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Functionalization Of 3,4-Ethylenedioxythiophene

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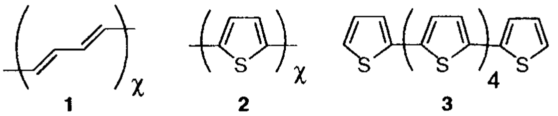
Abstract

Syntheses of 3,4-ethylenedioxythiophene-based vinylenes and oligomers are reported.

Key words

thiophenes; phosphoranes; Wittig reaction; coupling reactions; oligomers

The discovery of electrical conductivity in polyacetylene (**1**) after treatment with oxidizing agents (doping) in the late 1970's spurred the growth of the area of organic conducting polymers.[1] This world-wide activity has led to tremendous progress not only in the synthesis of a variety of conducting polymers, but also to a better understanding of the structural requirements for the design of materials with optimum electronic properties.[2,3] One such class of conducting polymers is polythiophene (**2**) which can be viewed as a sulfur-bridged *cis* polyacetylene.



1 **2** **3**

Polythiophene exhibits semiconducting properties upon oxidative doping. It has a band-gap (HOMO-LUMO energy difference) of ~2.0 electron volts (ev). The oligomer sexithiophene

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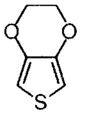
3, synthesized chemically is very insoluble, but it merits interest in that it has been shown to function as an organic transistor.[4] Recently polythiophene has also been fabricated into a high-performance plastic transistor.[5] Polythiophene is also of interest in the area of photonics. It has been shown that it exhibits a relatively high third-order optical susceptibility.[6] The major problems which have to be addressed if such materials are to become technologically functional are solubility, ease of access, capacity to produce regularly linked structures, mechanical and environmental stability, as well as low band-gap to approach metallic conductivity. During the last two decades researchers around the globe, in academia as well as industry, have been investigating these problems. The insolubility problem arising from chemical polymerization has been addressed by carrying out electrochemical oxidative couplings to give peelable films. The irregularity in intermolecular linkage (αα versus αβ or ββ) has also been addressed by blocking the β-positions, as for example, in thiophene with alkyl and alkoxy groups.[3] Alkoxy and dialkoxythiophene derived polymers have been shown to exhibit lower bandgaps than polythiophene as well as being more stable in humid environments.[7,8] The lowering of the bandgap compared to that of polythiophene or alkylpolythiophenes is due to the presence of donor oxygen atoms in the β-position(s) of the thiophene unit(s).

One of the most investigated member of these alkoxysubstituted polythiophenes is the polymer derived from 3,4-ethylenedioxythiophene (EDOT-**4**).[8] The monomer **4** has been known from 1938,[9] with subsequent reports of improvements in its synthesis.[10,11] The most valuable property of poly**4** is its antistatic function, discharging static electricity from photographic films, electronic components, etc. Whereas **4** and poly**4** are manufactured commercially by Bayer AG, investigations into other types of EDOT derived polymers like vinylenes, cyanovinylenes and polyheterocycles require fabrication starting from **4**. To some degree this is being done, taking advantage of the ready formation of organolithium and organomagnesium reagents from **4**.[12-16]



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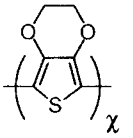
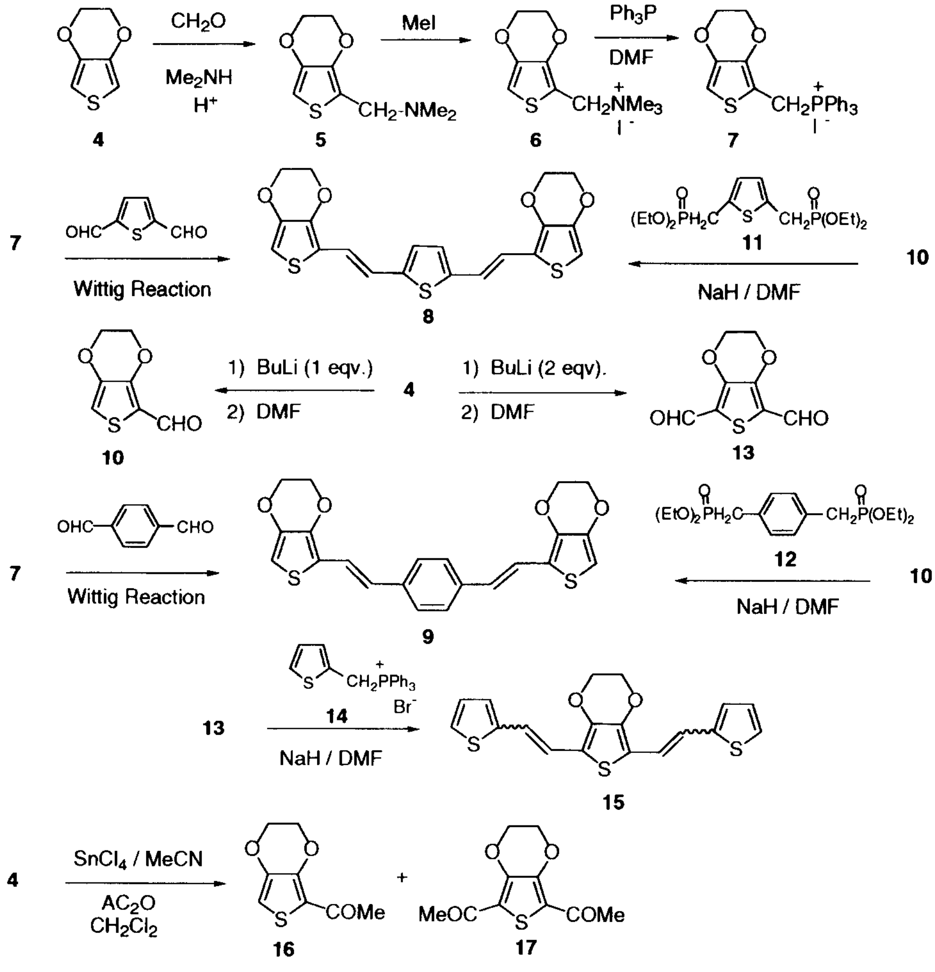


Poly**4**

In several instances, the synthetic details are unavailable due to the nonsynthetic emphasis of the journals. We now wish to describe in this paper our investigations into the basic chemistry of **4** as well as the formation of new oligomers.

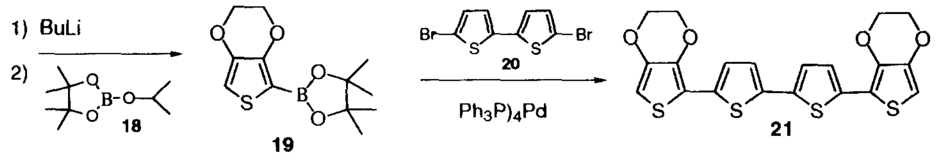
Discussion of Results

While thiophene undergoes Mannich reactions more sluggishly than furan or pyrrole, electron-rich EDOT (**4**) reacts with formalin/dimethylamine to give the Mannich base **5** and its methiodide **6** upon reaction of **5** with MeI. Methiodide **6** is transformed into the triphenylphosphonium salt **7** by reaction with triphenylphosphine in DMF. The Wittig reaction of **7** with 2,5-thiophenedicarboxaldehyde and terephthalaldehyde led to poor yields of the vinylenes **8** and **9** (4% each), respectively. In contrast, the Wittig-Horner reaction of the monoaldehyde **10** with the bisphosphonates **11** and **12** led to the vinylenes **8** and **9** in 91% and 87% yields, respectively. Dialdehyde **13** also underwent the Wittig reaction with phosphonium salt **14** to give vinylene **15**, in 74% yield, as an inseparable E/Z isomeric mixture. (Scheme 1)



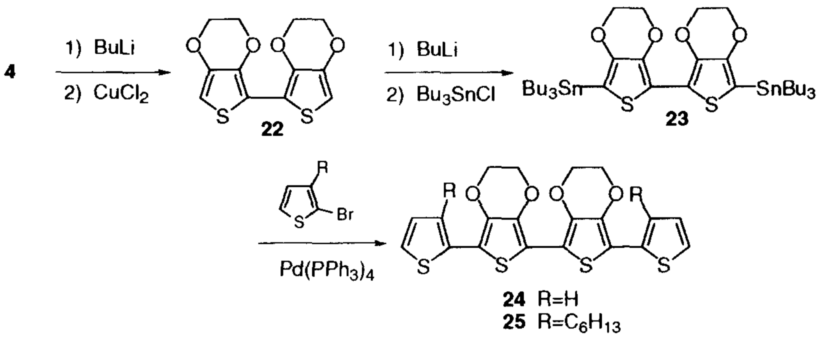
Scheme 1

In contrast to thiophene, EDOT (**4**) undergoes extensive decomposition under strongly acidic conditions, and in the presence of Lewis acid catalysts.[17] After several unsuccessful attempts at introducing acetyl function(s) in **4** to give ketone **16** and diketone **17**, it was found that the addition of one equivalent of stannic chloride in acetonitrile to a mixture of one equivalent of acetic anhydride and **4** in methylene chloride at room temperature led to ketone **16** and diketone **17** in 65% and 13% yield, respectively. The use of slightly over two equivalents of acetic anhydride and stannic chloride and refluxing conditions led to 12% of **16** and 70% of **17**. It is interesting to note that the electron donating capacity of the ethylenedioxy function predominates over the deactivating nature of the first ketone function at the 2-position to yield diketone **17** in good yield. (Scheme 1) These ketones are useful intermediates for further transformations similar to those carried out on acetyl thiophene. Lithiation of **4** followed by reaction with pinacol borate **18** gave the boronate **19**[18] in 71% yield. Coupling of the latter with αα'dibromobithiophene (**20**) in the presence of Pd° catalyst gave the tetracycle **21** in 20% yield. (Scheme 2)



Scheme 2

Copper-catalyzed coupling of the 2-lithio derivative of **4** as described in the literature led to a product with a higher melting point than previously reported.[19] This was recharacterized and structure **22** was confirmed. The bistributyltin derivative **23** was prepared and coupled with 2-bromothiophene and its 3-hexyl derivative to give two new tetramers **24** and **25**, respectively. (Scheme 3)



Scheme 3

Conclusion

In summary, we have described the preparation and properties of several new vinylenes, ketones and oligomers derived from 3,4-ethylenedioxythiophene (**4**) which are of potential use in the fabrication of polymers with interesting solid-state properties. The presence of the ethylenedioxy group in the 3,4-position confers considerable solubility to these molecules which can be further enhanced by the presence of the alkyl side chains on the thiophene moieties.

Experimental

General

All melting points are uncorrected. NMR spectra were determined in $CDCl_3$ solution containing TMS as internal standard unless otherwise stated. Mass spectra were obtained on an AEI MS-902 spectrometer at 70 ev. All UV-VIS spectra were obtained on a Shimadzu UV-VIS spectrophotometer. Organic extracts were dried over anhydrous Na_2SO_4.

*2-(N,N-Dimethylaminomethylene)-3,4-ethylenedioxythiophene (**5**).*

To a stirred solution of 3,4-ethylenedioxythiophene (**4**) (3.05 g, 0.0215 mol) in glacial acetic acid (5 mL) was added formalin (37%, 3.49 mL, 0.043 mol) and N,N-dimethylamine (4.84 mL, 0.043 mol). The mixture was then stirred at rt for 48 h. The brown solution was poured into water and the pH adjusted to 7 with 10% sodium hydroxide solution, and was extracted with methylene chloride. Removal of the solvent gave **5**, a brown oil (3.61 g, 84%) and it was used without further purification in the next step. ^1H NMR (360 MHz) δ 6.19 (s, 1H), 4.11-4.15 (2d, 4H, J=1 and 6 Hz), 3.44 (s, 2H), 2.22 (s, 6H). ^{13}C NMR (90 MHz) δ 141.09, 139.04, 113.98, 97.45, 64.45 (2C), 53.65, 44.75 (2C). UV ($CHCl_3$) λ_{max} (log ε) 259 (3.90), 228 (3.64). HRMS Calcd for $C_9H_{13}NO_2S$: 199.0667. Found: 199.0652.

*Methiodide (**6**).*

To a stirred solution of the Mannich base **5** (3.60 g, 0.018 mol) in dry toluene (100 mL) was added iodomethane (3.6mL, 0.058 mol). The mixture was stirred at rt overnight. The white solid was filtered and washed with hot hexane to give pure **6**, as a white powder (4.5 g, 73%). Mp 170-173 °C. ^1H NMR (360MHz) δ 6.58 (s 1H), 4.78 (s, 2H), 4.30-4.32 (dd, 2H, J=2 and 4 Hz), 4.23-4.25 (dd, 2H, J=2 and 4 Hz), 3.43 (s, 9H). ^{13}C NMR (90 MHz) δ 144.04 141.31, 104.44, 101.19, 65.24, 64.38, 61.46, 53.06 (3C). UV ($CHCl_3$) λ_{max} (log ε) 246 (4.34), 229 (3.97). Anal. Calcd for $C_{10}H_{16}INO_2S$: C, 35.20; H, 4.73; N, 4.10; S, 9.40. Found: C, 35.22; H, 4.68; N, 3.98; S, 9.54.

*Phosphonium Salt (**7**).*

To a solution of methiodide **6** (1.0 g, 2.94 mmol) in dry DMF (10 mL) was added triphenylphosphine (0.77 g, 2.94 mmol), and the resulting solution was refluxed until there was no further evolution of trimethylamine. The mixture was then cooled and diluted with diethyl ether and the resulting precipitate was collected by filtration and washed with diethyl ether. The precipitate was crystallized from CH_2Cl_2/hexanes to give **7**, as a light brown crystalline solid (1.35 g, 84%). Mp 205-206°C. ^1H NMR (360MHz) 7.66-7.82 (m, 15H), 6.18-6.19 (d, 1H, J=3.36 Hz), 5.08-5.16 (d, 2H, J=12 Hz), 3.91-3.93 (m, 2H), 3.76-3.78 (m, 2H). ^{13}C NMR 141.91, 141.19, 135.27, 135.24, 134.14, 134.03, 130.36, 130.22, 118.01, 117.07, 100.78, 100.71, 100.03, 64.56, 64.38. Anal. Calcd for $C_{25}H_{22}IO_2PS \bullet 0.5$ eq H_2O: C, 54.26; H, 4.19; S, 5.79. Found: C, 54.26; H, 4.19; S, 5.84.

*3,4-Ethylenedioxythiophene-2-carboxaldehyde (**10**).*

A solution of 3,4-ethylenedioxythiophene (**4**) (2 g, 0.0141 mol) in dry THF (30 mL) was cooled to -78 °C under N_2 and treated with 2.5 M solution of n-Buli (6.2 mL). The temperature was slowly raised to 0 °C and the mixture was stirred at the same temperature for 20 min. The reaction mixture was recooled to -78 °C and treated with dry DMF (2 mL, 0.026 mol). The resulting mixture was then stirred at rt for 1 h and poured into crushed ice containing HCl. The white precipitate of aldehyde was filtered, washed with water, and dried *in vacuo* to give **10** (2.26 g, 95%). Mp 142 °C (methanol). ^{1}H NMR (360 MHz) δ 9.90 (s, 1H), 6.79 (s, 1H), 4.37-4.35 (t, 2H, J=3.3 Hz), 4.28-4.25 (t, 2H, J=4.2 Hz). MS (m/z) 170 (m$^+$, 100%), 169 (81), 143 (24), 142 (12). ^{13}C NMR (90 MHz) δ 178.9, 128.3, 128.0, 127.7, 109.9, 64.7, 63.9. UV (CH_2Cl_2) λ_{max} (log ε) 413 (2.36), 293 (4.14). Anal. Calcd for $C_7H_6O_3S$: C, 49.39; H, 3.56; S, 18.84. Found: C, 49.56; H, 3.68; S, 18.74. (Previously prepared by Reynolds *et al.*,[12] but no analytical data was reported.)

3,4-Ethylenedioxythiophene-2,5-dicarboxaldehyde (13).

The dilithiation of 3,4-ethylenedioxythiophene **1** (1 g, 0.007 mol) was carried out using 6.2 mL of 2.5 M n-BuLi and was reacted with 2 mL of dry DMF as previously stated. The usual workup followed by recrystallization from methanol yielded pure dialdehyde **13** as pale brown needles (1 g, 72%). Mp 141 °C (methanol). ^{1}H NMR (360 MHz) δ 10.02 (S, 2H), 4.45 (S, 4H). MS (m/z) 198 (m$^+$, 100%), 197 (84), 169 (21). UV (CH_2Cl_2) λ_{max} (log ε) 358 (4.01), 324 (4.49), 230 (3.58). Anal. Calcd for $C_8H_6O_4S$: C, 48.47; H, 13.06; S, 16.18. Found: C, 48.53; H, 3.11; S, 16.28.

2,2'-(3,4-Ethylenedioxydithienyl)-ω,ω'-2,5-divinylthiophene (8).

Method A. To a stirred suspension of NaH (0.19 g, 0.004 mol) in dry DMF (30 mL) was added tetramethyl-2,5-thienyl)bis(methyl phosphonate) **11** (0.75 g, 0.002 mol) at 0 °C. After 15 min, a solution of aldehyde **10** (0.75 g, 0.0044 mol) in DMF (10 mL) was added and stirred at rt for 10 h. The orange-yellow solution was poured into ice water/HCl and the solid product was filtered and washed with methanol to give **8** (0.74 g, 91%), mp 176-177 °C. ^{1}H NMR (d_6-benzene, 360 MHz) δ 7.89-7.85 (d, 2H, 15.9 Hz), 7.83 (s, 2H), 7.81-7.77 (d, 2H, J=15.8 Hz), 6.69 (s, 2H), 4.09-4.05 (m, 8H). MS (m/z) 416 (m$^+$, 100%), 360 (11), 319 (44), 287 (17), 263 (12). UV (CH_2Cl_2) λ_{max} (log ε) 455 (4.62), 429 (4.71), 326 (4.08), 267 (3.36). Anal. Calcd for $C_{20}H_{16}O_4S_3$: C, 57.67; H, 3.88; S, 23.10. Found: C, 57.44; H, 3.97; S, 22.95.

Method B. To the phosphonium salt **7** (300 mg, 0.55 mmol) in dry THF (10 mL) at 0 °C, was added 2.5 M n-BuLi in hexane (0.22 mL, 0.55 mmol) with stirring. After 20 min a solution of thiophene-2,5-dicarboxaldehyde (39 mg, 0.28 mmol) in dry THF (1 mL) was added and the resulting mixture was stirred at rt for 48 h. The solution was then poured into crushed ice, filtered to remove unreacted phosphonium salt, and the filtrate was extracted with methylene chloride (3x25 mL). The dried extract was concentrated *in vacuo* and purified by column chromatography eluting with CH_2Cl_2 to give in addition to unreacted phosphonium salt (90 mg) **8**; orange powder (10 mg, 4%). Mp 176-177 °C. This sample was identical to **8** prepared by Method A.

2,2'-(3,4-Ethylenedioxy)dithienyl-ω,ω'-1,4-divinyl benzene. (9).

Method A. A solution of tetraethyl-1,4-phenylenebis(methylphosphonate) **12** (0.45 g, 0.0012 mol) in dry DMF (30 mL) was reacted with aldehyde **10** (0.144 g, 0.003 mol) in the presence of NaH (0.144 g, 0.003 mol) by using a similar procedure as described above. The usual workup yielded a bright yellow solid **9** (0.42 g, 87%), mp 233 °C. ^{1}H NMR (360 MHz) δ 7.40 (s, 4H), 7.16-7.11 (d, 2H, J=16.2 Hz), 6.86-6.81 (d, 1H, J=16.2 Hz), 6.22 (s, 2H), 4.30-4.27 (q, 4H, J=2.8 Hz), 4.23-4.21 (q, 4H, J=1.9 Hz). ^{13}C NMR (90 MHz) δ 142.0, 139.2, 136.4, 126.4, 125.8, 117.8, 117.3, 97.7, 64.8, 64.7. MS (m/z) 410 (m$^+$, 25%), 358 (44), 278 (75), 263 (100), 221 (25), 207 (34), 165 (47), 151 (48). UV (CH_2Cl_2) λ_{max} (log ε) 393 (4.60), 251 (3.09). Anal. Calcd for $C_{22}H_{18}O_4S_2$. C, 64.39; H, 4.42; S, 15.60. Found: C, 63.65; H, 4.55; S, 15.24. HRMS Calcd for $C_{22}H_{18}O_4S_2$ • 410.062130. Found: 410.0646.

Method B. To the phosphonium salt **7** (200 mg, 0.37 mmol) in dry THF (10 mL) at 0 °C, was added 2.5 M n-BuLi in hexane (0.15 mL, 0.37 mmol) with stirring. After 20 min a solution of terephthalaldehyde (25 mg, 0.18 mmol) in dry THF (1 mL) was added and the resulting mixture stirred at rt for 48 h. The mixture was poured into crushed ice, filtered to remove unreacted phosphonium salt, and the filtrate extracted with methylene chloride (3x25 mL). The dried extract was concentracted *in vacuo*, and purified by column chromatography eluting with CH_2Cl_2 to give in addition to unreacted phosphonium salt (30 mg) **9**; yellow powder (3 mg, 4%). Mp 233-234 °C. This sample was identical to **9** prepared by Method A.

*2,2'-Dithienyl-ω,ω'-2,5(2,4-ethylenedioxy)divinyl thiophene (**15**).*

To a stirred suspension of NaH (0.24 g, 0.005 mol) in dry THF (40 mL) was added 2-thienylmethyl triphenylphosphonium bromide **14** (1.8 g, 0.004 mol) and dialdehyde **13** (0.4 g, 0.002 mol). The reaction mixture was stirred at rt for 10 h and then poured into crushed ice. Extraction of the crude product using CH_2Cl_2 (3x20 mL) followed by column chromatographic purification on neutral alumina gave compound **15** as a pale yellow solid (0.53 g, 74%). Mp 117-120 °C. ^{1}H NMR (360 MHz) 7.44-7.21 (m, 4H), 7.07-6.99 (m, 1H), 6.91-6.72 (m, 4H), 6.42-6.35 (m, 1H), 3.55-3.45 (m, 4H). MS (m/z) 358 (m$^+$, 49%), 250 (69), 218 (23), 192 (47), 153 (100). UV (CH_2Cl_2) λ_{max} (log ε) 446 (4.57), 425 (4.65), 321 (4.16), 262 (3.53). Anal. Calcd for $C_{18}H_{14}O_2S_3$: C, 60.30; H, 3.94; S, 26.83. Found: C, 59.82; H, 3.85; S, 26.54.

*2-Acetyl-3,4-ethylenedioxythiophene (**16**).*

To a solution of 3,4-ethylenedioxythiophene (**4**) (3.13 g, 0022 mol) in dry methylene chloride (2 mL) was added a 0.25 M solution of acetic anhydride in dry methylene chloride (114.5 mL, 0.0286 mol) and a 0.25 M solution of stannic chloride in dry acetonitrile (114.5 mL, 0.0286 mol), and the resulting mixture stirred at rt, under anhydrous conditions for 24 h. The wine-red solution was then poured into crushed ice containing glacial acetic acid (50 mL). The organic layer was separated and the aqueous extracted with methylene chloride (3x50 mL). The combined organic layer was washed with 10% sodium hydroxide untl the washings were pH 7. Chromatographic purification on silica gel [eluting with CH_2Cl_2/hexanes (2:1)], followed by recrystallization from $CHCl_3$/hexanes gave **16**, yellow-orange needles (2.64 g, 65%) and **17** peach needles (0.64 g, 13%).

16. Mp 101-102.5 °C ($CHCl_3$/hexanes). ^{1}H NMR (360 MHz) δ 6.66 (s, 1H), 4.26-4.38 (dd, 2H, J=0.90 and 1.87 Hz), 4.23-4.25 (dd, 2H, J=1.1 and 1.9 Hz), 2.50 (s, 3H). ^{13}C NMR (90 MHz) δ 189.68, 144.78, 141.68, 120.08, 108.32, 65.24, 63.90, 28.96. IR (KBr) υ 1639 cm^{-1}. MS (m/z) 184 (m$^+$, 73%), 169 (100), 143 (15) 113 (12). UV ($CHCl_3$) λ_{max} (log ε) 287 (4.2). Anal. Calcd for $C_8H_8O_3S$: C, 52.16; H, 4.38; S, 17.41. Found: C, 52.13; H, 4.46; S, 17.56.

*2,5-Diacetyl-3,4-ethylenedioxythiophene (**17**).*

3,4-Ethylenedioxythiophene (**4**) (0.25 g, 1.76 mmol) in dry methylene chloride (1 mL) was stirred with a 0.196 M solution of acetic anhydride in dry methylene chloride (23 mL, 4.58 mmol) and a 0.1 M solution of stannic chloride in dry acetonitrile (46 mL, 4.58 mmol). The resulting mixture was then refluxed overnight under anhydrous conditions. The mixture was worked up as previously described. Chromatographic purification followed followed by recrystallization yielded **16** (0.04 g, 12%) and **17** (0.277 g, 70%).

17. Mp 200-203 °C ($CHCl_3$/hexane). ^{1}NMR (360 MHz) δ 6.66 (s, 1H), 4.26-4.38 (dd, 2H, J=0.90 and 1.87 Hz), 4.23-4.25 (dd, 2H, J=1.1 and 1.9 H 4.42 (s, 4H), 2.55 (s, 6H). ^{13}C NMR (90 MHz) δ 6.66 (s, 1H), 4.26-4.38 (dd, 2H, J=0.90 and 1.87 Hz), 4.23-4.25 (dd, 2H, J=1.1 and 1.9 H 190.21 (2C), 143.64 (2C), 124.22 (2C), 64.62 (2C), 29.62 (2C). IR (KBr) υ 1645, 1655 cm^{-1}. MS (m/z) 226 (m$^+$, 82%), 211 (100), 169 (20), 143 (10), 113 (7). UV ($CHCl_3$) λ_{max} (log ε) 314 (4.27). Anal. Calcd for $C_{10}H_{10}O_4S$: C, 53.09; H, 4.45; S, 14.17. Found: C, 53.29; H, 4.35; S, 13.95.

*Preparation of boronic ester **19**.*

Lithiation of 3,4-ethylenedioxythiophene (**4**, 2 g, 0.0141 mol) was carried out as described previously. To this solution 2-isopropoxy-4,4,5,5'-tetramethyl-1,3,2-dioxaborolane (**18**, 5.8 mL, 0.028 mol) in dry THF (10 mL) was added, and the mixture was stirred for 6 h. The mixture was then poured over crushed ice/NH_4Cl and crude product was extracted into Et_2O (3x30 mL), and dried. Removal of the solvent followed by trituration with methanol gave pure boronic ester **19** (2 g, 71%). Mp 87-88 °C. ^{1}H NMR (360 MHz) δ 6.62 (s, 1H, 4.29-4.28 (t, 2H, J=2.2 Hz), 4.18-4.17 (t, 2H, J=21 Hz), 1.33 (s, 12H). ^{13}C NMR (90 MHz) δ 150.1, 142.9, 128.3, 128.0, 127.7, 107.9, 83.5, 64.4, 64.0, 24.8. MS (m/z) 268 (m$^+$, 78%), 253 (35), 225 (58), 210 (29), 183 (47), 168 (100). UV (CH_2Cl_2) λ_{max} (log ε) 280 (3.95), 259 (4.14), 322 (3.63). Anal. Calcd for $C_{12}H_{17}BO_4S$: C, 53.74; H, 6.40; S, 11.96. Found: C, 53.61; H, 6.51; S, 12.08.

*Bis(3,4-ethylenedioxothienyl)-bithiophene (**21**).*

A solution of 5,5'-dibromo-bithiophene (**20**) (325 mg, 1 mmol), boronic ester **19** (805 mg, 3 mmol), $Pd(PPh_3)_4$ (230 mg, 0.2 mmol), and dry K_3PO_4 (200 mg) in 15 mL DMF was heated for 16 h at 100 °C (oil bath temperature) under N_2. The mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed several times with a conc aq NaCl solution and with water and then evaporated. Column chromatography of the residue [eluting with hexanes CH_2Cl_2 (3:2)] afforded **21** as an orange solid (90 mg, 20%). Mp 188-191 °C. ^{1}H NMR ($CDCl_3$) δ 7.11 (d, 2H, J=3.9 Hz), 7.07 (d, 2H, J=3.8 Hz), 6.23 (s, 2H), 4.36 (m, 4H), 4.25 (m, 4H). UV (CH_2Cl_2) λ_{max} (log ε) 412 (4.49), 251 (4.06). Anal. Calcd for $C_{20}H_{14}O_4S_4$: C, 53.81; H, 314; S, 28.70. Found: C, 54.25; H, 3.49; S, 27.59.

*2,2'-Bis(3,4-ethylenedioxythiophene) (**22**).*

A solution of 3,4-ethylenedioxy-thiophene (**4**) (5 g, 0.035 mol) in dry THF (100 mL) was cooled to -78 °C under N_2 and treated with 14.5 mL of 2.5 M n-BuLi (hexane). The temperature was slowly raised to 0 °C and the mixture was stirred at the same temperature for 30 min. To this was added $CuCl_2$ (5 g, 0.0372 mol) in one portion and stirring was continued for an additional 12 h. It was then poured into crushed ice, extracted into CH_2Cl_2 (3x50 mL), and passed through celite. Removal of the solvent gave 4.2 g (84%) of compound **22** as a white solid. Mp 203-204 °C (Lit.[19] 183-185 °C). ^{1}H NMR (360 MHz) δ 6.25 (s, 2H), 4.31-4.28 (t, 4H, J=3.6 Hz), 4.21-4.19 (t, 4H, J=4.1 Hz). ^{13}C NMR (90 MHz) δ 141.1, 136.9, 109.8, 97.4, 64.9, 69.5. UV (CH_2Cl_2) λ_{max} (log ε) 313 (4.17), 319 (4.23), 305 (4.07). Anal. Calcd for $C_{12}H_{10}O_4S_2$: C, 51.05; H, 3.58; S, 22.72. Found: C, 50.86; H, 3.59; S, 22.78.

*Ditributylstannyl-ethylenedioxythiophene (**23**).*

A 2.4 M solution of n-BuLi in hexane (16 mL, 0.038 mol) was added dropwise to a stirred solution of BiEDOT **22** (5 g, 0.018 mol) in 60 mL of dry THF at -60 °C under N_2. The mixture was allowed to come to rt and stirred for 30 min. To the grey suspension, a solution of tributyltin chloride (12.3 g, 0.038 mol) in 20 mL of dry THF was added dropwise at

-60 °C. The reaction mixture was raised to rt and stirred for 2 h. The mixture was poured into aqueous NH_4Cl solution and extracted two times with CH_2Cl_2. The organic layer was washed three times with water and dried. Evaporation of the solvent gave the tin compound **23** as brown oil (15.2 g, 100%). The compound was used without further purification. ^{1}H NMR ($CDCl_3$) δ 4.30 (m, 4H), 417 (m, 4H), 1.53 (m, 12H), 1.34 (m, 12H); 1.10 (t, 12H, J=7.9 Hz), 0.89 (t, 18H, J=7.3 Hz).

*Dithienyl-bis(3,4-ethylenedioxythiophene) (**24**).*

A solution of bistributylstannyl BiEDOT **23** (obtained from 5 g BiEDOT, 17.7 mmol), 2-bromothiophene (6.1 g, 37.4 mmol), and $Pd(PPh_3)_4$ (2 g, 1.7 mmol) in 120 mL THF was refluxed for 10 d under N_2. After concentration and cooling, the precipitate of the tetrathiophene **24** was filtered off, washed several times with EtOH and a small amount of Et_2O giving a red brown solid (3.7 g, 47%). Mp 306-309 °C. ^{1}H NMR ($CDCl_3$) δ 7.25 (d, 2H, J=3.7 Hz), 7.20 (d, 2H, J=5.0 Hz), 7.02 (2d, 2H, J=3.9 Hz), 4.39 (q, 8H), 2.72 (t, 4H, J=7.8 Hz), 1.62 (m, 4H), 1.31 (m, 12H), 0.88 (t, 6H, J=6.6 Hz). MS 446 (m^+, 97%), 418 (09), 390 (22), 312 (09), 267 (40), 251 (11), 127 (100). UV (CH_2Cl_2) λ_{max} (log ε) 440 (4.5), 416 (4.57), 256 (3.98). Anal. Calcd for $C_{20}H_{14}O_4S_4$: C, 53.81; H, 3.14; S, 28.70. Found: C, 53.69; H, 3.19; S, 28.84.

*Di-(3-hexylthienyl)-bisethylenedioxythiophene (**25**).*

A solution of bistributylstannyl BiEDOT **23** (1.4 g, 1.64 mmol), 2-bromo-3-hexylthiophene (870 mg, 3.52 mmol) and $Pd(PPh_3)_4$ (230 mg, 0.2 mmol) in 70 mL THF was refluxed for 11 d (on TLC still spots of bromothiophene and BiEDOT and/or tin BiEDOT; runs the same way) to give, after workup, pure **25** (180 mg, 18%). Mp 110-112 °C. ^{1}H NMR ($CDCl_3$) δ 7.24 (d, 2H, J=5.2 Hz), 6.93 (d, 2H, J=5.2 Hz), 4.36 (q, 4H), 4.31 (q, 8H), 2.72 (t, 4H, J=7.8 Hz), 1.62 (m, 4H), 1.31 (m, 12H), 0.88 (t, 6H, J=6.6 Hz). MS 614 (m^+, 100%) 543 (29), 515 (14), 351 (19), 237 (14). UV (CH_2Cl_2) λ_{max} (log ε) 388 (4.44), 232 (4.11). Anal. Calcd for $C_{32}H_{38}O_4S_4$: C, 62.54; H, 6.19; S, 20.85. Found: C, 62.26; H, 6.21; S, 20.73.

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References and Notes

[1] Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc. Chem. Commun.* **1977**, 578. See also "Handbook of Conducting Polymers" Vol. 1 and Vol. 2, Skotheim, T. A., Ed.: Marcell Dekker: New York; 1986.

[2] McCullough, R. D. *Advanced Materials* **1998**, *10*, 93.

[3] Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

[4] Horovitz, G.; Deloffre, F.; Garnier, F.; Hajlaoui, R.; Hmyene, M.; Yassar, A. *Synth. Metals* **1993**, *54*, 435.

[5] Bao, Z.; Feng, Yi; Dodabalapur, A.; Raju, V. R.; Lovinger, A. J. *Chem. Mater.* **1997**, *9*, 1299.

[6] Logsdon, P.; Pfleger, J.; Prasad, P. N. *Synthetic Metals* **1988**, *26*, 369.

[7] Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.

[8] Bayer, A. G. Eur. Pat. 339 340, **1989**. C. A. Vol. 112, **1990**, 1592132.

[9] Guha, P. C.; Iyer, B. H. *J. Ind. Inst. Sci.* **1938**, A21, 115.

[10] Fager, E. W. *J. Am. Chem. Soc.* **1945**, *67*, 2217

[11] Gogte, V. N.; Shah, L. G.; Tilak, B. D.; Gudekar, K-N.; Schasvabudhe, M. B. *Tetrahedron* **1967**, *23*, 2437.

[12] Fu, Y.; Cheng, H.; Elsenbaumer, R. L. *Chem. Mater.* **1997**, *9*, 1720.

[13] Sotzing, G. A.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1995**, 703.

[14] Reddinger, J. L.; Sotzing, G. A.; Reynolds, J. R. *ibid* **1996**, 1777.

[15] Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1996**, *8*, 882.

[16] Sotzing, G. A.; Thomas, C. A.; Reynolds, J. R.; Steel, P. J. *Macromolecules* **1998**, *31*, 3750.

[17] Mohanakrishnan, A. K.; Cava, M. P. Unpublished observations.

[18] In contrast to thiophene boronic acid, the pinacol boronate is not labile.

[19] Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Adv. Mater.* **1997**, *10*, 795.