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Novel Terthiophene and Bis(thienyl)furan Derivatives as Precursors to Highly Electroactive Polymers

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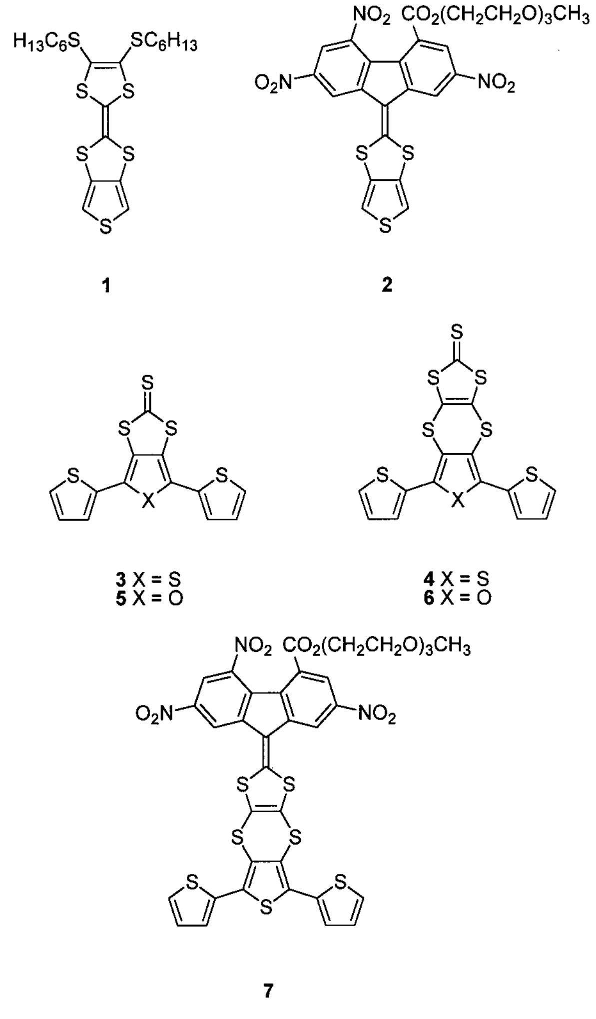
The syntheses of a series of 1,3-dithiole-2-thione derivatives (**3**−**6**), bearing fused terthiophene or bis(2-thienyl)-2,5-furan units, are reported. These novel heterocycles are readily polymerized electrochemically to give stable electroactive materials. The target compounds were obtained in moderate to high yield via the cyclization of the corresponding diketones or hydroxyketones, using phosphorus pentasulfide or acidic conditions. The ketones **12** and **17** were prepared directly from their hydroxy precursors by treatment with MnO_2. The trans configuration of diketone **20** was confirmed by X-ray crystallography.

Introduction

The role of terthiophene systems in materials chemistry is 2-fold. First, unsubstituted 2,5″-derivatives can be used as efficient trimers for oxidative polymerization reactions. The corresponding poly(thiophene)s represent a major group in the highly topical field of conjugated polymers.[1] Due to the highly electroactive nature of poly(thiophene) and its derivatives, these materials can been used in applications such as batteries,[2] chemical[3] and biological[4] sensors, and light-emitting diodes.[5] Second, terthiophenes are useful synthetic precursors to sexithiophenes, which are materials currently being investigated as components in field-effect transistors.[6]

Recently, we have been investigating the syntheses of thiophene monomers bearing strongly redox-active substituents, viz. the electron-donating tetrathiafulvalene in **1**[7] and the electron-accepting fluorene unit in **2** (Chart 1).[8] Both species represent highly redox-active systems with the potential of exhibiting unusual electronic properties in conjunction with the conducting polymer.[9] Due to unfavorable electronic interactions, together with additional steric reasons in **2**, we have been unable to polymerize these monomers. Subsequently, we have developed the syntheses of terthiophenes **3** and **4**, which are functionalized by a 1,3-dithiole-2-thione moiety; synthetically, this unit is extremely versatile and is a

Chart 1



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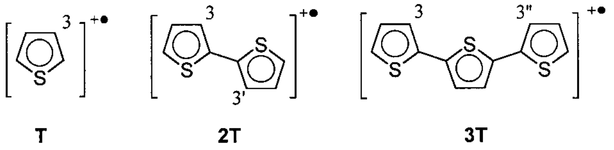
10.1021/jo990198+ CCC: $18.00

Chart 2



well-known precursor to tetrathiafulvalene systems.[10] The extended chains in terthiophenes **3** and **4** reduce the adversity of steric hindrance from substituents on the central ring, while in **4**, the cation radical intermediate obtained by oxidation will be affected less by the electronic behavior of the 1,3-dithiole unit, due to the fused 1,4-dithiino spacer group. Using this approach, we have succeeded in the preparation and electrochemical polymerization of fluorene derivative **7**, which has been the subject of a preliminary communication.[11]

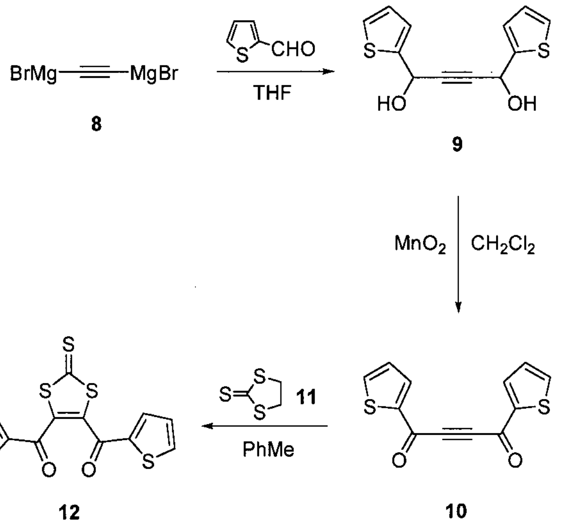
The synthesis and properties of mixed heterocyclopentadiene co-oligomers[12] and copolymers[13] are also of interest; in the latter case, theoretical studies have shown that the incorporation of mixed repeating units of different band gaps lowers the overall band gap (E_g) of the polymer.[14] This type of methodology can be used for tuning the value of E_g, which is an important criterion in the application of light-emitting devices.

According to Smith et al.,[15] density functional theory calculations (also supported by experimental ESR measurements in some cases) show that differences in the spin densities between the 2(5) and 3(4) positions in radical cations of thiophene (T), bithiophene (2T), and terthiophene (3T) decrease in the order T > 2T > 3T (Chart 2). Thus, for thiophene, $\rho_\pi(2,5) = 0.456$(DFT), 0.492 (ESR), $\rho_\pi(3,4) = 0.098$ (DFT), 0.095 (ESR); for terthiophene, $\rho_\pi(5) = 0.151$ (DFT), 0.127 (ESR); $\rho_\pi(3) = 0.075$ (DFT), 0.077 (ESR). Consequently, there is a greater chance of $\alpha-\alpha'$-coupling between bithiophene and terthiophene systems; this type of “imperfection” within poly(thiophene)s is detrimental to the conjugation in the polymer chain and results in a decrease in conductivity (compared to the corresponding polymer derived from exclusive $\alpha-\alpha'$-coupling).[9] On the other hand, steric factors have not been taken into consideration and should be significant if, for example, the central ring in terthiophene is substituted at the 3′ and 4′ positions. Thus, compounds **3**−**6** are well-suited for the synthesis of substituted poly(terthiophene) and poly[bis(thienyl)furan] systems with a good control of regiospecificity. Herein, we discuss the detailed syntheses and electrochemistry of **3** and **4**, together with the dithienyl furan analogues **5** and **6**.

Results and Discussion

Synthesis. The terthiophenes **3** and **4** were obtained in 70% and 57% yields, respectively, by heating the corresponding diketones **12** and **20** with phosphorus pentasulfide and sodium bicarbonate[16] in dioxane. The reaction proved to be suitable for the cyclization of saturated as well as unsaturated diketones, as previously seen for 1,2-dibenzoylnaphthalene.[17]

Scheme 1



We have explored two synthetic pathways toward compound **12**. First, the diketone was obtained by the reaction of acetylene **10** with ethylene trithiocarbonate **11**[18] by analogy with the synthesis of dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate.[19] The starting dithienoyl acetylene **10** was isolated in 55% yield, by the oxidation of the corresponding diol **9**, which was in turn obtained from the addition of acetylene dimagnesium bromide **8**[20] to 2-thiophenecarboxaldehyde (50% yield) (Scheme 1). The diol **9** was first reported as a byproduct in the synthesis of the monofunctionalized acetylene.[21] In the same work, several acetylenic monoketones were obtained by the oxidation of the corresponding monoalcohols with chromium trioxide; however, to the best of our knowledge, the synthesis of diketone **10** has not yet been described. Since, in the presence of acids employed in CrO_3 oxidations, one could expect **9** to undergo acid-catalyzed rearrangements (e.g. ring closure to the furan derivative), we chose manganese dioxide as the oxidizing agent which has been used for the synthesis of a number of acetylenic ketones of the thiophene series.[22] The yield of **10** was found to be essentially independent of the solvent choice (dichloromethane, diethyl ether, benzene), while the reaction efficiency increased with the quantity of manganese dioxide used (ca. 40% with MnO_2:diol = 6:1 w/w and 55% with 12:1). Dichloromethane was chosen for convenience, since it proved to be the best solvent for the subsequent purification of the product by column chromatography. The

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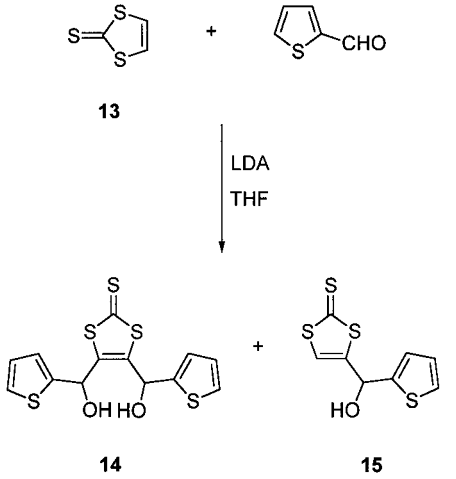
Scheme 2

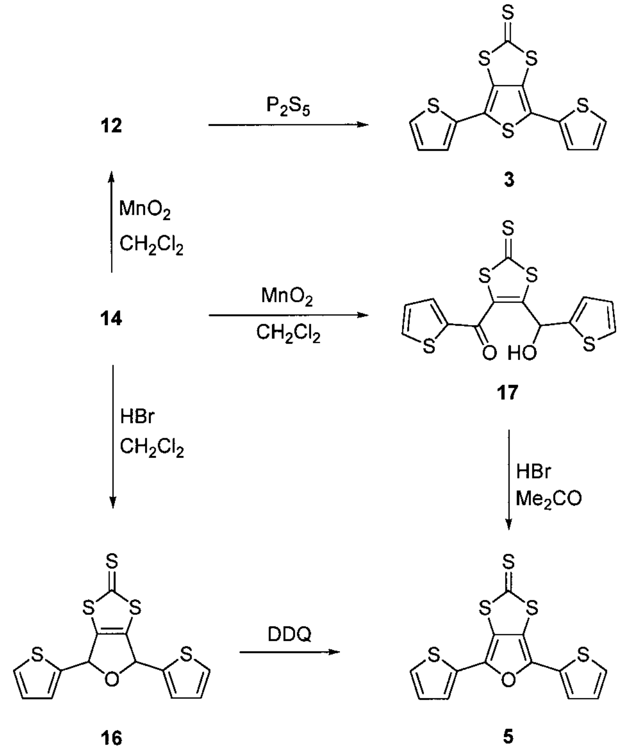


optimum reaction time for the oxidation process was very short (2 min), while prolonged treatment led to the decomposition of the product. Although diketone **10** was obtained in a satisfactory yield, its reaction with **11** gave a very low yield (8%) of the key intermediate **12**, which urged us to find an alternative synthetic strategy for the diketone **12**.

A much more efficient route to diketone **12** involved the oxidation of the diol **14**. Compound **14** was obtained in good yield (82%), via the lithiation of vinylenetrithiocarbonate[23] **13** and subsequent trapping of the carbanion species with thiophenecarboxaldehyde (Scheme 2). The reaction necessitated a stepwise process, such that 1 equiv of reagents was allowed to react with **13**, before the second equivalent was added. This exact procedure was necessary, since our attempts to obtain the dilithio derivative of **13**, in one step under mild conditions (THF, −60 °C), led to the predominant formation of the monofunctionalized product **15**, even in the presence of a large excess of LDA. The use of a less polar solvent (e.g. toluene and petroleum ether), which is known to favor the formation of dilithiothiophenes,[24] did not lead to an increase in the yield of **14**, while the use of *n*-BuLi or raising the reaction temperature (−30 °C) led to the decomposition of the starting material.

The diastereomers of **14** were separated easily by column chromatography, fraction **14a** having a higher R_f value than **14b**. Whereas the NMR signal (acetone-d_6) of the methine proton in **14a** showed normal splitting due to coupling of the hydroxyl group (J = 3.6 Hz), the same peak for **14b** appeared as a broad singlet ($W_{1/2}$ = 3 Hz). When the coupling of methine to hydroxyl protons was quenched (by the addition of a trace amount of acid or by using $CDCl_3$), both spectra showed methine doublets, due to the interaction with the 3-H proton of the thiophene ring (J = 0.8 Hz). Thus, the coupling constant between methine and hydroxyl protons in **14b** does not exceed 2 Hz, which suggests an unfavorable value for the H−C−O−H dihedral angle, possibly due to a dominant H-bonded conformation of the molecule.

Scheme 3



A quantitative yield was obtained for the conversion of **14** to the diketone **12**, using MnO_2 as the oxidizing agent (Scheme 3). For this reaction, a 10-fold excess (by weight) of MnO_2 was required to achieve an optimum yield, whereas the mono-oxidized derivative **17** was obtained by limiting the oxidizing reagent to a 3-fold excess (50% yield, with **12** as a side product). Under ambient conditions, the hydroxy ketone **17** underwent slow conversion to the furan **5**; the cyclization was efficiently catalyzed by the addition of acid (HBr or $HClO_4$) to give **5** in 89% yield. The same furan was obtained by the aromatization of dihydrofuran **16** with DDQ. Compound **16** was prepared in turn as a product of the acid-catalyzed rearrangement of **14**. The preparation of dithienyl furan **5** from diol **14**, via **17**, gave an overall yield of 45%; however, the overall yield via **16** was far lower (ca. 5%) and the product required further purification, proving that the latter method is an inferior route toward the synthesis of furan **5**. We discovered that, due to its allylic nature, diol **14** was able to undergo several acid-catalyzed rearrangement pathways, depending on the choice of acid and solvent; a study of the product distribution and kinetics of these processes, along with relevant mechanistic considerations, has recently been reported in a separate paper.[25]

The diketone **20** was obtained by the Diels−Alder coupling of oligo(1,3-dithiole-2,4,5-trithione) **19**[26] with 1,4-bis(2-thienyl)but-2-ene-1,4-dione **18**[27] (73% yield, Scheme 4). The efficiency of the cycloaddition step was complicated by side reactions between the product and the oligomer **19**. Consequently, the use of an excess of **19** led to a decrease in the product yield.

Diketone **20** proved to be quite stable and remained unchanged under the normal conditions used for the

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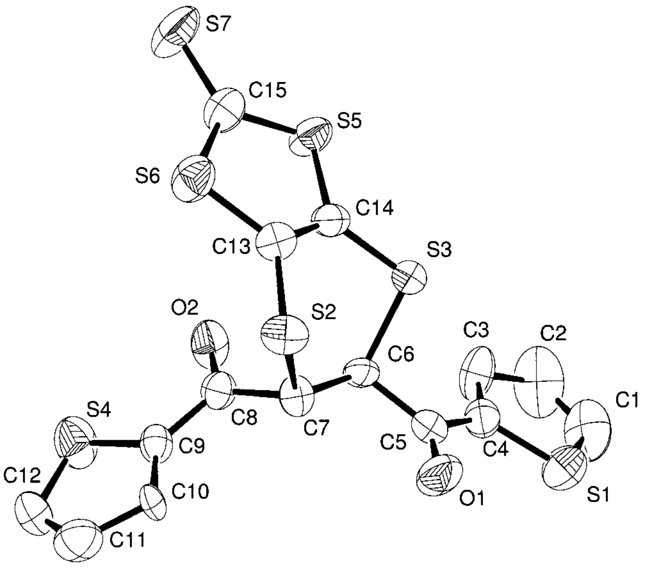
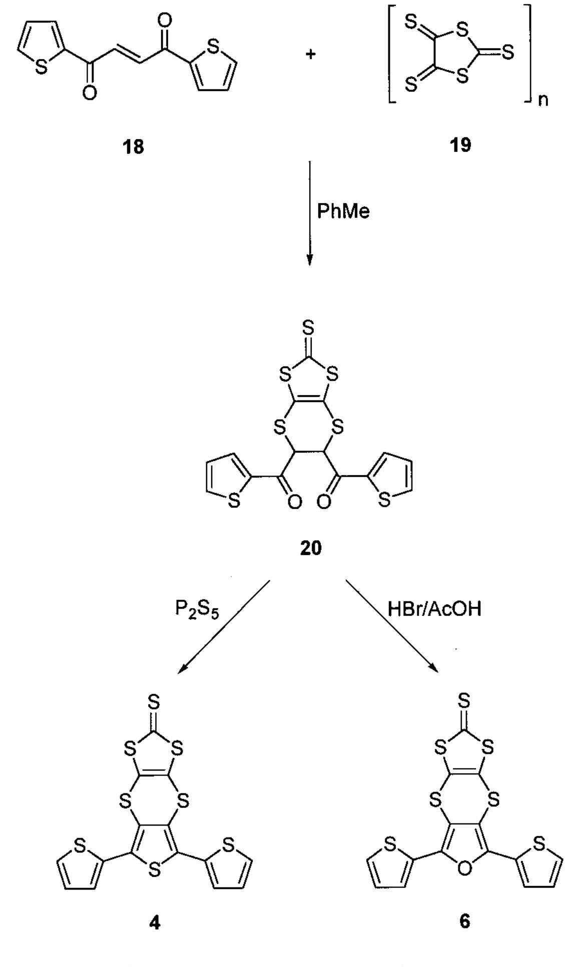


Figure 1. Molecular structure of *trans*-diketone **20**.

Scheme 4



preparation of thiophene derivatives from 1,4-diketones (Lawesson's reagent in refluxing toluene or phosphorus pentasulfide and sodium bicarbonate in ether at room temperature).[16] The inert behavior of **20** could be explained by the trans arrangement of the carbonyl groups, with respect to the dithiin ring, which was confirmed by single-crystal X-ray crystallography (Figure 1). The absence of any classical intra- or intermolecular hydrogen bonds in diketone **20** is noteworthy, since it is this type of arrangement which normally causes such stability in the solid state. Hence, we suspect that the low reactivity of **20** toward cyclization is due to steric hindrance arising from the conformation of the 1,4-dithiin ring, which limits the approach of the sulfur reagents. The structure of **20** consists of a 1,3-dithiole-2-thione fused to a 1,4-dithiin ring with 2,3-diketone substituents, each bearing a thienyl ring bound in the 2 position. The bond lengths and angles are within the expected ranges. In addition, the orientations of the thienyl rings are determined by the arrangement of the carbonyl groups, due to 1,4-intramolecular interactions between O1−S1 and O2−S4 (2.958 and 2.951 Å which, respectively, are 0.36 and 0.37 Å less than the sum of the contact radii). Similar 1,4-interactions between "nonbonded" O and S atoms have been observed previously.[28] When compared, the orientations of these substituents on the dithiin ring are somewhat different. The angle of the substituents to the mean plane of the dithiin ring are 17.64° (axial substituent) and 50.20° (bisectional substituent) for the C7−C8 and C6−C5 arms, respectively. A Cremer−Pople[29] puckering analysis of the rings showed them to be planar, apart from the dithiin ring. The lone pairs on the two sulfur atoms cause a puckering of the ring, with an angle between the two least squares mean planes (S2−C7−C6−S3 and S2−C13−C14−S3) of 116.25(12)°. Puckering analysis of this ring gave $\theta = 94.2$E and $\phi = 184.27$E, which corresponds to a boat conformation.

Assuming the reaction stereochemistry of the cycloaddition mechanism, the conformation of **20** proves the suggested trans conformation of its precursor **18**.[27] Ultimately, the trans configuration of **20** did not render the cyclization impossible; terthiophene **4** was prepared successfully under more vigorous conditions (P_2S_5 + $NaHCO_3$, dioxane, 90 °C) in 57% yield.

Bis(thienyl)furan **6** was obtained by the acid-catalyzed cyclization of diketone **20** (35%). However, in parallel with the corresponding terthiophene **4**, the yield of **6** was substantially lower than that expected for a nonhindered system.[16,27]

Electrochemistry. The cyclic voltammogram (CV) of terthiophene **3** reveals two oxidation processes corresponding to $E_1^{1/2}$ (+1.23 V) and E_2 (+1. 73 V), with the latter being irreversible. Thiophene derivative **21**,[7] however, displays unusual redox behavior: a broad oxidation peak is observed between +1.30 and +1.70 V, which is accompanied by a distinct reduction peak at +0.81 V. The difference between these two peaks is quite large and does not correlate with the electrochemical behavior of terthiophene **3**. The overall redox properties of **3**, therefore, are probably independent of the central fragment (represented by **21**), and it can be assumed that the first redox process in **3** is due to the terthiophene moiety, while the second, irreversible peak arises from the fused 1,3-dithiole ring. This assumption is supported by the voltammogram of **5**, which shows only one redox wave ($E^{1/2} = +1.13$ V): the absence of a second, irreversible peak (analogous to that of **3**), is probably due to the greater electron-withdrawing ability of the furan ring in

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5 than that of the corresponding thiophene ring in **3**, suppressing the electroactivity of the 1,3-dithiole unit.

The CVs of compounds **4** and **6** are almost identical: an ill-defined oxidation peak is observed between +1.30 and +1.90 V, together with the corresponding reduction waves at +0.85 and + 0.88 V, respectively. Again, the differences between these peak potentials is quite noticeable. The CV of thiophene derivative **22**[30] is also similar, this time with a clear oxidation peak at +1.48 V and a reduction peak at +0.94 V. In predicting the electroactive sites in compounds **4**, **6**, and **22**, one cannot discount the potential electroactivity of the 1,4-dithiino unit; therefore, assignment of the redox processes in **4** and **6** becomes somewhat ambiguous.

Although compounds **21** and **22** cannot be polymerized under electrochemical conditions, derivatives **3**−**6** form the corresponding polymers and copolymers via repetitive scanning in the range from 0.00 to +(1.60−2.00) V. The polymers are deposited at the working (Au) electrode as dark red films and appear to be stable over several scans, however, poly(**5**) permanently loses its electroactivity after cycling below −0.50 V and gives extremely broad oxidation waves above +0.90 V. The polyterthiophene derived from **3** gives an almost indistinguishable oxidation peak, but the reduction peak is quite pronounced and occurs in the region from +0.50 to +0.80 V, depending upon the anodic limit of the CV run. Successive cyclic voltammograms were taken from 0.00 V to maxima ranging from +1.00 to +3.25 V (at 0.25 V intervals). The current of the reduction peak is zero for the run from 0.00 to +1.00 V, but steadily increases to a maximum of +167 μA when the limit of the experiment reaches +2.50 V. Over the next two runs, the peak current for reduction falls steadily (+111 μA at $E_{\max} = +2.75$ V and −83 μA at $E_{\max} = +3.00$ V), and the polymer is finally destroyed at $E_{\max} = +3.25$ V. Despite the indeterminate nature of the oxidation peak in poly(**3**), these results indicate that the polymer is truly being oxidized over a broad range.

Although poly(**6**) is stable to cathodic analysis (up to −2.00 V), its electroactivity is poorly defined. Once more the oxidation process is broad and covers the range from +1.00 to +2.00 V with a more noticeable reduction at +0.44 V. The polyterthiophene prepared from **4**, however, gives a very stable polymer and is the only one in the series showing cathodic redox activity. A clear, almost irreversible oxidation peak is observed with a maximum at +1.79 V, while the polymer is reduced at −0.25 V (Figure 2). The band gap of poly(**4**) can be estimated from the onset potentials of these oxidation/reduction peaks (corresponding to p and n doping), and the resulting value observed (ca. 1.04 eV) is among the lowest reported for any polyterthiophene system.[31]

Conclusions

We have presented the synthesis of a series of novel trimers based on terthiophene and bis(thienyl)furan derivatives (**3**−**6**), functionalized by a 1,3-dithiole unit. These materials are highly suitable precursors toward fascinating electroactive molecular species and conducting polymers incorporating strong redox active units.

We are currently investigating the reactivity and electrochemistry of the thiophene systems presented in this work. Early results have shown that trimers **3**−**6**, and their derivatives, are readily polymerized using chemical and electrochemical techniques.

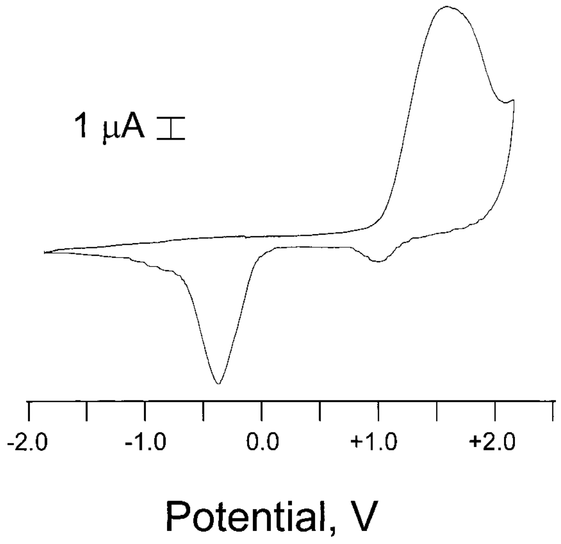
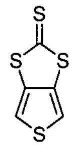


Figure 2. Cyclic Voltammogram of electrodeposited poly(**4**) on a gold working electrode in acetonitrile at a scan rate of 300 mV s^{-1}.

Chart 3



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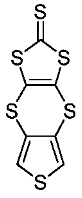

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Experimental Section

General. All melting points are uncorrected. All solvents were dried and purified by standard methods. The reactions were carried out under dry N_2. All reagents were purchased from Aldrich unless referenced.

Cyclic Voltammetry. The measurements for compounds **3**−**6** and their electropolymerization were performed on a BAS CV50W voltammetric analyzer at a scan rate of 200 mVs^{-1}, with *iR* compensation, using anhydrous dichloromethane as the solvent, Ag/AgCl as the reference electrode, and platinum wire and gold disk as the counter and working electrodes, respectively. All solutions were degassed (N_2) and contained the substrate in concentrations ca. 10^{-2} M, together with Bu_4NPF_6 (0.1 M) as the supporting electrolyte. Voltammograms of the polymer (scan rate 300 mVs^{-1}) films were obtained in monomer-free solutions (anhydrous acetonitrile) containing Bu_4NPF_6 (0.1 M) as the supporting electrolyte.

Single-Crystal X-ray Structure Determination. Crystal data for **20**: $C_{15}H_8O_2S_7$, $M = 444.63$, monoclinic, space group $P2_1/n$ (alternative setting of $P2_1/c$, No. 14), $a = 8.773(2)$, $b = 20.104(4)$, $c = 10.983(2)$ Å, $\alpha = 111.08(3)°$, $U = 1807.5(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, μ(Mo−Kα) = 0.878 mm^{-1}, $F(000) = 904$, 7039 reflections collected, θ range 2.03−25.07° (index ranges; $h = -8$ to 9, $k = -22$ to 22 and $l = -12$ to 11), which merged to give 2657 unique reflections ($R_{\text{int}} = 0.0620$) to refine against 217 parameters. Final *R* indices were $wR_2 = 0.1037$ and $R_1 = 0.0482$ [$I > 2\sigma(I)$] and 0.1112 and 0.0802 respectively for all data. Residual electron densities were 0.406 and −0.492 e Å^{-3}.

Data were collected for a crystal of size 0.45 × 0.2 × 0.2 mm on a Delft instruments FAST TV area detector diffractometer at the window of a rotating anode FR591 generator (50

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kV, 55 mA), using a molybdenum target (λ(Mo−Kα) = 0.71069 Å], controlled by a MicroVax 3200 and driven by MADNES[32] software.

The structure was solved by direct methods (SHELXS-97[33]) and then subjected to full-matrix least squares refinement based on F_o^2 (SHELXL−97[33]). Non-hydrogen atoms were refined anisotropically with hydrogens included in idealized positions (C−H distance = 0.97 Å) with isotropic parameters free to refine. The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$. An absorption correction was deemed unnecessary, as the structure had been fully refined to a satisfactory standard.

Additional material, containing atomic coordinates, thermal parameters, bond lengths and angles are available from the Cambridge Crystallographic Data Center.[34]

1,4-Bis(2-thienyl)but-2-yne-1,4-diol (9). A solution of ethylmagnesium bromide was prepared from Mg (1.42 g, 59 mg-atom) and ethyl bromide (4.92 mL, 64 mmol) in THF (50 mL), under standard Grignard conditions. Acetylene gas was purified by passing the reagent through a trap cooled to −70 °C and a second trap with concentrated sulfuric acid; the gas was immediately transferred into the Grignard solution, over 2 h at 50 °C, at a rate of 2−3 L/min on vigorous stirring. After this time, the flow of acetylene was interrupted and a fraction of the solvent (10−15 mL) was removed by distillation at ambient pressure, to ensure the complete decomposition of acetylene monomagnesium bromide. 2-Thiophenecarboxaldehyde (5 mL, 54 mmol) was then added at room temperature and the mixture was allowed to stir overnight. The reaction contents were poured into 20% aqueous NH_4Cl (200 mL) and the product was extracted with ethyl acetate (2 × 30 mL). The organic phase was dried over $MgSO_4$, the solvent was removed in vacuo, and the residue was purified by column chromatography (silica, CH_2Cl_2 with a gradual change to CH_2Cl_2:ethyl acetate = 2:1) to afford **5** (3.30 g, 50%), mp 110−113 °C (lit.[21] mp 116 °C).

1,4-Bis(2-thienyl)but-2-yne-1,4-dione (10). To a solution of **9** (50 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) was added MnO_2 (600 mg). The mixture was stirred for 2 min at room temperature, slowly filtered through a (i.d.) 2 × 5 cm layer of silica and the silica was washed with dichloromethane (30 mL). Evaporation of the solvent under reduced pressure afforded **10** (28 mg, 55%): mp 133−135 °C; ^{1}H NMR (acetone-d_6) δ 8.21 (dd, 2 H, J = 3.9 and 1.1 Hz), 8.17 (dd, 2H, J = 4.9 and 1.3 Hz), 7.36 (dd, 2H, J = 4.9 and 3.9 Hz); ν_{max}/cm^{-1} (KBr) 1628 (C═O); HRMS calcd for $C_{12}H_6O_2S_2$ 245.98093, found 245.98165.

4,5- Bis(2-thienoyl)-1,3-dithiol-2-thione (12). Method A. A solution of **10** (33 mg, 0.13 mmol) and **11**[17] (20 mg, 0.15 mmol) in toluene (1 mL) was heated in a sealed tube under nitrogen at 100 °C for 16 h. The solvent was removed in vacuo and the residue was subjected to flash chromatography (silica, dichloromethane:petroleum ether = 1:1), affording **12** (4 mg, 8%).

Method B. To a solution of **14a** or **14b** (300 mg, 0.83 mmol) in dichloromethane (15 mL) was added MnO_2 (3.0 g). The mixture was stirred at room temperature for 2 min and immediately filtered through a layer of silica (2 (i.d.) × 3 cm), while eluting with CH_2Cl_2 (25 mL). The solvent was removed in vacuo to afford **12** as a yellow tar which gradually solidified on standing (298 mg, 100%): mp 92 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (m, 4H), 7.11 (dd, 2H, J = 5.0 and 3.9 Hz); MS 354 (M^+, 100); ν_{max}/cm^{-1} (KBr) 1636 (C═O). Anal. Calcd for $C_{13}H_6O_2S_5$: C, 44.1; H, 1.7. Found: C, 44.1; H, 1.6.

***dl*- and *meso*-4,5-Bis(2-thienylhydroxymethyl)-1,3-dithiole-2-thione (14a and 14b) and 4-(2-Thienylhydroxymethyl)-1,3-dithiole-2-thione (15).** To a solution of vinylenetrithiocarbonate[22] (2.15 g, 16.1 mmol) in dry THF (60 mL), at −55 °C, was added lithium diisopropylamide (12.4 mL, 1.5 M solution in hexanes, 18.5 mmol); the mixture was stirred under dry nitrogen for 20 min. The reaction was then cooled to −70 °C, 2-thiophenecarboxaldehyde (1.50 mL, 16.1 mmol) was added over 1−2 min, and after stirring for 3 min, the second portion of LDA (11.6 mL, 17.4 mmol) was added. The mixture was stirred at −55 °C for 15 min, after which 2-thiophenecarboxaldehyde (1.50 mL, 16.1 mmol) was added over 1−2 min. The reaction was heated quickly to −30 °C and poured into saturated $NaHCO_3$ solution (200 mL), to which KBr (20 g) was added. The product was extracted with ethyl acetate (1 × 100 mL and 3 × 50 mL), and the combined organic layers were dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography (silica, CH_2Cl_2 with gradual change to CH_2Cl_2:ethyl acetate = 10:1), to afford essentialy pure (NMR evidence) **15**, **14a**, and **14b**, respectively, in order of elution. The analytical samples were obtained by treating the methanolic solutions with charcoal, removing the solvent in vacuo, and reprecipitation of the residues (only for **14a** and **15**) with petroleum ether from dichloromethane.

14a: pale green-yellow crystals (3.88 g, 67%); mp 109−110 °C; ^{1}H NMR (acetone-d_6) δ 7.50 (dd, 2H, J = 5.2 and 1.0 Hz), 7.20 (m, 2H), 7.03 (dd, 2H, J = 5.2 and 3.6 Hz), 6.35 (d, 2H, J = 3.4 Hz), 6.11 (d, 2H, J = 3.8 Hz); ν_{max}/cm^{-1} (KBr) 3330 (O−H, br); MS 358 (M^+, 100). Anal. Calcd for $C_{13}H_{10}O_2S_5$: C, 43.6; H, 2.8. Found: C, 43.3; H, 2.6.

14b: yellow-brown tar (0.85 g, 15%); ^{1}H NMR (acetone-d_6) δ 7.50 (dd, 2H, J = 5.2 and 1.0 Hz), 7.20 (m, 2H), 7.03 (dd, 2H, J = 5.2 and 3.6 Hz), 6.35 (d, 2H, J = 3.4 Hz), 6.11 (d, 2H, J = 3.8 Hz); ν_{max}/cm^{-1} (neat on KBr) 3330 (O−H, br); HRMS calcd for $C_{13}H_{10}O_2S_5$ 357.92844, found 357.92605.

15: pale green-yellow crystals (0.44 g, 12%); mp 67−69 °C; ^{1}H NMR (acetone-d_6) δ 7.47 (dd, 1H, J = 5.1 and 1.2 Hz), 7.33 (d, 1H, J = 1.2 Hz), 7.14 (m, 1H), 7.02 (m, 1H), 6.21 (dd, 1H, J = 4.4 and 0.9 Hz), 6.03 (dd, 1H, J = 4.4 and 0.9 Hz); ν_{max}/cm^{-1} (KBr) 3363 (O−H, br); HRMS calcd for $C_8H_6S_4O$ 245.93015, found 245.93090.

4,6-Bis(2-thienyl)-4,6-dihydrofuro[3,4-*d*]-1,3-dithiole-2-thione (16). Two drops of concentrated HBr were added to a suspension of **14** (400 mg, 1.13 mmol) in dichloromethane (10 mL). After the mixture was stirred at room temperature for 20 min, the product was isolated by column chromatography (silica, CH_2Cl_2:petrol ether = 1:1). The major fraction was treated with cold acetone−water (10:1, 15 mL), and the insoluble yellow precipitate was filtered and washed with a small amount of cold acetone to give **16** (55 mg, 14%); mp 134 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.40 (dd, 2H, J = 5.1 and 1.0 Hz), 7.17 (dd, 2H, J = 3.6 and 1.0 Hz), 7.02 (dd, 2H, J = 5.1 and 3.6 Hz), 6.38 (s, 2H); HRMS calcd for $C_{13}H_8S_5O$ 339.91788, found 339.91634.

4-(2-Thienoyl)-5-(2-thienylhydroxymethyl)-1,3-dithiole-2-thione (17). To a solution of **14** (50 mg) in dichloromethane (2 mL) was added MnO_2 (150 mg), and the mixture was stirred at room temperature for 2 min. The product was purified directly from the reaction mixture by column chromatography, using silica and CH_2Cl_2 as the eluent. The solvent was evaporated under reduced pressure to afford **17** as a yellow tar (25 mg, 50%): ^{1}H NMR ($CDCl_3$) δ 7.91 (dd, 1H, J = 3.9 and 1.0 Hz), 7.81 (dd, 1H, J = 5.0 and 1.0 Hz), 7.31 (dd, 1H, J = 5.1 and 1.2 Hz), 7.19 (dd, 1H, J = 3.9 and 5.0 Hz), 7.14 (m, 1H), 6.98 (dd, 1H, J = 5.1 and 3.6 Hz), 6.41 (d, 1H, J = 0.8 Hz), 3.6 (br, 1H); ν_{max}/cm^{-1} (neat on KBr) 3420 (O−H, br) and 1623 (C═O); HRMS calcd for $C_{13}H_8O_2S_5$ 355.91278, found 355.91103.

***trans*-5,6-Bis(2-thienoyl)-5,6-dihydro-1,4-dithiino[2,3-d]-1,3-dithiole-2-thione (20).** A mixture of **18** (1.0 g, 4.0 mmol), **19** (860 mg, 2.2 mmol) and toluene (100 mL) was stirred at 90−100 °C for 20−30 min. The product was purified from the hot solution by column chromatography (silica, toluene) The volume of the eluate from the second fraction was reduced in vacuo (to 30−40 mL), and left to crystallize affording **20** as red-brown crystals (960 mg, 53%): mp 174−179 °C (with fast decomposition at 182 °C). The remainder of **18** together with some amount of the product was eluted from

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(32) Pflugrath, J. W.; Messerschmidt, A. MADNES, version 11, Sep. 1989; Delft Instruments: Delft, The Netherlands, 1989.

(33) Sheldrick, G. M. SHELXL-97, Program for crystal structure refinement, University of Göttingen, Germany, 1997.

(34) The authors have deposited atomic coordinates for **20** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

the column with toluene:ethyl acetate mixture (10:1) and was used in an analogous synthesis affording additionally 360 mg (20%) of **20** (overall yield 73%): ^{1}H NMR (CDCl$_3$, 50 °C) δ 7.92 (dd, 2H, J = 4.6 and 0.8 Hz), 7.75 (dd, 2H, J = 3.8 and 0.8 Hz), 7.21 (dd, 2H, J = 4.6 and 3.8 Hz), 5.51 (s, 2H); ν_{max}/cm^{-1} (KBr) 1641 (C=O); MS 444 (M$^+$, 100). Anal. Calcd for $C_{15}H_8O_2S_7$: C, 40.5; H, 1.8. Found: C, 40.8; H, 1.9.

4,6-Bis(2-thienyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (3). A mixture of **12** (1.0 g, 2.80 mmol), P_2S_5 (3 g, 13 mmol), and $NaHCO_3$ (1 g) in 1,4-dioxane (20 mL) was stirred under nitrogen while the temperature was increased from 60 to 100 °C over 1 h. The mixture was poured into water (150 mL) (**CAUTION**! H_2S and CO_2 evolution) and the suspension was refluxed for 15−20 min. The crude product was filtered, dried, and purified by column chromatography (silica, toluene). The volume of the eluent was reduced in vacuo to 15−20 mL and petroleum ether (50 mL) was added to afford **3** as an orange powder (0.70 g, 70%): mp 195−196 °C; ^{1}H NMR (CDCl$_3$, 55 °C) δ 7.38 (dd, 2H, J = 5.1 and 1.0 Hz), 7.21 (dd, 2H, J = 3.7 and 1.2 Hz), 7.11 (dd, 2H, J = 5.1 and 3.7 Hz); MS 354 (M$^+$, 100). Anal. Calcd for $C_{13}H_6S_6$: C, 44.0; H, 1.7. Found: C, 43.6; H, 1.8.

5,7-Bis(2-thienyl)thieno[3′,4′:5,6]-1,4-dithiino[2,3-*d*]-1,3-dithiole-2-thione (4). A suspension of **20** (1.0 g, 0.90 mmol), P_2S_5 (4.5 g, 20 mmol), and $NaHCO_3$ (1.5 g) in dry 1,4-dioxane (50 mL) was stirred at 90 °C for 1.5 h on vigorous stirring. After cooling, the mixture was diluted with water (100 mL) (**CAUTION**! H_2S and CO_2 evolution), heated to 50 °C, and filtered. The precipitate was refluxed with water (50 mL) for 10 min, filtered, and dried. The solid was treated with boiling toluene (150 mL), filtered while still hot through a layer of silica (5 (i.d.) × 5 cm) and the silica was washed with hot toluene (150 mL). The volume of the filtrate was reduced to ca. 40 mL in vacuo, affording **4** as yellow-orange needles (567 mg, 57%): mp 230−232 °C; ^{1}H NMR (acetone-d_6, 50 °C) δ 7.67 (dd, 2H, J = 5.2 and 1.0 Hz), 7.43 (dd, 2H, J = 3.6 and 1.0 Hz), 7.21 (dd, 2H, J = 5.2 and 3.6 Hz); HRMS calcd for $C_{15}H_6S_8$ 441.82352, found 441.82323.

4,6-Bis(2-thienyl)furo[3,4-*d*]-1,3-dithiole-2-thione (5). Method A: A mixture of **16** (25 mg, 0.073 mmol), DDQ (23 mg, 0.10 mmol), and toluene (10 mL) was refluxed for 3 h and the volume of the mixture was reduced to 2−3 mL. Flash chromatography (silica, toluene) afforded crude **5** (9 mg, 35%), mp 178−186 °C.

Method B. A solution of **17** (20 mg) and 3 drops of concentrated HBr in acetone (1 mL) was allowed to stand at room temperature for 24 h. Water (0.5 mL) was added and the precipitate was filtered and washed with a small amount of cold acetone: petroleum ether (1:3) mixture to afford **5** as scarlet thin needles (17 mg, 89%): mp 193−195 °C; ^{1}H NMR (CDCl$_3$, 55°C) δ 7.39 (dd, 2H, J = 5.1 and 1.0 Hz), 7.22 (dd, 2H, J = 3.8 and 1.1 Hz), 7.14 (dd, 2H, J = 5.0 and 3.8 Hz); HRMS calcd for $C_{13}H_6OS_5$ 337.90222, found 337.90424.

5,7-Bis(2-thienyl)furo[3′,4′:5,6]-1,4-dithiino[2,3-*d*]-1,3-dithiole-2-thione (6). To a solution of **20** (20 mg) in boiling acetic acid (7 mL) was added concentrated HBr (0.5 mL) and the mixture was allowed to reflux for 3 h. After addition of water (3 mL) the precipitate was filtered, dried, and chromatographed (silica, toluene) to afford **6** as a yellow powder (7 mg, 35%): mp 180−210 °C (dec); ^{1}H NMR (CDCl$_3$, 50 °C) δ 7.42 (m, 4H), 7.14 (dd, 2H, J = 5.1 and 3.7 Hz); MS found 426, required for 425.84637. Anal. Calcd for $C_{15}H_6S_7O$: C, 42.2; H, 1.4. Found: C. 42.3; H, 1.7.

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Supporting Information Available: X-ray data for diketone **20**; ^{1}H NMR spectra for compounds **4**, **5**, **10**, **15**, and **16**; cyclic voltammograms for compounds **3**−**6** and their polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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