Synthesis of 2,3-Dihydrothieno[2,3-*b*]-1,4-dithiine, 2,3-Dihydrothieno-[3,2-*b*]-1,4-oxathiine, 2,3-Dihydrothieno[2,3-*b*]-1,4-oxathiine and Their Transformation into Corresponding End-Capped Oligomers[1]

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Abstract: Three new heterocyclic parent compounds, 2,3-dihydrothieno[2,3-*b*][1,4]dithiine (TDT), 2,3-dihydrothieno[3,2-*b*][1,4]oxathiine (TOT), and 2,3-dihydrothieno[2,3-*b*][1,4]oxathiine, have been synthesized by acid-catalyzed transformations starting from 3-methoxythiophene. Two of the new compounds have been transformed to the corresponding end-capped dimeric, trimeric and tetrameric oligothiophenes. These oligomers show very stable cationic and dicationic states as judged by cyclic voltammetry, and their UV-Vis spectra are considerably red-shifted compared to previously synthesized end-capped oligomers.

Key words: ring-closure, tandem reactions, oligothiophenes, Suzuki coupling

Introduction

During the last decade, organic compounds have contributed significantly to the progress towards new lightweight, high-performing materials in several electronic applications, such as light-emitting diodes, superconductors and thin-film transistors.[5] Polymeric materials have been in focus of much research towards technological applications, while molecular materials have dominated the search for high conductivity and superconductivity. Polymers hold several advantages in processing and synthesis, but oligomers have become increasingly popular, giving well-defined materials with many of the classical polymers' advantages. In the sense of being model compounds, oligomers offer the possibility to study the 'true' behaviour of longer polymers.[6] The oligomers can often be strictly purified, to give well-defined compounds, whereas the dispersity and defect distribution for the commonly used conjugated polymers varies significantly from batch to batch. Optical and electronic properties vary only slightly with chain length above a certain critical number of repeating units. In the field of oligomer research, oligothiophenes **1** (Figure 1) have attracted a lot of interest, since it has been possible to synthesize and characterize a large number of substituted and unsubstituted oligomers. Substitution may be chosen to enhance solubility or affect electronic properties. If substituents are placed at the terminal positions (as in, e.g. **2**), the result is a more stable oligomer, resistant to further polymerization.[7]

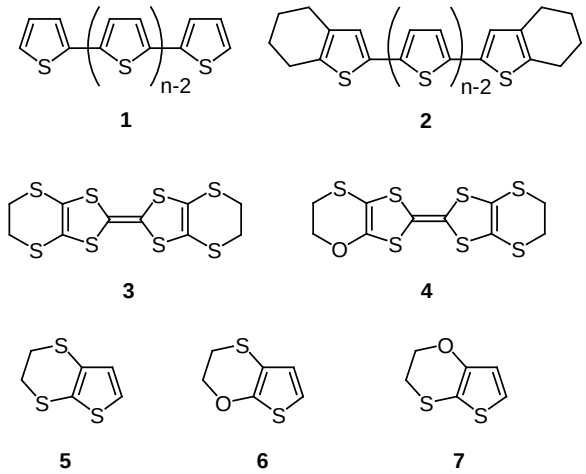

Figure 1 The structures of compounds **1**–**7**

The blocking terminal substituents can also play a more active role in building up the electroactive structure. Most organic superconductors are based on the π-donor BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene, **3**], and the sulfur atoms in the fused dihydrodithiine ring in **3** are responsible for much of the interstack connections leading to a two-dimensional material.[8] We therefore decided that the dihydrodithiino-fused thiophene **5** (TDT), would be a valuable building block for both condensed π-donors and for 'end-capped' oligothiophenes. We were also interested in applying our experience of thioxane-condensed donor molecules like **4**,[9] to investigate compounds like 2,3-dihydrothieno[2,3-*b*][1,4]oxathiine (**6**) and 2,3-dihydrothieno[3,2-*b*][1,4]oxathiine (**7**, TOT)[10] (Figure 1). Using these parent compounds of surprisingly rare heterocyclic systems,[11] we should be able to synthesize interesting new electroactive systems. Furthermore, electroactive terminal groups should also pave the way for alternative conduction pathways, which in turn could make these oligomers more attractive for high-mobility applications such as field-effect transistors.

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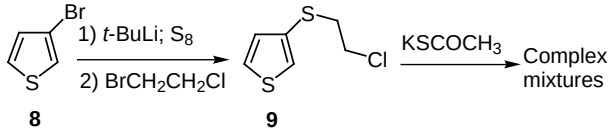
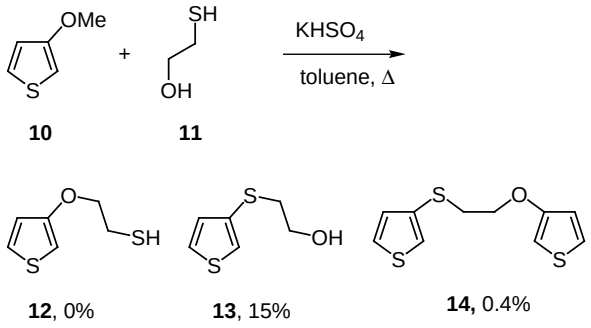
Results and Discussion

Our original approach to synthesize TDT (**5**) was to react 3-bromothiophene (**8**) with *tert*-butyllitihum and then sulfur, and treat the resulting sulfide anion with 1-bromo-2-chloroethane to give the chloroethylthio-substituted thiophene **9**. Reaction with potassium thioacetate followed by hydrolysis was anticipated to give the thiol, which then could be cyclized to **5** after umpolung with sulfuryl chloride. However, when **9** was treated with thioacetate, a mixture was formed, containing at least four different inseparable thiophene products (Scheme 1).



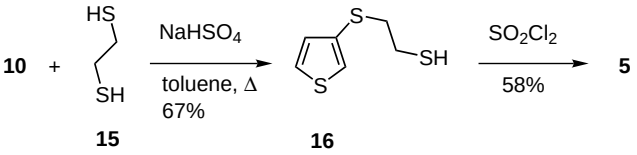
Scheme 1

An important method for the synthesis of 3-alkoxy and 3-alkylthio thiophenes is the acid-catalyzed transetherification[12] of 3-methoxythiophene (**10**).[13] This should allow for a very simple synthesis of **5**. Transetherification of 3-methoxythiophene (**10**) with mercaptoethanol (**11**) has been reported to give **12**,[12b] that would probably provide a fast route to the interesting and unknown parent compound **7**. In practice, however, only the thioether **13** and small amounts of **14** were isolated[14] (cf. Scheme 2). Moreover, the mass balance indicated only 23% conversion after 3 hours. When the reaction was performed without solvent at 90 °C, with excess mercaptoethanol and a catalytic amount of *p*-toluenesulfonic acid, **13** was formed selectively and rapidly. Higher reaction temperatures resulted in extensive decomposition of starting materials.



Scheme 2

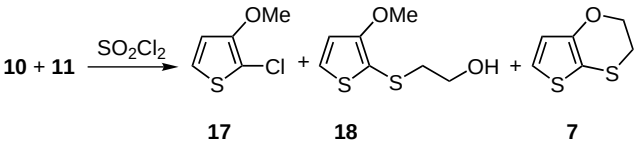
In order to prepare **5**, we treated **10** with an excess of ethanedithiol (**15**), and we could easily isolate **16** in 67% yield after short-path distillation (see Scheme 3). Addition of sulfuryl chloride to a dilute solution of **16** in diethyl ether effected ring-closure to the target molecule 2,3-dihydrothieno[2,3-*b*][1,4]dithiine (**5**) in up to 58% yield after distillation.



Scheme 3

The reaction mechanism for the transetherification probably involves rapid and reversible protonation at C-2,[15] nucleophilic attack at C-3, followed by elimination of methanol.

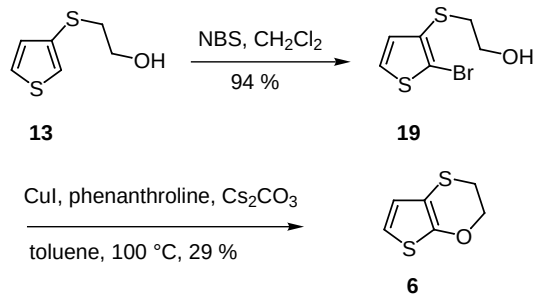
We envisaged that an analogous ring-closure of compound **18** would provide an efficient route to TOT (**7**). In order to prepare **18**, we treated a solution of 3-methoxythiophene (**10**) and mercaptoethanol (**11**) in dichloromethane with sulfuryl chloride. To our surprise, the product mixture contained not only the expected product **18** and the chlorinated by-product **17**, but also the target molecule **7** (Scheme 4).



Scheme 4

By adjusting the conditions, we were able to suppress chlorination and achieve a good yield (61%) of the ring-closed product TOT (**7**) by this tandem reaction. Presumably, **7** can be formed directly via ring-closure of the initially formed sigma-complex from the reaction of **10** with 2-hydroxyethylsulfenyl chloride. However, equilibration between different tautomers of protonated **18** is likely to be faster than the cyclization.

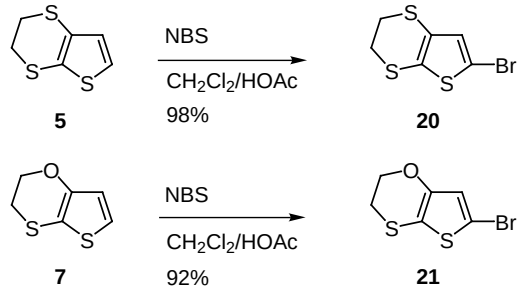
In order to support further the structure proposed for TOT (**7**), we decided to prepare the regioisomer **6**. Compound **13** was regioselectively brominated using NBS, and ring-closure was done by Buchwald's alkoxylation procedure[16] (Scheme 5).



Scheme 5

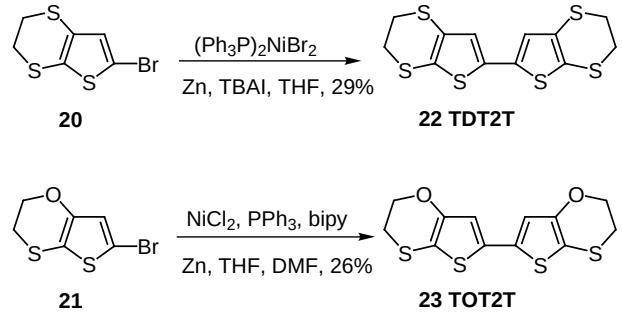
Oligomer Synthesis

Having the building blocks TDT (**5**) and TOT (**7**) in hand, we started to transmogrify these to the corresponding oligomeric electroactive systems. Monobromination of TDT (**5**) occurred smoothly with NBS in a dichloromethane–acetic acid mixture, giving **20** in excellent yield. Applying the same procedure on TOT (**7**) produced the brominated dihydrothioxino analogue **21** (Scheme 6). Both **20** and **21** showed limited stability in air and light. It is therefore best to prepare these immediately prior to their further conversions.



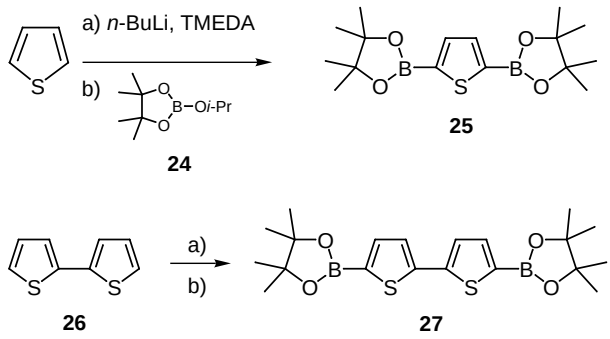
Scheme 6

The first obvious oligomer is of course the dimer, and dimerization of a haloaromatic can be achieved by several methods. Oxidative coupling of the lithiated aromatic is a versatile method which has been used extensively.[17] However, treatment of **20** with *n*-butyllithium and then copper(II) chloride resulted only in reduction of **20**, giving **5** as the sole product. This demonstrates the low stability of metalated, chalcogen-rich aromatics, in accord with previous observations in our group. In the same way, direct lithiation of **5** with LDA failed, probably due to the relative inertness of **5** under these conditions. We found instead that the nickel-catalyzed method of Iyoda[18] gave a modest yield of dimer **22** (TDT2T) from **20** (Scheme 7). Reduction to the thiophene **5** is the major side reaction. Preparation of **23** turned out to be a more difficult task. Analogously with the dithia analogue, lithiation of **2** failed both by direct or halogen–metal exchange methods. A series of procedures for homocoupling were tested and best yields of the dimer **23** (TOT2T) were obtained with a bipyridine-ligated nickel catalyst (Scheme 7). This method gave only a few percent of reduced material.

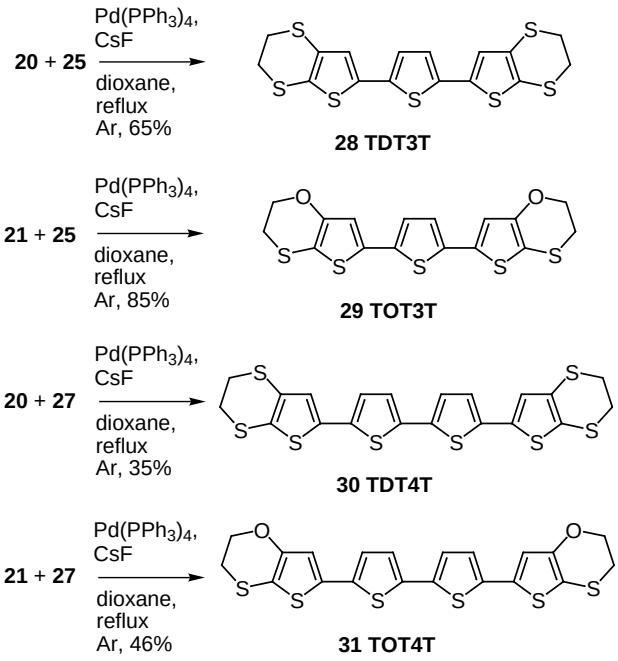


Scheme 7

Inspired by the results of Cava et al.,[19] we decided to apply the Suzuki methodology for the higher oligomers. The original Suzuki–Gronowitz procedure[20] with sodium carbonate in dimethoxyethane–water gave inseparable mixtures of different oligomers. Change of solvent and base/activator proved to be essential.[21] Thus, the bis(pinacolboronic ester)-substituted thiophene **25**[19] (Scheme 8) was reacted with **20** in refluxing dioxane with cesium fluoride, to give the bis(ethylenedithio) end-capped trimer **28** in an useful yield (Scheme 9). This procedure was also successful when **25** reacted with **21** to yield the dihydrothioxino end-capped trimer **29** in good yield.



Scheme 8



Scheme 9

To reach beyond trimers, we decided to synthesize the bithiophene homologue of **25** by direct dilithiation of bithiophene **26** with *n*-butyllithium/TMEDA and subsequent reaction with the mixed boronic ester **24**. This procedure gave the bifunctional compound **27**[22] in good yield (Scheme 8).

The tetramers were now readily obtained with the analogous CsF/Pd(0) procedure, i.e. **20** and **27** gave the dihy-

drodithiino end-capped tetramer **30**. Reaction between **21** and **27** produced the dihydrothioxino end-capped tetramer **31** in modest, but still useful yield (Scheme 9). The tetramers are highly insoluble materials, which simplifies their isolation.

UV-Vis Spectroscopy

The UV-Vis spectrum was recorded for each oligomer in chloroform (see Table 1). The spectra are more or less identical for the ethylenedithio and thioxano oligomer series. This clearly illustrates that the two different end-capping moieties have the same influence on the electronic spectra. The spectra show a considerable red-shift induced by the heterofusion when compared to end-capped oligomers, ECnT (**2**), synthesized by Bäuerle et al.[7] Compared to the ECnT series, the values are red-shifted for the trimer and tetramer by 36 nm and 17 nm respectively. It seems that the heterobridge induces a red-shift in the UV-Vis spectrum, which is equal to a one-unit extension of the oligomer number.

Table 1 UV/Vis Data for Oligomers

Compound	λ_{max} (nm)	λ_{max} (eV)
EC3T[a]	375	3.31
EC4T[a]	411	3.02
EC5T[a]	432	2.87
TDT2T (**22**)	380	3.27
TDT3T (**28**)	411	3.02
TDT4T (**30**)	428	2.90
TOT2T (**23**)	374	3.32
TOT3T (**29**)	412	3.02
TOT4T (**31**)	431	2.88

[a] Literature values for oligomers synthesized by Bäuerle et al.[7]

Cyclic Voltammetry

The cyclic voltammetric behaviors of the new oligomers were recorded in dichloromethane (Table 2). The different influences of the two fused six-membered heterocycles are clear. Thioxano condensation lowers the first oxidation potential by 60–100 mV compared to the dihydrodithiino series. This clearly shows the superior π-donating ability of oxygen. The values for Bäuerle's oligomers fall in between these values. All oligomers synthesized in this work nicely show reversible first and second oxidation half-waves, except TOT2T (**23**), for which we were unable to record a reversible redox pair at normal sweep rates. In the second oxidation, our two series show their ability to host charge and reduce the on-site coulombic repulsion; the difference between the two oxidation values (ΔE) is considerably lower (150–200 mV) than for the comparison series. However, oligomers end-capped with only α-methylsulfanyl group show an even lower ΔE, the trimer coming down to only 130 mV.[23]

Table 2 Cyclic Voltammetric Data for Oligomers[a]

Compound	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)	ΔE (V)
EC3T[b]	0.38	0.79 (irr.)	0.41
EC4T[b]	0.32	0.66	0.34
EC5T[b]	0.26	0.55	0.29
TDT2T (**22**)	0.42	0.79	0.37
TDT3T (**28**)	0.40	0.60	0.20
TDT4T (**30**)	0.35	0.51	0.16
TOT2T (**23**)	0.32	0.74[c]	0.42
TOT3T (**29**)	0.32	0.56	0.24
TOT4T (**31**)	0.29	0.43	0.14

[a] Measured at 30 °C in CH_2Cl_2, 0.15 M Bu_4NPF_6 with 100 mV/s scan rate. Values are given vs. the ferrocene-ferrocenium couple.
[b] Literature values for oligomers synthesized by Bäuerle et al.[7]
[c] The second half-potential for TOT2T was recorded at 7.0 V/s.

Conclusion

We have synthesized three new parent heterocyclic compounds **5**, **6** and **7**. The compounds **5** and **7** have been used as building blocks for the synthesis of end-capped bi–, ter and quaterthiophenes. The synthesis clearly shows the versatility and usefulness of 3-methoxythiophene as a starting material for electronic materials.

NMR spectra were recorded on a Bruker AM 400 (400 MHz) or Bruker AMX 500 (500 MHz) spectrometer. Mass spectra were recorded on a Finnigan SSQ 7000 spectrometer. Elemental analyses were performed by Analytische Laboratorien GmbH, Lindlar, Germany. High-Resolution MS was performed at the Department of Organic Chemistry, Stockholm University and at the Department of Bioorganic chemistry, Lund University. THF was distilled from sodium/benzophenone, all other solvents were distilled or HPLC grade. $MgSO_4$ was used as drying agent during work-up in all reactions. Starting materials were commercially available and used as received. Melting points were measured on a Bibby Sterilin Stuart SMP3 melting point apparatus, or by DSC on a Mettler-Toledo DSC820, 1st heating, 10 °C/min, N_2 (80 mL/min), 150–350 °C. Cyclic voltammetry was performed at 25 °C in CH_2Cl_2 at 100 mV/s with Bu_4NPF_6 (0.15 M) as electrolyte and measured vs. a SCE reference electrode. The halfwave potential for the ferrocene/ferrocenium couple was 0.42 V in our system.

2-(3-Thienylsulfanyl)ethanol (13) and 3-[3-Thienoxyethylsulfanyl)thiophene (14)
(Unoptimized Procedure, cf. Scheme 2)

3-Methoxythiophene (**10**; 1.14 g, 9.99 mmol), mercaptoethanol (**11**; 964 mg, 12.3 mmol) and oven-dried $KHSO_4$ (182 mg, 1.34 mmol) were heated in refluxing toluene (25 mL) for 3 h. After cooling to r.t., the mixture was filtered through glass wool and concentrated to a yellow oil (362 mg, 23% of theory). Chromatography on silica

gel, eluting with toluene, CH_2Cl_2 and then 30% MeOH in CH_2Cl_2 gave **13** (242 mg, 15%) and **14** (10 mg) as yellow oils.

13

^{1}H NMR ($CDCl_3$): δ = 7.34 (dd, J_1 = 3.0 Hz, J_2 = 5.0 Hz, 1 H), 7.26 (dd, J_1 = 1.3 Hz, J_2 = 3.0 Hz, 1 H), 7.06 (dd, J_1 = 1.3 Hz, J_2 = 5.0 Hz, 1 H), 3.72 (dt, $J_1 = J_2$ = 6.0 Hz, 2 H), 3.02 (t, J = 6.0 Hz, 2 H), 2.03 (t, J = 6.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 130.63, 130.59, 127.0, 125.6, 60.8, 39.0.

MS (EI): *m*/*z* (%) = 160 (48, M^+), 116 (100).

HRMS: *m*/*z* calcd for $C_6H_8OS_2$: 160.0017; found: 160.0024.

14

^{1}H NMR ($CDCl_3$): δ = 7.34 (dd, J_1 = 4.9 Hz, J_2 = 3.1 Hz, 1 H), 7.26 (dd, J_1 = 3.1 Hz, J_2 = 1.2 Hz, 1 H), 7.17 (dd, J_1 = 5.3 Hz, J_2 = 3.1 Hz, 1 H), 7.08 (dd, J_1 = 4.90 Hz, J_2 = 1.2 Hz, 1 H), 6.73 (dd, J_1 = 5.3 Hz, J_2 = 1.5 Hz, 1 H), 6.19 (dd, J_1 = 3.1 Hz, J_2 = 1.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 157.2, 130.7, 130.3, 126.5, 125.3, 124.9, 119.5, 97.8, 68.8, 34.3.

MS (EI): *m*/*z* (%) = 242 (8, M^+), 143 (100).

2-(3-Thienylsulfanyl)ethanol (13)

3-Methoxythiophene (**10**; 10.00 g, 87.59 mmol), mercaptoethanol (**11**; 12.38 g, 158.5 mmol, 1.81 equiv), and *p*-TsOH·H_2O (53 mg, 0.28 mmol) were heated at 90 °C under a stream of N_2. After 3 h, NMR indicated 90% conversion. The product was diluted with toluene, and distilled from K_2CO_3 at 15 mmHg, collecting the fraction between 100–165 °C. The product was obtained as a yellowish oil (7.451 g, 53%); analyses as above.

2-[3-(2-Bromothienyl)sulfanyl]ethanol (19)

2-(3-Thienylsulfanyl)ethanol (**13**; 3.185 g, 19.87 mmol) was dissolved in CH_2Cl_2 (120 mL) and cooled in an ice–water bath for 30 min. NBS (3.926 g, 22.16 mmol, 1.12 equiv) was added in portions over 5 min. The mixture was left with stirring for 90 min, and the organic layer was washed with 10% aq $Na_2S_2O_3$, aq 2 M NaOH and H_2O, dried ($MgSO_4$), and concentrated to give **19** as a yellowish oil (4.471 g, 94% of theory), sufficiently pure for further transformations.

^{1}H NMR ($CDCl_3$): δ = 7.27 (d, J = 5.7 Hz, 1 H), 6.96 (d, J = 5.7 Hz, 1 H), 3.65 (t, J = 5.9 Hz, 2 H), 2.99 (t, J = 5.9 Hz, 2 H), 2.32 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 131.6, 131.3, 126.8, 116.7, 60.8, 39.0.

MS (EI): *m*/*z* (%) = 237.9 (44, M^+), 114.9 (46), 69.0 (52), 45.0 (100).

HRMS: *m*/*z* calcd for $C_6H_7BrOS_2$: 237.9122; found: 237.9129.

2,3-Dihydrothieno[2,3-*b*][1,4]oxathiine (6)

2-[3-(2-Bromothienyl)sulfanyl]ethanol (**19**; 1.405 g, 5.875 mmol), Cs_2CO_3 (3.860 g, 11.85 mmol, 2.02 equiv), CuI (122 mg, 0.641 mmol, 11%), 1,10-phenanthroline monohydrate (238 mg, 1.20 mmol, 20%) and toluene (15 mL) were charged in a vial, which was sealed and heated at 100 °C for 68 h, allowed to cool to r.t. and left at r.t. for 24 h. The mixture was diluted with Et_2O and filtered through a short plug of silica gel to yield crude **6** as a yellow oil (854 mg). Chromatography on silica gel, with gradient elution going from hexane to 20% EtOAc in hexane gave **6** as a yellow oil (263 mg, 29%).

^{1}H NMR ($CDCl_3$): δ = 6.53 (d, J = 6.0 Hz, 1 H), 6.50 (d, J = 6.0 Hz, 1 H), 4.48 (m, 2 H), 3.12 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 151.3, 124.5, 110.8, 104.2, 68.6, 25.3.

MS (EI): *m*/*z* (%) = 158 (79), 130 (21), 102 (100).

HRMS: *m*/*z* calcd for $C_6H_6OS_2$: 157.9860; found: 157.9860.

2-(3-Thienylsulfanyl)ethanethiol (16)

3-Methoxythiophene (**10**; 15.00 g, 0.131 mol) and ethanedithiol (**15**; 32 mL, 0.38 mol) in toluene (300 mL) was heated to 110 °C. $NaHSO_4$ (2 g) was added in 4 portions during 2 h. The MeOH–toluene azeotrope was continuously collected and when no more azeotrope could be observed, the temperature was raised and the toluene was distilled off. Distillation under reduced pressure (12 mm Hg) removed the ethanedithiol (31–35 °C) and 3-methoxythiophene (38–40 °C). Further distillation under reduced pressure at 90–110 °C/10^{-2} mbar to a trap cooled by dry ice gave 15.55 g of pure **16** (67%).

^{1}H NMR ($CDCl_3$): δ = 7.32 (dd, J_1 = 4.9 Hz, J_2 = 3.1 Hz, 1 H), 7.23 (dd, J_1 = 3.1, J_2 = 1.2 Hz, 1 H), 7.04 (dd, J_1 = 4.9 Hz, J_2 = 1.2 Hz, 1 H), 3.01 (m, 2 H), 2.69 (m, 2 H), 1.70 (t, 1 H).

^{13}C NMR ($CDCl_3$): δ = 130.4, 130.3, 126.6, 125.6, 39.5, 24.5.

MS (EI): *m*/*z* (%) = 176 (44, M^+), 116 (100).

Anal. Calcd for $C_6H_8S_3$: C, 40.87; H, 4.57; S, 54.55. Found: C, 41.01; H, 4.55.

2,3-Dihydrothieno[2,3-*b*][1,4]dithiine (TDT, 5)

To a solution of 2-(3-thienylsulfanyl)ethanethiol (**16**; 18.14 g, 0.103 mol) in Et_2O (1.5 L) under argon, was added SO_2Cl_2 (14.02 g, 0.104 mol) in one portion. After 3 h at r.t., the mixture was washed several times with H_2O and aq 2 M NaOH, dried and concentrated to yield 17.64 g of crude product. The product was distilled at 85–90 °C under reduced pressure ($5\cdot10^{-3}$ mbar) to a flask cooled with dry ice; yield: 10.39 g (58%).

^{1}H NMR ($CDCl_3$): δ = 7.09 (d, J = 5.2 Hz, 1 H), 6.73 (d, J = 5.2 Hz, 1 H), 3.35–3.32 (m, 2 H), 3.30–3.27 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 127.1, 123.2, 121.8, 121.6, 28.8, 28.0.

MS (EI): *m*/*z* (%) = 174 (100, M^+), 70 (32), 146 (59).

Anal. Calcd for $C_6H_6S_3$: C, 41.35; H, 3.47; S, 55.18. Found: C, 41.50; H, 3.49.

6-Bromo-2,3-dihydrothieno[2,3-*b*][1,4]dithiine (20); Typical Procedure

2,3-Dihydrothieno[2,3-*b*][1,4]dithiine (**5**; 10.39 g, 59.6 mmol) was dissolved in a mixture of AcOH (100 mL) and CH_2Cl_2 (50 mL). The reaction mixture was cooled to 0 °C, and NBS (10.61 g, 59.6 mmol) was added in portions during 30 min. After 3 h at r.t., the solution was diluted with CH_2Cl_2 (200 mL) and washed with 10% aq $Na_2S_2O_3$ and H_2O. The aqueous phases were back-extracted with CH_2Cl_2, and the combined organic fractions were washed with 2 M NaOH and H_2O, dried and concentrated to yield 14.76 g (98%) of crude **20**. The purity of the product was sufficient for further transformations.

^{1}H NMR ($CDCl_3$): δ = 6.68 (s, 1 H), 3.33–3.30 (m, 2 H), 3.27–3.24 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 129.6, 124.4, 123.1, 107.9, 28.9, 28.4.

HRMS: *m*/*z* calcd for $C_6H_5BrS_3$: 251.8737; found: 251.8733.

2,3-Dihydrothieno[3,2-*b*][1,4]oxathiine (TOT, 7)

Mercaptoethanol (**11**; 6.85 g, 88 mmol) was dissolved in CH_2Cl_2 (500 mL) under argon, and cooled to 0 °C. The argon source was removed, the system closed and SO_2Cl_2 (11.82 g, 88 mmol) was added. After 15 min, 3-methoxythiophene (**10**; 10.00 g, 88 mmol) was added. The cooling bath was removed and the reaction mixture was left with stirring overnight. After cautiously opening the system, aq 2 M NaOH was added to the reaction mixture. The organic layer was washed several times with aq 2 M NaOH and H_2O. After drying and filtration through neutral Al_2O_3, the solution was concentrated to yield an oil. After a quick distillation from Na_2CO_3 ($8\cdot10^{-3}$ mbar,

75–80 °C), the oil was purified by chromatography on silica gel using 10% toluene in hexanes as eluent; yield: 8.48 g (61%).

^{1}H NMR ($CDCl_3$): δ = 6.94 (d, *J* = 5.5 Hz, 1 H), 6.63 (d, *J* = 5.5 Hz, 1 H), 4.45 (m, 2 H), 3.10 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 148.3, 119.81, 119.78, 103.6, 66.4, 25.8.

^{13}C NMR (DMSO-d_6): δ = 148.0, 120.4, 119.8, 102.7, 66.0, 25.0.

MS (EI): *m*/*z* (%) = 158 (100, M^+), 130 (42), 102 (49).

Anal. Calcd for $C_6H_6OS_2$: C, 45.54; H, 3.82. Found: C, 45.44; H, 3.76.

6-Bromo-2,3-dihydrothieno[3,2-*b*][1,4]oxathiine (21)
The same procedure as for **20** was used. Compound **7** (2.99 g, 18.9 mmol) gave 4.14 g (92%) of **21.**

^{1}H NMR ($CDCl_3$): δ = 6.60 (s, 1 H), 4.43 (m, 2 H), 3.09 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 147.7, 122.8, 106.6, 104.7, 66.6, 26.0.

HRMS: *m*/*z* calcd for $C_6H_5BrOS_2$: 235.8965; found: 235.8965.

2,3,2′,3′-Tetrahydro-6,6′-bi(thieno[2,3-*b*][1,4]dithiinyl) (TDT2T, 22)
6-Bromo-2,3-dihydrothieno[2,3-*b*][1,4]dithiine (**20**; 5.00 g, 19.75 mmol) was dissolved in THF (40 ml) under N_2. To the solution was added Bu_4NI (7.30 g, 19.75 mmol), Zn (2.00 g, 29.6 mmol) and $NiBr_2(PPh_3)_2$ (1.41 g, 1.89 mmol). The mixture was heated to 50 °C for 2 h and left at r.t. overnight. Most of the solvent was removed under reduced pressure, and the mixture was diluted with Et_2O. Filtration through a pad of neutral alumina and concentration gave 2.14 g of crude product. An additional 1.53 g of crude product was extracted from the alumina with CH_2Cl_2. Recrystallization from EtOH or MeOH gave in total 1.00 g (29%) of the dimer.

^{1}H NMR ($CDCl_3$): δ = 6.68 (s, 2 H), 3.37–3.28 (m, 8 H).

^{13}C NMR ($CDCl_3$): δ = 132.2, 124.0, 123.2, 121.2, 28.8, 27.9.

MS (EI): *m*/*z* (%) = 346 (100, M^+), 318 (40), 242 (21).

Anal. Calcd for $C_{12}H_{10}S_6$: C, 41.59; H, 2.91. Found: C, 41.55; H, 3.04.

2,3,2′,3′-Tetrahydro-6,6′-bi(thieno[3,2-*b*][1,4]oxathiinyl) (TOT2T, 23)
Anhyd $NiCl_2$ (531 mg, 4.18 mmol), Ph_3P (5.24 g 20.0 mmol) and 2,2′-bipyridine (648 mg, 4.15 mmol) were mixed with anhyd DMF (20 mL) in an oven-dried flask and heated at 70 °C under a stream of N_2 for 70 min. 6-Bromo-2,3-dihydrothieno[3,2-*b*][1,4]oxathiine (**21**; 4.71 g, 19.9 mmol) was added as a solution in anhyd THF (20 mL), followed, after another 10 min, by Zn (3.31 g, 50.6 mmol). After 10 min, the outlet for N_2 was removed and the mixture was stirred at 80 °C for 22 h. After cooling to r.t., the mixture was diluted with CH_2Cl_2, washed with 2 M HCl, aq 10% $NaHCO_3$, dried and evaporated to afford 7.36 g of a dark brown oil. The oil was treated with Et_2O, and the insoluble material was purified by chromatography on silica gel with gradient elution using mixtures of heptane and EtOAc. Analytically pure **23** was obtained as yellow crystals; yield: 827 mg (26%); mp 181–183 °C.

^{1}H NMR ($CDCl_3$): δ = 6.60 (s, 2 H), 2.45 (m, 4 H), 3.10 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 148.5, 131.2, 115.8, 103.6, 66.7, 26.3.

MS (EI): *m*/*z* (%) = 314 (100, M^+), 287 (21), 182 (33), 154 (32).

5,5′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene (27)
Bithiophene (**26**; 2.91 g, 17.5 mmol) with TMEDA (4.69 g, 40.4 mmol) in hexanes (dried over CaH_2) under N_2 was cooled to –78 °C, and *n*-BuLi in hexanes (1.5 M, 25 ml, 38 mmol) was added over 5 min. After 10 min, the cooling bath was removed, and 45 min later, the mixture was refluxed for 30 min, and again cooled to –78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**24**; 8.38 g, 45.0 mmol) was added and the mixture left to attain r.t. overnight (16 h). After dilution with CH_2Cl_2 and washing with aq 10% $NaHCO_3$ and brine, the solution was dried ($MgSO_4$) and concentrated to give a brownish-white solid (6.80 g, 93% of theory) which was recrystallized from MTBE to give pure **27** (4.15 g, 57%).

^{1}H NMR ($CDCl_3$): δ = 7.52 (d, *J* = 3.7 Hz, 2 H), 7.29 (d, *J* = 3.7 Hz, 2 H), 1.35 (s, 24 H).

^{13}C NMR ($CDCl_3$): δ = 144.3, 138.4, 129.1 (br s), 126.0, 84.6, 25.2.

MS (EI): *m*/*z* (%) = 418 (100, M^+), 218 (17).

Anal. Calcd for $C_{20}H_{28}S_2BO_4$: C, 57.44; H, 6.75. Found: C, 57.42; H, 6.65.

TDT3T (28); Typical Procedure
6-Bromo-2,3-dihydrothieno[2,3-*b*][1,4]dithiine (**20**; 2.68 g, 10.60 mmol) was dissolved in dioxane (120 mL) under argon. $Pd(PPh_3)_4$ (0.62 g, 0.54 mmol) was added, and after 5 min **25** (1.78 g, 5.30 mmol), and CsF (9.66 g, 63.6 mmol) were added. The mixture was refluxed for 48 h. The reaction mixture was concentrated and partitioned between CH_2Cl_2 and H_2O. The organic layer was dried and concentrated to give a dark brownish powder as crude product. The product was treated with absolute EtOH overnight and filtered to yield a light-brown powder (1.40 g, 62%). This powder contained the trimer and small (<5%) amounts of the dimer. Pure fractions could be obtained either by treatment overnight with $CHCl_3$ and filtering off the pure trimer, or by chromatography.

^{1}H NMR ($CDCl_3$): δ = 6.93 (s, 2 H), 6.77 (s, 2 H), 3.36–3.28 (m, 8 H).

^{13}C NMR ($CDCl_3$): δ = 135.2, 132.8, 124.3, 124.1, 123.3, 121.3, 28.8, 28.0.

MS (EI): *m*/*z* (%) = 428 (46, M^+), 400 (18), 280 (100).

Anal. Calcd for $C_{16}H_{12}S_7$: C, 44.83; H, 2.82. Found: C, 44.57; H, 2.74.

TOT3T (29)
In a procedure analogous to the synthesis of **28**, **21** (2.11 g, 8.9 mmol) was reacted with **25** (1.57 g, 4.67 mmol) in the presence of CsF (4.07 g, 26.8 mmol) and $Pd(PPh_3)_4$ (0.26 g, 0.24 mmol), to give 1.14 g (65%) of pure **29**; mp (DSC) 246 °C.

^{1}H NMR ($CDCl_3$): δ = 6.92 (s, 2 H), 6.68 (s, 2 H), 4.60 (m, 4 H), 3.13 (m, 4 H).

^{13}C NMR (CS_2–$CDCl_3$): δ = 148.3, 135.9, 131.0, 123.7, 116.2, 104.0, 66.3, 26.7.

MS (EI): *m*/*z* (%) = 396 (100, M^+), 264 (74).

Anal. Calcd for $C_{16}H_{12}S_5O_2$: C, 48.46; H, 3.05. Found: C, 48.40; H, 2.97.

TDT4T (30); Typical Procedure
Compound **20** (2.14 g, 8.46 mmol) was dissolved in dioxane (120 mL) under argon. To this solution was added $Pd(PPh_3)_4$ (0.49 g, 0.42 mmol). After 5 min, **27** (1.77 g, 4.23 mmol) and CsF (7.71 g, 50.8 mmol) were added, and the mixture was heated at reflux for 48 h. The mixture was concentrated, and partitioned between CH_2Cl_2 and H_2O. The organic layer was dried, filtered through Celite and concentrated to give 3.30 g of a dark oil as crude product. The product was treated with EtOH, yielding a crystalline residue, which was treated with $CHCl_3$ to give 200 mg of NMR pure tetramer. The Celite was transferred to a Soxhlet apparatus and extracted with EtOH, followed by extraction with $CHCl_3$ for 2 d. The $CHCl_3$ extract was concentrated to afford 556 mg of product. The total yield of tetramer was 756 mg (35%). Analytically pure fractions could be obtained by chromatography through Al_2O_3 with toluene as eluent; mp (DSC) 276 °C.

^{1}H NMR ($CDCl_3$): δ = 7.02 (d, *J* = 3.7 Hz, 2 H), 6.96 (d, *J* = 3.9 Hz, 2 H), 6.80 (s, 2 H), 3.33 (m, 8 H).

^{13}C NMR ($CDCl_3$): δ = 136.4, 135.9, 133.4, 124.9, 124.8, 124.7, 123.8, 121.9, 29.7, 28.8.

MS (EI): *m*/*z* (%) = 510 (100, M^+), 482 (26), 362 (37).

Anal. Calcd for $C_{20}H_{14}S_8$: C, 47.03; H, 2.76. Found: C, 46.81; H, 2.94.

TOT4T (31)

In a procedure analogous to the synthesis of **30**, **21** (1.98 g, 8.4 mmol) was reacted with **27** (1.75 g, 4.18 mmol) in the presence of CsF (3.76 g, 24.8 mmol) and $Pd(PPh_3)_4$ (0.26 g, 0.24 mmol), to give 0.934 g (47%) of pure **31**; mp (DSC) 302 °C.

^{1}H NMR ($CDCl_3$): δ = 7.27 (d, *J* = 3.7 Hz, 2 H), 7.20 (d, *J* = 3.7 Hz, 2 H), 6.99 (s, 2 H), 4.60 (m, 4 H), 3.15 (m, 4 H).

^{13}C NMR (DMSO-d_6, 95 °C): δ = 149.5, 136.5,135.8, 130.6, 126.2, 125.4, 117.3, 105.3, 67.3, 26.5.

MS (EI): *m*/*z* (%) = 478 (97, M^+), 450 (24), 346 (100), 214 (56).

Anal. Calcd for $C_{20}H_{14}S_6O_2$: C, 50.12; H, 2.95. Found: C, 49.93; H, 2.90.

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