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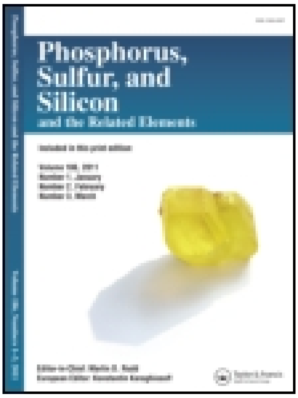

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Synthesis and Properties of Thiophene and Dithiin Functionalized Tetrathiafulvalenes

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SYNTHESIS AND PROPERTIES OF THIOPHENE AND DITHIIN FUNCTIONALIZED TETRATHIAFULVALENES

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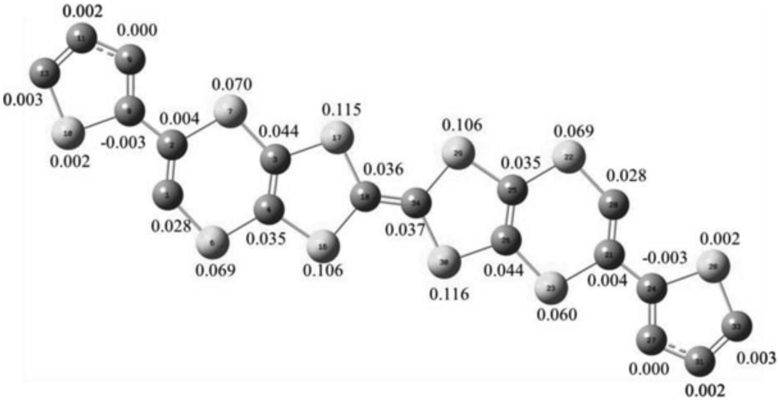
GRAPHICAL ABSTRACT



Abstract *Syntheses of two analogues of tetrathiafulvalene (TTF), fused to 1,4-dithiin and thiophene rings, substituted with thiophene moieties, have been illustrated. The syntheses were accomplished through the reaction of a 1,8-diketone with phosphorus pentasulfide or Lawesson's reagent in boiling dry toluene. Conversion of the thioketones to their the oxo forms with mercury (II) acetate, was followed by self-coupling in freshly distilled boiling triethyl phosphite. Attempts for their electro-polymerizations through the thiophene groups at the peripherals were unsuccessful. Computational chemistry studies revealed that the thiophene groups did not exhibit enough spin densities to perform polymerization.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

Keywords Thiophene; tetrathiafulvalene; 1,8-diketone; phosphorus pentasulfide; Lawesson's reagent

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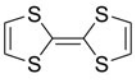
INTRODUCTION

The discovery of metallic conductivity of charge transfer complexes of tetrathiafulvalene (TTF) **1** with tetracyanoquinodimethane (TCNQ) goes back to the end of 1973.[1–5] Since then great efforts have been devoted to improve and understand its properties. Various derivatives, among which the most important one is bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, or ET) **2**, have been synthesized and their charge transfer salts with TCNQ or mono anions have been prepared.[4,6–10] They displayed interesting properties such as superconductivity at very low temperatures, conductivity, and semiconductivity.[2] As generally accepted, crystal structures of the charge-transfer salts and π-extension of the donor molecules are two important parameters for improving the properties of organic materials.[11–15] As TTF is a strong organic donor molecule, various research groups devoted immense interest in synthesizing π-extended TTF derivatives to improve its properties.[16–21]

TTF derivatives, having thiophene groups on the peripherals, are of interest for research groups. Although some studies have appeared in the literature, among which Bryce and co-workers reported first TTF linked to thiophene, [22–27] and our group reported first TTF fused to 1,4-dithiin and thiophene groups, more efforts are required to explore such TTF derivatives.[16,17,20] In the present work, we report syntheses, electronic and electrochemical properties of new TTF derivatives, consisting of fused thiophene and 1,4-dithiin rings, both having thiophene groups.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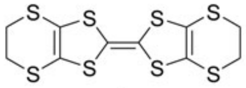
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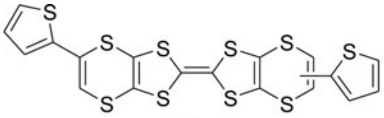
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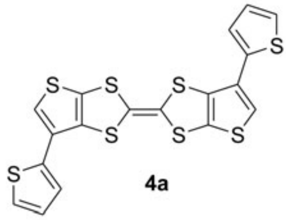
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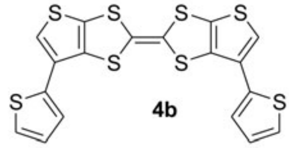
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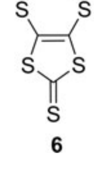
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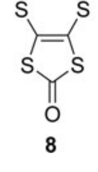
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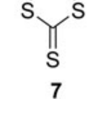
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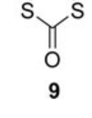
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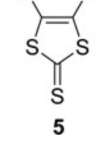
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RESULTS AND DISCUSSION

Syntheses

The syntheses of TTF **3** fused to 1,4-dithiin and TTF **4** fused to thiophene, both having thiophene moieties, were accomplished with self-coupling reactions of 5-(thien-2-yl)-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one **8** and 6-(thien-2-yl)thieno[3,2-*d*][1,3]dithiol-2-one **9** in boiling dry triethyl phosphite, respectively, which were prepared by converting the thione groups of **6** and **7** to oxo groups with mercuric acetate in acetic acid (Scheme 1).[28] The TTF derivatives **3** and **4** were obtained as mixtures of non-separable *cis*- and *trans*-isomers **3** and **4a** and **4b**. The syntheses of the crucial compounds, the thiones, **6** and **7**, exhibiting 1,4-dithiin and thiophene rings, respectively, fused to TTF were conducted by employing the reaction of 1,8-diketone **5** with P_4S_{10}[29] and Lawesson's reagent (LR).[30] The diketone **5** was synthesized by reaction of the readily available zinc-complex **10**[31] with 2-(2-bromoacetyl)thiophene **12**, which was obtained by treatment of 2-acetylthiophene **11** with bromine.[32] It is an established method now that fused 1,4-dithiins and thiophenes can be synthesized in a one pot reaction from 1,8-diketones through their reactions with P_4S_{10} or LR,[33] which then require a separation process of the dithiins and the thiophenes, in general by employing column chromatography. Considering our previous experience,[34] it could be possible to shift the reaction toward the dithiin or the thiophene, by performing the reaction in acid or base. Thus, the ring closure reaction of 1,8-diketone **5** was conducted in neutral, acidic, and basic conditions and the results are summarized in Table 1. The reactions were also conducted in acid and base without P_4S_{10} or LR to demonstrate that these reagents are required for the ring closure. The best overall yield (82%) and selectivity with 1,4-dithiine **6** as major product (75%) and thiophene **7** as minor product (7%) was obtained with P_4S_{10} under basic conditions. Unfortunately, such selectivity could not be achieved with the thiophene **7**. After an intensive study, the best selectivity with the thiophene **7** as major product (55%) and the dithiin **6** as minor product (10%) was obtained with P_4S_{10} under acidic conditions. A possible mechanism for the formation of **7** is given in Scheme 2, which may explain how the rearrangement of **6**, with the help of acid and through the

Table 1 Reaction conditions and yields for the synthesis of **6** and **7**

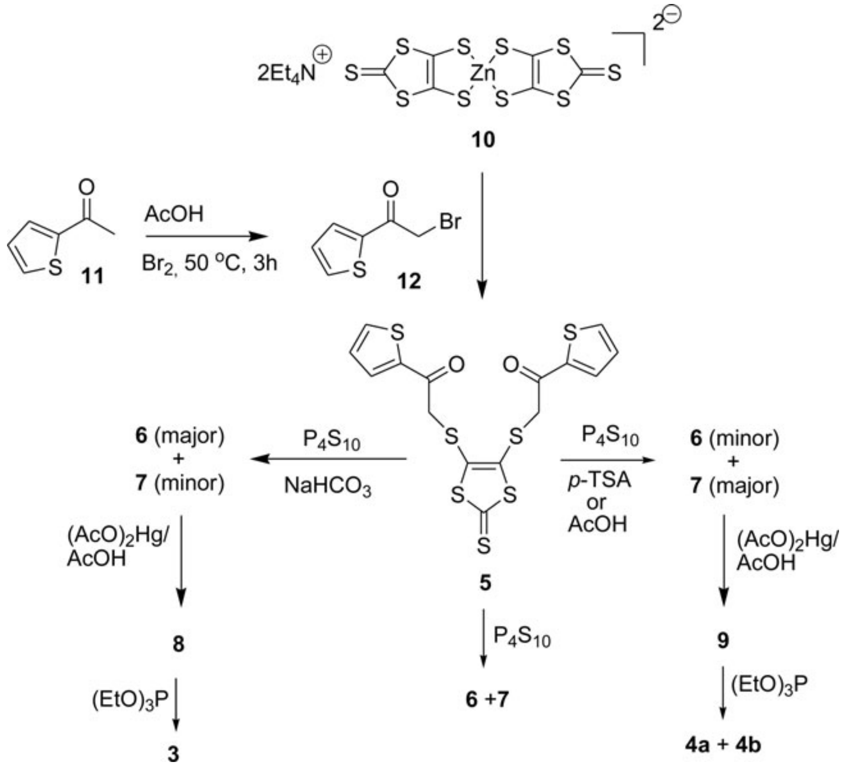
Reagent		Reaction Condition	**6** (%)	**7** (%)	Total Conversion
P_4S_{10}	neutral	A: dry toluene, reflux, 3 h	35	26	61
		B: dry toluene, reflux, 6 h	30	35	65
	acidic	A[a]: dry toluene, reflux, p-TSA, 3 h	45	20	65
		B[a]: dry toluene, reflux, p-TSA, 6 h	42	25	67
		A[b]: dry toluene, reflux, glacial acetic acid, 3 h	10	55	65
		B[b]: dry toluene, reflux, glacial acetic acid, 6 h	15	57	72
	basic	A[c]: dry toluene, reflux, $NaHCO_3$, 3 h	75	5	80
		B[c]: dry toluene, reflux, $NaHCO_3$, 6 h	75	7	82
LR	neutral	dry toluene, reflux, 3 h	25	30	55
	acidic[a]	dry toluene, reflux, p-TSA, 3 h	20	40	60
	basic[c]	toluene, reflux, $NaHCO_3$, 3 h	30	20	50

[a] equal amounts of *p*-TSA (*p*-toluenesulfonic acid) and reagent (P_4S_{10} or LR).

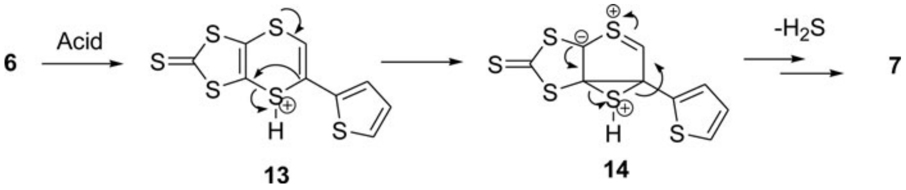
[b] 1 mL of glacial acetic acid.

[c] equal amounts of $NaHCO_3$ and reagent (P_4S_{10} or LR).

intermediates **13** and **14**, to form the thiophene **6** takes place. All efforts using LR did not yield any better result than P_4S_{10}.



Scheme 1



Scheme 2

Cyclic Voltammetry and Polymerization Studies

The electrochemical properties of the compounds **3** and **4** in dichloromethane containing $TBABF_4$ were studied by cyclic voltammetry (CV) (Figure 1). While compound **3** exhibiting a fused 1,4-dithiin ring displayed oxidation at 1.02 V, compound **4** with a fused thiophene ring showed oxidation at 1.41 V, both of which are irreversible steps. As they had thiophene groups at the peripherals, their electro-polymerization was attempted. Unfortunately all our efforts to produce any polymer were not successful. When the CV of

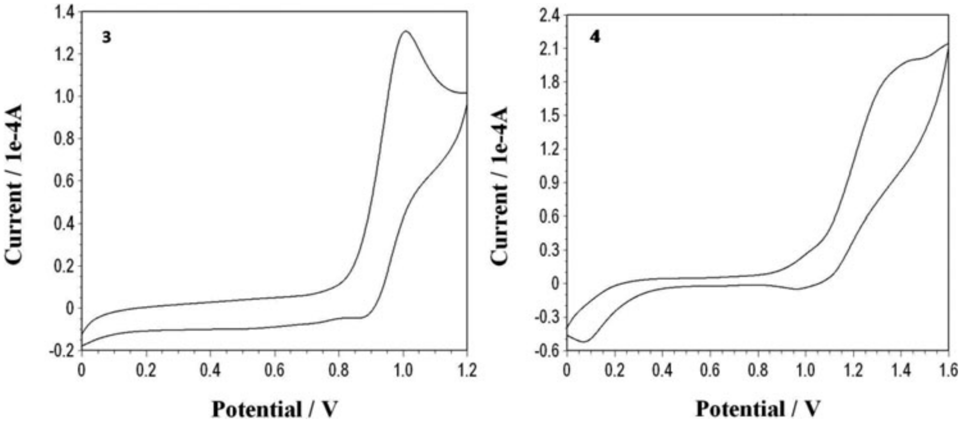


Figure 1 Cyclic voltammogram of **3** and **4** in 0.1 M TBAPF$_6$/DCM with a scan rate of 100 mV/s.

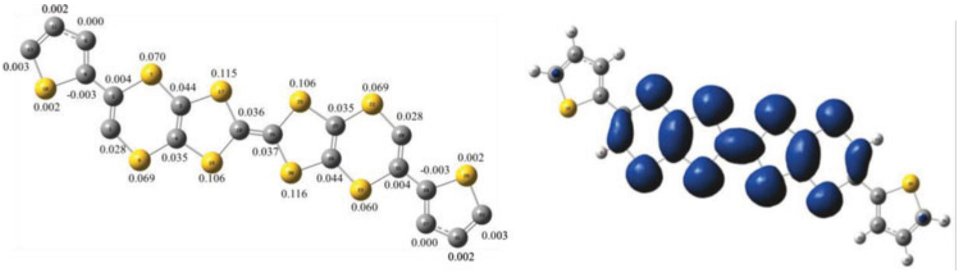


Figure 2 Spin density and SOMO of **3**. (Color figure available online).

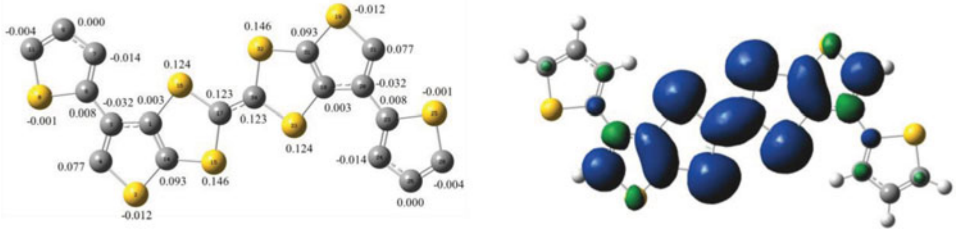


Figure 3 Spin density and SOMO of **4**. (Color figure available online).

4 was examined closely, small oxidation and reduction peaks at 1.0 and 0.9 V, respectively, were observed which could be an indication of the formation of an oligomer. Then, a computational study was initiated to understand if the thiophene rings at the peripherals had enough spin density at the carbon atoms next to the sulfur atoms, where polymerization is expected to take place. Unfortunately, those carbon atoms either exhibited a very small positive spin density such as 0.003 for the compound **3** (Figure 2) or a negative spin density of −0.004 for the compound **4** (Figure 3), which explains why the electro-polymerization did not take place. As the spin density studies are compatible with the experimental results, no further study was performed for electro-polymerization.

CONCLUSIONS

Analogues of TTF exhibiting fused thiophene and 1,4-dithiin rings which, furthermore, exhibit thien-2-yl substituents were synthesized. The synthesis was achieved by cyclization of the 1,8-diketone **5** with both phosphorus pentasulfide and Lawesson's reagent, which resulted in the formation of the two analogues **6** and **7** in one batch. In order to obtain them selectively, neutral, acidic, and basic conditions were applied for the ring closure reaction, which indicated that the best selectivity for the formation of TTF with fused dithiin rings is achieved with phosphorus pentasulfide under basic conditions whereas phosphorus pentasulfide under acidic conditions provided the best selectivity for the formation of the TTF with a fused thiophene ring. Unfortunately, all attempts to electro-polymerize the analogues failed. Spin density calculations indicated that the peripheral thiophene moieties did not exhibit enough spin density at the carbon atoms next to the sulfur atoms, where electro-polymerizations was expected to take place.

EXPERIMENTAL

Chemicals

All chemical reagents were obtained from Sigma-Aldrich-Fluka Co. Ltd. (Steinheim, Germany), unless otherwise stated. Toluene and bromine were obtained from Merck (Darmstadt, Germany).

Instrumentation

A CH-Instruments Model 400A was used as potentiostat for the CV studies. FTIR spectrum was recorded on a Thermo Nicolet 6700 FT-IR-ATR spectrometer. UV measurements were performed on a HITACHI U-0080D instrument. NMR spectra were recorded in $CDCl_3$ on a 400 MHz Bruker DPX system (^1H: 400 MHz, ^{13}C: 100 MHz). HR-Mass spectra were recorded on Bruker Daltonics MicroTof ESI-TOF Mass Spectrometer.

Cyclic Voltammetry (CV)

Cyclovoltamograms were recorded to investigate the electroactivity of **3** and **4**. A CV compartment with Pt-working, Pt-counter, and Ag-wire reference electrodes was employed. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.1 M) in dichloromethane was used as solvent supporting electrolyte. All measurements were recorded at room temperature under nitrogen atmosphere.

Computational Studies

Full geometry optimizations of gas-phase stationary points were performed with a 6–311++G(d,p)[35] basis set, where the functions of atomic orbital descriptors are augmented with polarization and diffuse functions on both heavy atoms and hydrogens, using Becke's three-parameter exchange functional (B3)[36] with the Lee–Yang–Parr correlation functional (LYP)[37] as implemented in Gaussian 03.[38] While the restricted method was applied for closed-shell molecules, unrestricted calculations were performed for radical cations. The minima of calculated structures were verified by analyzing the harmonic vibrational frequencies, using analytical second derivatives with NIMAG = 0. Visualization of spin densities was done with GaussView 5.08[39] using an isocontour value of 0.0004 ebohr^{-3}, respectively.

2-(2-Bromoacetyl)thiophene 12. Ketone **12** was synthesized according to the literature method.[32] Bromine (15.6 g, 97.6 mmol) in 10 mL glacial acetic acid was added drop-wise into the stirred solution of 2-acetylthiophene (11.7 g, 92.8 mmol) in 10 mL glacial acetic acid. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h, and then at 45°C for 2 h. The dark brown mixture was poured into ice water (2 × 300 mL). Water, formed as a separate layer, was decanted and the remaining trace amounts of water and 2-acetylthiophene were removed by vacuum distillation at 40°C at 25 mbar. The oily brown liquid **12** (16.77 g, 88.21%) was checked with the reference, purchased from Aldrich (Steinheim, Germany).

4,5-Bis[2-oxo-2-(thien-2-yl)ethylthio]-1,3-dithiol-2-thione 5. A solution of 2-(2-bromoacetyl)thiophene (5.70 g, 27.8 mmol) **12** in 20 mL acetone was added drop-wise to a stirred solution of zinc complex **10** (5 g, 7.0 mmol) in 30 mL acetone and the reaction mixture was stirred at room temperature for 5 h. After filtration, the solvent was removed by use of a rotary evaporator. The red crude product was extracted with CH_2Cl_2 (2 × 200 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was crystallized from hexane/CH_2Cl_2 (1:1) to yield **5** as a yellow powder (4.99 g, 80.6%), mp. 112–113°C; ^{1}H NMR: δ 7.76 (dd, J = 3.9/1.1 Hz, 2H), 7.74 (dd, J = 4.9/1.1 Hz, 2H), 7.18 (dd, J = 3.9/4.9 Hz, 2H); 4.23 (s, 4H, 2 CH_2); ^{13}C NMR: δ 210.9, 185.7, 142.1, 137.8, 135.7, 133.6, 128.9, 43.3; HRMS (ESI) m/z $C_{15}H_{10}O_2S_7$ (M^++1) requires 446.8787, found 446.8799; IR ν_{max} 1656 (C=O), 1058 (C=S) cm^{-1}.

5-(Thien-2-yl)-[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione 6 and 6-(Thien-2-yl)thieno[3,2-*d*][1,3]dithiole-2-thione 7.

Neutral Reaction: A solution of 0.50 g (1.12 mmol) 1,8-diketone **5** in 20 mL dry toluene was added to a hot (70°C) solution (20 mL) of P_4S_{10} (0.75 g, 1.6 mmol). The reaction mixture was refluxed at 110°C for 3 h. The solvent was removed by blowing nitrogen gas. The remaining crude product was dissolved in CH_2Cl_2 and filtered to remove undissolved solids. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography eluting with hexane/CH_2Cl_2 (5:1) to obtain **6** as first fraction as a brown solid (0.12 g, 35%) and **7** as second fraction as a dark brown solid (0.08 g, 26%). **6**: Mp. 144–145°C; ^{1}H NMR: δ 7.34 (dd, J = 5.1/1.1 Hz, 1H), 7.30 (dd, J = 3.7/1.1 Hz, 1H), 7.1 (dd, J = 5.1/3.7 Hz, 1H), 6.7 (s, 1H); ^{13}C NMR: δ 213.9, 138.5, 135.6, 130.8, 128.8, 128.4, 128.1, 127.5, 116.3; HRMS (ESI) m/z M^++1 calculated for $C_9H_4S_6$ m/z 304.8707, found 304.8710; IR ν_{max} 1062(C=S) cm^{-1}. – **7**: Mp. 134–136°C, ^{1}H NMR:

δ 7.66 (s, 1H), 7.31 (dd, $J = 5.1/1.1$ Hz, 1H), 7.20 (dd, $J = 3.6/1.1$ Hz, 1H), 7.10 (dd, $J = 5.1/3.6$ Hz, 1H); ^{13}C NMR: δ 214.6, 137.2, 135.9, 133.2, 129.6, 128.4, 126.1, 125.2, 124.6; HRMS (ESI) *m/z* M^{+}+1 calculated for $C_9H_4S_5$ *m/z* 272.9002, found 272.8989; IR ν_{max} 1063(C=S) cm^{-1}.

The same procedure was applied for the reactions with LR. Yields are given in Table 1.

Reaction in the Presence of *p*-TSA or Glacial Acetic Acid. To the mixture of *p*-TSA (0.75 g) and P_4S_{10} (0.75 g) dissolved in dry toluene (20 mL) at 70°C, was drop-wise added the 1,8-diketone **5** (0.50 g, 1.10 mmol) dissolved in toluene (20 mL). After employing the same work up and separation techniques described above, **6** and **7** were obtained with 45% and 20% yield, respectively. The same reaction conditions, work up and separation techniques were applied when glacial acetic acid (1 mL) was used in place of *p*-TSA. Yields for each reaction condition are given in Table 1.

Reaction with $NaHCO_3$. The same reaction conditions and separation techniques as described for the reaction with *p*-TSA were employed. The yields are given in Table 1.

5-(Thien-2-yl)-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one, 8. Mercuric acetate (1.57 g, 4.95 mmol) was added to a solution of **6** (0.5 g, 1.65 mmol) in $CHCl_3$/glacial acetic acid (3:1, 30 mL). The reaction was stirred at room temperature for 2 h. It was filtrated through celite and the filtrate was extracted with $NaHCO_3$ solution (2 × 20 mL) and water (2 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduce pressure to yield **8** as a light yellow powder (0.31 g, 65%). Mp. 138–139°C; ^{1}H NMR: δ 7.32 (m, 2H), 7.02 (dd, $J = 5.04/3.8$ Hz, 1H), 6.70 (s, 1H); ^{13}C NMR: δ 192.2, 138.8, 135.2, 128.3, 127.9, 127.5, 121.3, 119.2, 116.2; HRMS (ESI) *m/z* $C_9H_4OS_5$ (M^{+}+1) requires 288.8942, found 288.8938; IR ν_{max} 1682 (C=O) cm^{-1}.

6-(Thien-2-yl)thieno[3,2-*d*][1,3]dithiol-2-one, 9. The reaction conditions and separation techniques described above were employed to obtain **9** as a yellow powder (0.36 g, 85%). Mp. 92–94°C; ^{1}H NMR: δ 7.52 (s, 1H), δ 7.28 (dd, $J = 3.6$ / 1.0 Hz, 1H), 7.17 (dd, $J = 3.6/1.1$ Hz, 1H), 7.14 (s, 1H), 7.04 (dd, $J = 5.1/3.6$ Hz, 1H); ^{13}C NMR: δ 193.6, 139.3, 135.7, 128.4, 127.9, 125.9, 125.1, 123.9, 117.7; HRMS (ESI) *m/z* $C_9H_4OS_4$ (M^{+}+1) requires 256.9221, found 256.9218; IR ν_{max} 1662 cm^{-1}.

2,2′-Bi{5-(thien-2-yl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene} 3. Compound **8** (0.2 g, 0.7 mmol) in freshly distilled $(EtO)_3P$ (15 mL) was heated at 110°C under N_2 for 3 h. $(EtO)_3P$ was distilled off under reduced pressure to obtain **3** as a brown powder (0.3 g, 80%). Mp. 168–170°C, ^{1}H NMR: δ 7.29 (dd, $J = 5.1/1.0$ Hz, 2H), 7.27 (dd, $J = 4.7/1.1$, Hz, 2H), 7.01 (dd, $J = 5.1/3.8$ Hz, 2H), 6.6 (s, 2H); ^{13}C NMR: δ 140.3, 137.3, 135.6, 130.4, 129.5, 128.4, 128.1, 128.0, 123.9; HRMS (ESI) *m/z* $C_{18}H_8S_{10}$ (M^{+}+1) requires 544.7854, found 544.7906.

(*E*)- and (*Z*)-2,2′-Bi{6-(thien-2-yl)thieno[2,3-*d*][1,3]dithiol-2-ylidene} (4a + 4b). The same reaction conditions and separation techniques were employed to obtain the mixture of **4a** and **4b** as a brown powder (0.21 g, 75%). Mp. 155–159°C; ^{1}H NMR: δ 7.53 (s, 4H), 7.32 (dd, $J = 5.1/1.0$ Hz, 4H), 7.23 (dd, $J = 3.6/1.0$, 4H), 7.10 (dd, $J = 5.1/3.6$ Hz, 4H), ^{13}C NMR: δ 139.3, 135.7, 128.9, 128.5, 128.3, 125.1, 123.9, 121.3, 117.7; EIMS *m/z* 479.84 (M^{+}+1). Anal. Calcd. for $C_{18}H_8S_8$: C 44.97, H 1.68. Found C 44.20, H 1.72.

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