgBr_2 \cdot THF$ in situ, which was transferred to the 2-lithio-3,4-ethylenedioxythiophene adduct to form the Grignard reagent, which was transferred to the dibromo derivative and catalyst which formed the title products with yields ranging from 60 to 67%. BEDOT-3BT was obtained as a tan solid whereas BEDOT-3OT was a highly viscous tan oil, which failed to crystallize under high (10^{-3} mmHg) vacuum. The BEDOT-TOL was obtained as a light green solid.

BEDOT-TZ was synthesized via a Negishi cross-coupling using organopalladium chemistry; however, the yield at best was only a moderate 35%. This was partly due to separation problems encountered during column chomatography. A further purification step after column chomatography involved dissolution in DMF and precipitation in H_2O. Synthesis of BEDOT-TZ at higher temperatures (25−45 °C) did not improve the yield, but led to the formation of a pseudo-Wurtz coupled product with little if any yield of the desired product. The unstable pseudo-Wurtz coupled product is currently under investigation.

The cyanovinlyene derivatives, BEDOT-CNV and BEDOT-CNVMOB, were synthesized by a Knoevenagel condensation using 3,4-ethylenedioxythiophene-2-carboxaldehyde and the corresponding benzene-1,4-diacetonitrile derivative. Potassium *tert*-butoxide was employed as the base, but a 25 wt % solution of tetramethylammonium hydroxide in methanol also gave similar results. Unfortunately, incorporation of the methoxy substituents did not enhance the solubility of these materials as much as we would have anticipated, but a 28-nm red shift in the emission spectra was obtained. Larger alkoxy chain 1,4-bis benzene derivatives were synthesized, but the yields during the chloromethylation and Knoevenagel condensation were very low or zero. This was probably due to increasing steric hindrance of the larger alkoxy chains. The chloromethylation reaction itself proved to be a good synthetic scheme, but due to the possible toxic hazards associated with the formation of bis(chloromethyl) ethers, alternative pathways are being investigated.

BEDOT-OXA was synthesized via the hydrazide method in good yield. The precursor 1,2-bis[(3,4-ethylenedioxy)thiophene-2-carbonyl]-hydrazine exhibited very poor solubility in common solvents, which made characterization difficult. However, FTIR spectra of the precursor and BEDOT-OXA do show the disappearance of the carbonyl stretching and N−H stretching at 1622 and 3366 cm^{-1}, respectively, and the addition of peaks at 1585 and 1040 cm^{-1} of the 1,3,4-oxadiazole ring stretching. The ^1H NMR spectrum of BEDOT-OXA was obtained using DMF-d_7, but the solubility was still too low to obtain a good ^{13}C NMR spectrum on the Bruker AC-300 FT-NMR (75 MHz). The ^1H NMR spectra obtained was accomplished by using the parameters of DMSO-d_6 because of the lack of a DMF probe on the instrument. Therefore, the actual chemical shifts are relative to the DMSO-d_6 parameters of the instrument, but are fairly close to what is expected.

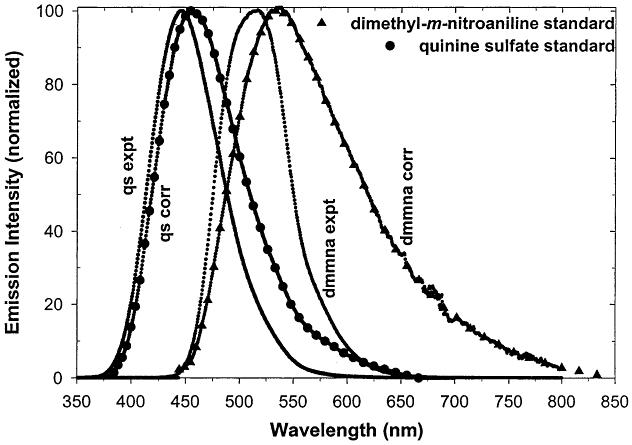

Figure 1. Apparent and corrected emission spectra: (●) Quinine sulfate corrected emission spectrum from the literature.[17] (▲) *N*,*N*′-dimethyl-*m*-nitroaniline corrected emission spectrum from the literature.[17]

It is important to recognize that because the photomultiplier in the emission monochomator is less sensitive to longer wavelengths, the emission spectra should be corrected to account for instrumental response. Figure 1 presents the observed emission spectra of the two standard materials employed in this work along with the standard (from literature) and corrected spectra. The corrected spectra are red-shifted with respect to the apparent emission. However, the decreasing sensitivity to longer wavelengths not only results in a shift in the peak wavelength but also significantly influences the peak shape, broadening the low-energy tail. The spectroscopic results for the BEDOT-Q derivatives are shown in Figure 2, with spectra of EDOT for comparison. Due to the insolubility of the cyanovinylene-containing derivatives, the excitation spectra of these two materials are presented in parts e and f of Figure 2 rather than the absorbance spectra. The BEDOT-OXA exhibited poor solubility in acetonitrile, so spectra were obtained in DMF, shown in Figure 2g. One will note that the soluble materials exhibited emission λ_{max} ranging from 401 nm for the BEDOT-TOL to 452 nm for the BEDOT-TZ. The emission λ_{max} of the 3-alkylthiophene derivatives were nearly identical at 441 nm. Orange (λ_{max} = 629 nm) and red (λ_{max} = 657 nm) emissions were observed for the insoluble BEDOT-CNV and BEDOT-CNVMOB derivatives, respectively.

Cyclic voltammagrams of the soluble materials are shown in Figure 3, with oxidation occurring at positive

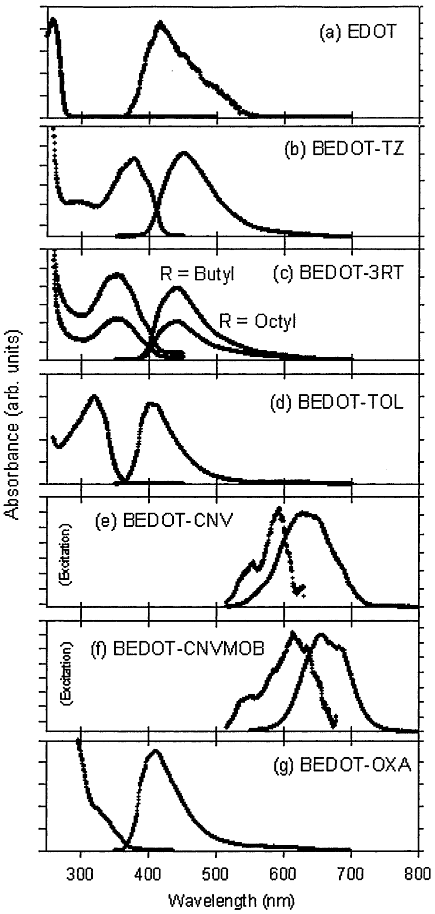

Figure 2. Electronic spectra of BEDOT-Q derivatives. (a) EDOT, (b) BEDOT-TZ **1**, (c) BEDOT-3RT **2** and **3**, (d) BEDOT-TOL **4**, (e) BEDOT-CNV **5**, (f) BEDOT-CNVMOB **6**, and (g) BEDOT-OXA **12**. (a–d) in $CHCl_3$; (e and f) excitation and emission spectra of solid, 30° incidence angle; (g) in DMF. (a–d, g) emission spectra corrected with quinine sulfate standard. (e and f) emission spectra corrected with *N*,*N*′-dimethyl-*m*-nitroaniline standard.

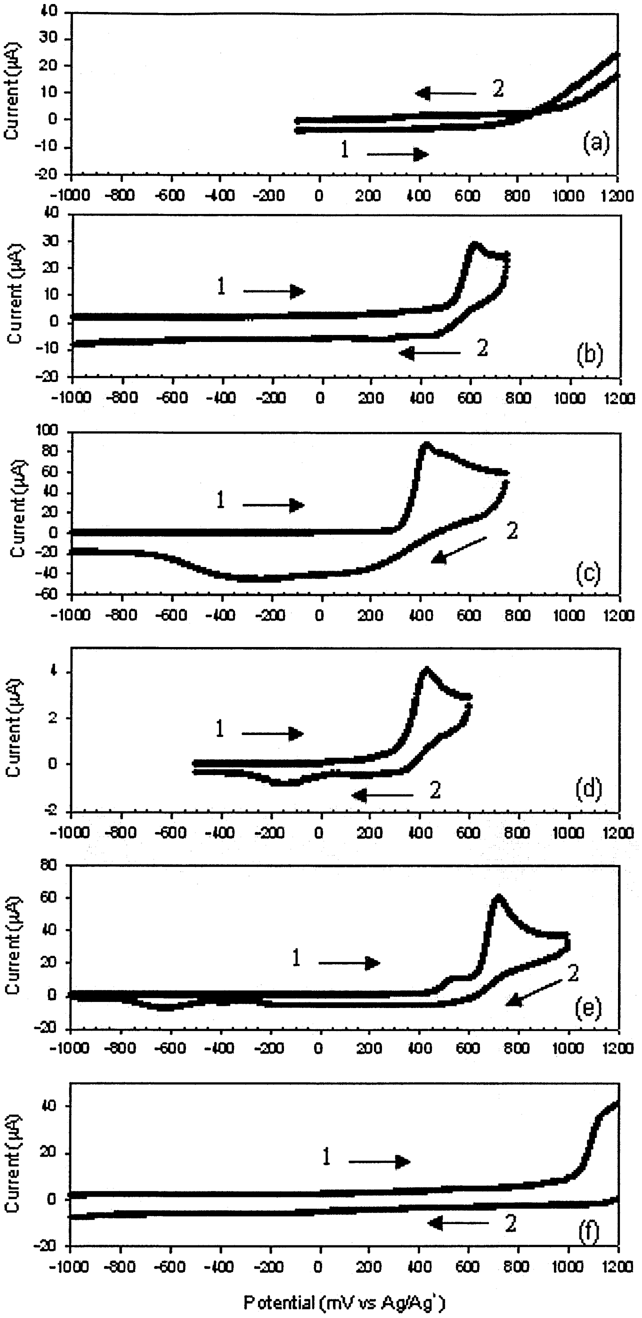

Figure 3. Cyclic voltammagrams of BEDOT-Q derivatives. Oxidation occurs with positive current. Sweep number and direction are indicated. (a) EDOT 1 mM; (b) BEDOT-TZ **1**, 1.0 mM; (c) BEDOT-3BT **2**, 1.4 mM; (d) BEDOT-3OT **3**, 1.4 mM; (e) BEDOT-TOL **4**, 1.0 mM; (f) BEDOT-OXA **12,** unknown concentration (see text). Electrolyte: 0.1 M Bu_4NPF_6/CH_3CN. Reference: Ag/0.01 M $AgNO_3$/electrolyte; glassy carbon working electrode; Pt auxiliary electrode; 100 mV/s except (c) 50 mV/s.

current. The initial and reversal sweeps are indicated. The cyclic voltammagram of EDOT is shown for comparison. Since the energy gap of these soluble monomers is greater than 2.9 eV (429 nm) and the most negative potential available with Bu_4NPF_6/acetonitrile is limited to about −2.0 V, the energy gap of these monomers could not be determined electrochemically. Although not evident from the presented voltammagram of the 1,3,4-oxadiazole derivative, there appears to be a very small oxidation wave at a lower potential ($E_{ox,onset} = 485$ mV, $E_{ox,peak} = 617$ mV) than the larger oxidation wave at $E_{ox,onset} = 1014$ mV. The small, lower potential wave is much more reasonable in comparison with the oxidation potentials of the other BEDOT-Q compounds. The low anodic current is likely due to the very low solubility of the BEDOT-OXA in acetonitrile. Characterization of this monomer will require more sensitive instrumentation or use of better solvents. All of the soluble monomers with the exception of the BEDOT-OXA can be deposited on ITO electrodes by repeated cyclic voltammetric sweeps beyond the oxidation potential. When BEDOT-OXA was subjected to repeated potential cycling, a purple film formed at the ITO working electrode; however, when the driving force was removed, the film dissolved. Characterization of the successfully deposited polymer films will be reported in a timely manner.

Table 1 presents the spectral and electrochemical data for the BEDOT-Q derivatives along with the emission quantum yield observed for the soluble materials. As expected, it is seen in Figure 2 that the materials with the highest quantum yield were those having the minimum overlap between the absorption and emission spectra. The quantum yield of the cyanovinylene derivatives was not measured.

Table 1. Spectroscopic and Electrochemical Data for BEDOT-Q Compounds

material	$E_{\mathrm{ox,onset}}$ (mV vs Ag/Ag$^+$)[a]	$E_{\mathrm{ox,peak}}$ (mV vs Ag/Ag$^+$)[a]	absorption λ_{onset} (nm)[b]	absorption λ_{max} (nm)[b]	emission λ_{max} (nm)[b]	ϕ_f[c]
BEDOT-TZ	479	619	429	377	452	0.054
BEDOT-3BT	329	422	418	361	441	0.034
BEDOT-3OT	312	426	419	361	441	0.032
BEDOT-TOL	453	557	373	321	401	0.071
BEDOT-CNV			620[d]	595[d]	629	
BEDOT-CNVMOB			674[d]	614[d]	657	
BEDOT-OXA	1014 (485)[e]	1191 (617)[e]	383	<320	413	0.090

[a] Solvent is ACN; electrolyte is Bu_4NPF_6. [b] Solvent is ACN except DMF for BEDOT-OXA. BEDOT-CNV and −CNVMOB are solid. [c] Quantum yield determined by comparison with quinine sulfate standard. [d] Excitation spectra. [e] Values in parentheses indicate a very low current oxidation wave not evident in Figure 3e due to poor solubility.

While it is true that there is a causal link between molecular structure and oxidation potential, absorption and emission wavelength, and quantum yield, it is nevertheless difficult at this time to conclusively correlate experimental behavior with structure. The electron-donating or -withdrawing characteristics of the derivatizing moieties as well as conformational effects will certainly influence the properties; however, the behavior is complex and requires more work to understand the relationship.

Conclusion

This work reports the synthesis of five new compounds based on 3,4-ethylenedioxythiophene. The three-ring bis-EDOT derivatives synthesized by organonickel, organopalladium, and functional group interconversions exhibited blue emission ($\lambda_{\mathrm{max,emission}} = 401-452$ nm) with quantum yields ranging from 3.2 to 9.0%. The cyanovinylene class of compounds exhibited poor solubility in common organic solvents, but afforded compounds which provided orange or red emission when interrogated in the solid state at a 30° angle of incidence. Cyclic voltammetry was employed to characterize the electrochemical behavior of the soluble systems. The onset of the oxidation wave, $E_{\mathrm{ox,onset}}$, for BEDOT-TZ was found to be 479 mV versus Ag/Ag$^+$. The 3-alkylthiophene class materials had onset oxidation potential of 329 and 312 mV for BEDOT-3BT and BEDOT-3OT, respectively. That of BEDOT-TOL was 453 mV, while BEDOT-OXA was only very sparingly soluble in acetonitrile, resulting in an extremely low current oxidation with $E_{\mathrm{ox,onset}}$ of about 485 mV. With the exception of BEDOT-OXA, the soluble monomers could be electrochemically polymerized by repeated potential cycling, giving well-adhered films on ITO electrodes. The deposition and characterization of the polymer films from BEDOT-Q are currently under investigation. Such materials as described in this work have the potential to form active luminescent constituents, covering a broad spectral band for a variety of optical device applications.

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Supporting Information Available: Spectroscopic data of **1**−**5**, **7**−**10**, and **12** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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