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Pyrrolo-Annelated Tetrathiafulvalenes: The Parent Systems

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The synthesis of a number pyrrolo-annelated tetrathiafulvalenes, including the parent bis(pyrrolo-[3,4-*d*])tetrathiafulvalene (**7**) is decribed. Starting from readily available 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (**14**) and sodium tosylamide, the parent **7** and the asymmetric monopyrrolo tetrathiafulvalenes **23a**,**b** were prepared in good yields via a nonclassical and simple pyrrole synthesis. Furthermore, a series of asymmetrical *N*-alkylated monopyrrolo/monodihydropyrrolotetrathiafulvalenes was prepared starting from primary amines and **14**. A detailed study of the fundamental redox behavior of this class of heterocycles is reported. NMR spectroscopy, cyclic voltammetry, and PM3 MO calculations revealed that the pyrrolo-annelated tetrathiafulvalenes have highly extended π-surfaces. The X-ray crystallographic analyses of the monopyrrolo tetrathiafulvalenes **22b** and **24b**, together with preliminary formation of a charge-transfer complex between the parent donor **7** and TCNQ, are also reported.

Introduction

The chemistry of tetrathiafulvalene (TTF, **1**) and its derivatives has been intensively studied since the discovery of the first metallic charge-transfer TTF complex.[1] The TTF skeleton has been extensively modified over the past two decades to enhance dimensionality in the related charge-transfer salts.[2] Among those modifications, the heterocyclic-fused TTF donor, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, **2**), has given rise to more superconducting salts than any other TTF derivative, with κ-(BEDT-TTF)$_2$-Cu[N(CN)$_2$]Br as the current record holder.[3]

A variety of donor molecules have been synthesized in which the TTF core is annelated to benzenoid **3**,[4] furan,[5] thiophene,[6] or selenophene[7] units **4** (Figure 1); all of these compounds have oxidation potentials appreciably higher than that of TTF (**1**) itself. Furthermore, there has been an increasing interest in incorporating tetrathiafulvalenes into macrocyclic and supramolecular structures.[2d,8] Cava and co-workers have recently presented a detailed study of bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (**5**), the related monopyrrolo-annelated tetrathiafulvalene **6**, and their *N*-alkylated derivatives (Figure 1).[9] The synthesis of **5** involves classical pyrrole chemistry, building up the 1,3-dithiole-2-thione moiety from a 2,5-dimethylpyrrole core.[10] Annelation of TTF to two electron-

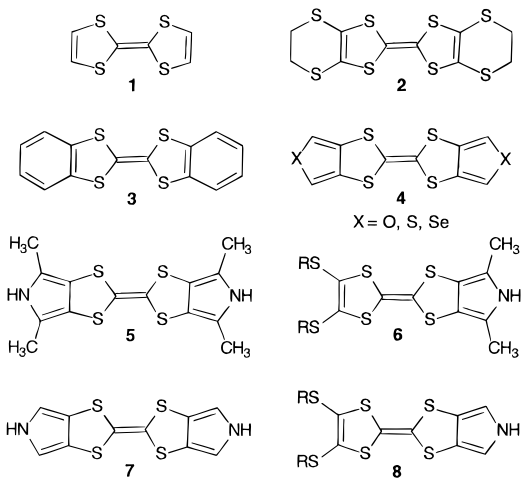

Figure 1.

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(10) The two methyl groups are mandatory in this synthesis because the first step is an electrophilic thiocyanation at the β-positions and they serve to block the more reactive α-positions.

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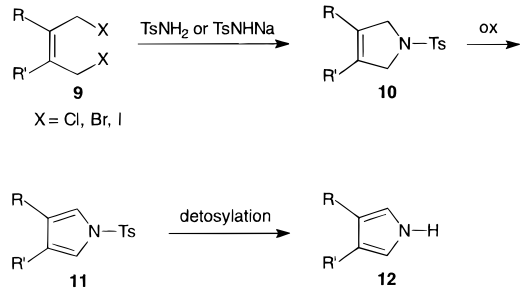
Scheme 1



rich 2,5-dimethylpyrrole rings produces a donor system with a lower oxidation potential than that of the parent TTF (**1**), and this in connection with the higher symmetry suggests **5** to be a useful building block in supramolecular chemistry, devoid of *cis*/*trans* isomerism as in the simple TTFs.[11] However, the four methyl groups in **5**, acting as protecting groups during the synthesis, block the α-positions in the pyrrole units, excluding the possibility for further *C*-functionalization in addition to *N*-alkylations. Furthermore, steric hindrance can be expected from the methyl groups, when **5** is incorporated in macrocyclic systems.

In this context, the parent bis(pyrrolo[3,4-*d*])tetrathiafulvalene (**7**) appeared to be interesting (Figure 1), and we present here a straightforward route to **7** and the related monopyrrolo annelated TTFs **8**, through a nonclassical pyrrole synthesis.[12,13]

The construction of α,α′-unsubstituted *N*-tosyl-2,5-dihydropyrrolo annelated heterocycles **10** from tosylamide/sodium tosylamide (Scheme 1) and unsaturated 1,2-bishalomethyl precursors **9** has been sporadically described in the literature.[14] However, to the best of our knowledge subsequent oxidations to the corresponding *N*-tosylpyrroles **11** and complete detosylation to give α,α′-unsubstituted pyrroles **12** have apparently not been reported.[15]

In our approach, the pyrrole ring is constructed in two steps from a 1,3-dithiole-2-thione core bearing two vicinal bromomethyl groups. The first step is a ring closure reaction with sodium tosylamide followed by oxidation of the annelated dihydropyrrole ring with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give the *N*-tosyl-protected pyrrole. The tosyl group plays a triple role during this synthesis. First, it activates the nitrogen in

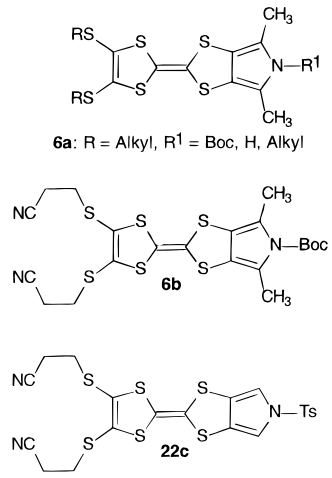


Figure 2.

the ring closure reaction. Second, it works as an excellent protecting group for the pyrrole nitrogen during the harsh triethyl phosphite coupling reaction. Finally, the tosyl groups can be removed almost quantitatively under mild conditions from the aromatic pyrrole ring.

We have previously demonstrated that the cyanoethyl group works as an excellent protecting group for 1,3-dithiole-2-chalcogenone and tetrathiafulvalene thiolates, and shown that selective and stepwise deprotection of the cyanoethyl thiolate protecting groups is possible, by treatment with 1 equiv of cesium hydroxide monohydrate.[16] Although the simple *S*-alkyl derivatives of **6a** recently have been reported,[9c] similar cross-couplings of 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-chalcogenones with 5-*tert*-butoxycarbonyl-4,6-dimethyl-(1,3)-dithiolo-[4,5-*c*]-pyrrole-2-chalcogenones to give **6b** were unsuccessful (Figure 2).[17]

These results encouraged us to synthesize **22c**, and we describe here the potential of **22c** as a promising building block for macrocyclic and supramolecular chemistry.

To study the difference between annelation of a dihydropyrrole- and a pyrrole unit to tetrathiafulvalene, a series of asymmetrical *N*-alkylated monopyrrolo/monodihydropyrrolotetrathiafulvalenes was prepared starting from primary amines and **14**.

The π-donor ability of the new systems was investigated by cyclic voltammetry and theoretical methods together with preliminary formation of a tetracyanoquinodimethane (TCNQ) complex. We also report the X-ray crystal structures of the monopyrrolo-TTFs **22b** and **24b**.

Results and Discussion

Synthesis of (1,3)-Dithiolo[4,5-*c*]pyrrole-2-chalcogenones. The starting material in our synthesis is the

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(13) A preliminary account on the synthesis of compounds **7** and **23a** has recently been published, see: Jeppesen, J. O.; Takimiya, K.; Jensen, F.; Becher, J. *Org. Lett.* **1999**, *1*, 1291−1294.

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(15) The dehydrogenation of *N*-alkyl/arylsulfonyl-2,5-dihydropyrroles with different oxidation agents has been described, see: (a) Suzuki, T.; Ohyabu, H.; Takayama, H. *Heterocycles* **1997**, *46*, 199−202. (b) Xu, Z.; Lu, X. *Tetrahedron Lett.* **1997**, *38*, 3461−3464. (c) Ando, K.; Kankake, M.; Suzuki, T.; Takayama, H. *Tetrahedron* **1995**, *51*, 129−138. (d) Suzuki, T.; Takayama, H. *J. Chem. Soc., Chem. Commun.* **1995**, 807−808. (e) Ando, K.; Kankake, M.; Suzuki, T.; Takayama, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1100−1102.

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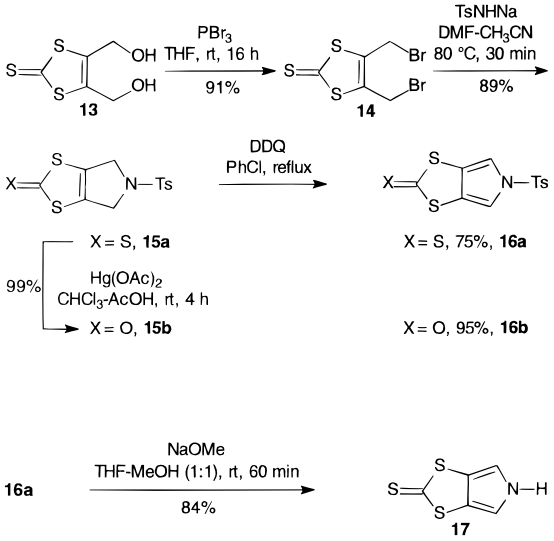
(19) Recently an experimental procedure using CBr_4/PPh_3 has been reported by Müllen and co-workers, see: Skabara, P. J.; Müllen, K.; Bryce, M. R.; Howard, J. A. K.; Batsanov, A. S. *J. Mater. Chem.* **1998**, *8*, 1719−1724.

(20) The use of PBr_3 has been reported in a communication from Gorgues and co-workers, see: Durand, C.; Hudhomme, P.; Duguay, G.; Jubault, M.; Gorgues, A. *Chem. Commun.* **1998**, 361−362.

Scheme 2



diol **13**,[18] which was dibrominated with phosphorus tribromide (PBr_3) to give dibromide **14**.[19,20] Cyclization was performed by treatment of **14** with 2 equiv sodium tosylamide affording the dihydropyrrolo compound **15a** in 89% yield (Scheme 2).

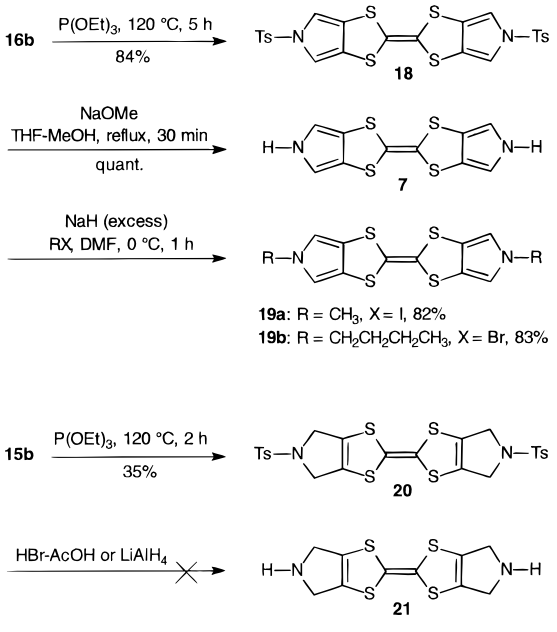
Transchalcogenation of thione **15a** with mercuric acetate in a mixture of chloroform and glacial acetic acid gave ketone **15b** in 99% yield. Dehydrogenation of the dihydropyrroles **15a**,**b** using 2 equiv of DDQ in chlorobenzene afforded the *N*-tosylated (1,3)-dithiolo[4,5-*c*]-pyrrole-2-chalcogenones **16a**,**b** in 75% and 95% yields, respectively. Detosylation of **16a** was carried out by treatment of **16a** with sodium methoxide in a 1:1 mixture of THF−MeOH, affording the pyrrole **17** in 84% yield.[21]

Synthesis of Bis(pyrrolo[3,4-*d*])tetrathiafulvalenes. Self-coupling of the ketone **16b** to form the TTF **18** using triethyl phosphite proceeded in 84% yield (Scheme 3).

Removal of the tosyl protecting groups of **18** was carried out by refluxing a suspension of **18** and sodium methoxide in a 1:1 mixture of THF−MeOH, affording the novel bis(pyrrolo)-TTF **7** in quantitative yield. Finally, **7** was dialkylated to give the *N*,*N*′-dialkyl derivatives **19a**,**b** in 82−83% yields (Scheme 3). Treatment of the ketone **15b** with triethyl phosphite gave bis(2,5-dihydro-*N*-tosylpyrrolo[3,4-*d*])tetrathiafulvalene (**20**) in 35% yield as a very insoluble solid (Scheme 3). Although several attempts were performed to remove the tosyl groups in **20**, we never succeeded in obtaining bis(2,5-dihydro[3,4-*d*])tetrathiafulvalene (**21**) probably on account of the high chemical stability of the sulfamide bonds and the low solubility of **20**.

Synthesis of Monopyrrolo[3,4-*d*]tetrathiafulvalenes. Cross-coupling of **16b** with 2 equiv of 4,5-bis(methylthio)-1,3-dithiole-2-thione, 4,5-bis(pentylthio)-1,3-dithiole-2-thione, and 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione, respectively, in neat triethyl phophite afforded the *N*-tosyl-protected asymmetrical monopyrrolo-TTFs **22a**−**c** in 55−69% yields (Scheme 4).[22]

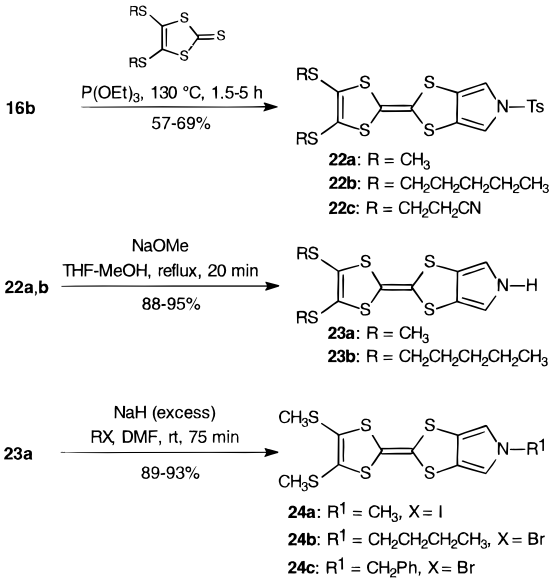
Scheme 3



Deprotection of the tosyl group in **22a**,**b** with sodium methoxide in a 1:1 mixture of THF−MeOH afforded the asymmetrical monopyrrolo-TTFs **23a**,**b** in high yields (Scheme 4). Alkylation of **23a** proceeded smoothly to give the *N*-alkylated derivatives **24a**−**c**.

Potential of 22c as a Building Block for Supramolecular Chemistry. To study the potential of **22c** as a building block for macrocyclic and supramolecular chemistry, the following regioselective deprotection and realkylation reactions were carried out. Treatment of a THF solution of **22c** with 1 equiv of cesium hydroxide monohydrate generated the TTF-monothiolate selectively, without interfering with the tosyl protecting group, evidenced by quenching of the thiolate with iodomethane to give the methylthio substituted TTF **25** in near quantitative yield. Subsequently, the remaining cyanoethyl thiolate protecting group in **25** was deprotected using 1 equiv of cesium hydroxide monohydrate followed by addition of iodomethane, affording the bis(methylthio)

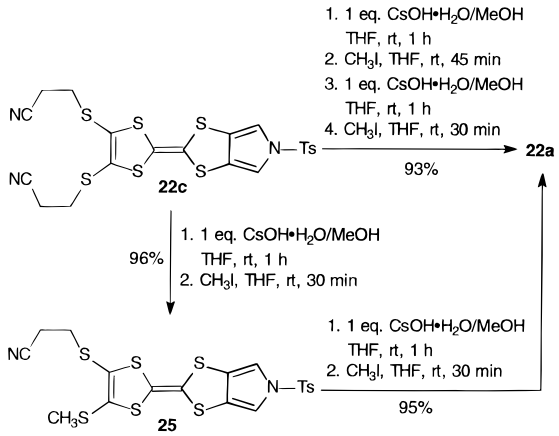
Scheme 4



(21) Care must be taken during workup, especially with regard to temperature; otherwise ring opening occurs in the 1,3-dithiole ring and a mixture of **17** and 3,4-bis(methylthio)pyrrole is isolated.

(22) Cross-coupling of thione **16a** and 2 equiv of 4,5-bis(methylthio)-1,3-dithiol-2-one in neat triethyl phosphite afforded TTF **22a** in a considerably lower yield (26%), compared to the cross-coupling reaction between ketone **16b** and 4,5-bis(methylthio)-1,3-dithiole-2-thione.

Scheme 5

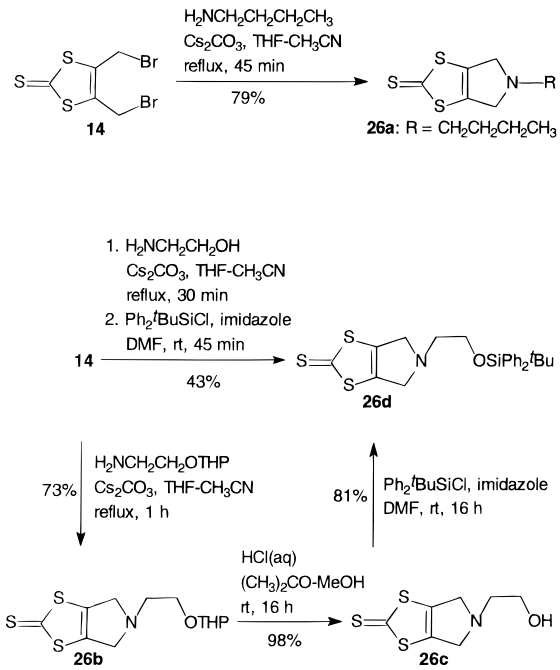


substituted TTF **22a** in 95% yield.To obtain **22a** directly from **22c**, the following reaction sequence was necessary.[23] A THF solution of **22c** was treated with 1 equiv of cesium hydroxide monohydrate and the resulting monothiolate realkylated with iodomethane, whereupon excess iodomethane was removed.[24] The residue was then treated with 1 equiv of cesium hydroxide monohydrate, followed by addition of iodomethane, which effected the second deprotection/realkylation sequence and afforded **22a** in 93% yield (Scheme 5).

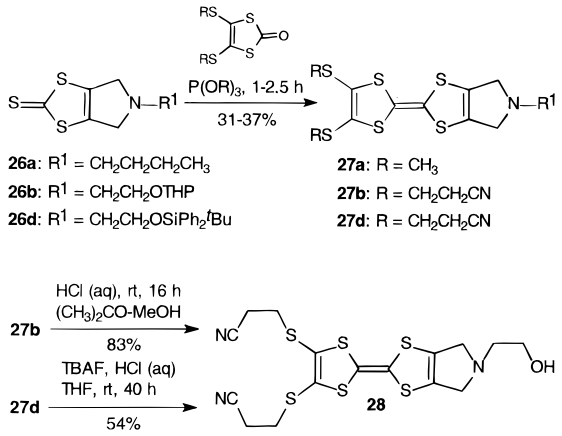
Synthesis of Asymmetrical *N*-Alkylated Monopyrrolo/Monodihydropyrrolotetrathiafulvalenes. Treatment of dibromide **14** with butylamine in a refluxing mixture of THF and CH_3CN, in the precence of excess cesium carbonate, gave the *N*-butyldihydropyrrole **26a** in 79% yield (Scheme 6).

Using similar reaction conditions, **26b** was obtained in 73% yield by treatment of dibromide **14** with THP-protected ethanolamine (Scheme 6). The THP protecting group in **26a** was removed using aqueous hydrochloric acid, affording the alcohol **26c** in almost quantitative yield, which subsequently was protected as the *tert*-butyldiphenylsilyl ether, using *tert*-butyldiphenylchlorosilane in the presence of imidazole, giving the silyl protected 1,3-dithiole-2-thione **26d** in 81% yield.[25] The THP protected ethanolamine was synthesized in a two-step reaction from commercially available ethanolamine,[26] which implies that five steps are necessary in this approach to **26d**. Instead, **26d** can be synthesized in a one-pot synthesis starting from **14** and ethanolamine, followed by treatment with *tert*-butyldiphenylchlorosilane in the presence of imidazole (Scheme 6), affording **26d** in an acceptable yield. The advantage of the second route is obvious.

Scheme 6



Scheme 7



Cross-coupling of the dihydropyrroles **26a**,**b**,**d** with 3 equiv of 4,5-bis(methylthio)-1,3-dithiol-2-one or 4,5-bis-(2-cyanoethylthio)-1,3-dithiol-2-one in neat triethyl phosphite gave the asymmetrical *N*-alkyl-dihydropyrrolo-TTFs **27a**,**b**,**d** in moderate yields (Scheme 7).

The TTF-alcohol **28** was obtained in optimum yield by removal of the THP protecting group in **27b** using aqueous hydrochloric acid. Deprotection of the silyl group in **27d** with tetrabutylammonium flouride (TBAF) afforded **28** in 54% yield after recrystallization (Scheme 7).

Oxidation of the dihydropyrroles **26a**,**d** with DDQ proceeded in high yields under mild conditions affording the corresponding pyrroles **29a**,**d**, which subsequently were cross-coupled with 4,5-bis(methylthio)-1,3-dithiol-2-one or 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one, giving the asymmetrical *N*-alkyl-monopyrrolo-TTFs **24b** and **30** in 52% and 31% yields, respectively (Scheme 8).

Deprotection of the *tert*-butyldiphenylsilyl protecting group in **30** with TBAF afforded the TTF-alcohol **31** in 92% yield.

Electrochemistry of Compounds 7, 18, 19, and 22−25. Solution oxidation potentials obtained from cyclic voltammograms (CVs) of pyrrolo-TTF π donors (D) and

(23) Treatment of **22c** with 2.1 equiv of cesium hydroxide monohydrate dissolved in MeOH, followed by addition of excess iodomethane, afforded only **22a** in 42% yield, together with byproducts where the tosyl group had been partially deprotected and/or the cyanoethyl thiolate protecting groups partially deprotected.

(24) At this point it was verified by TLC and PDMS that clean monodeprotection had taken place.

(25) Previous results have shown that a primary alcohol functionality is unable to survive the standard trialkyl phosphite coupling, whereas the *tert*-butyldiphenylsilyl alcohol protecting group is able to withstand the standard coupling conditions, see: (a) Marshallsay, G. J.; Bryce, M. R.; Cooke, G.; Jørgensen, T.; Becher, J.; Reynolds, C. D.; Wood, S. *Tetrahedron* **1993**, *49*, 6849−6862. (b) Marshallsay, G. J; Hansen, T. K.; Moore, A. J.; Bryce, M. R.; Becher, J. *Synthesis* **1995**, 926−930.

(26) Passon, M.; Antoine, M.; Chabassier, S.; Geiger, S.; Girard, P.; Richer, D.; Lajudie, P.; Hovath, E.; Leriche, B.; Patte, S. *Eur. J. Med. Chem., Chemi Ther.* **1974**, *9*, 591−594.

Scheme 8

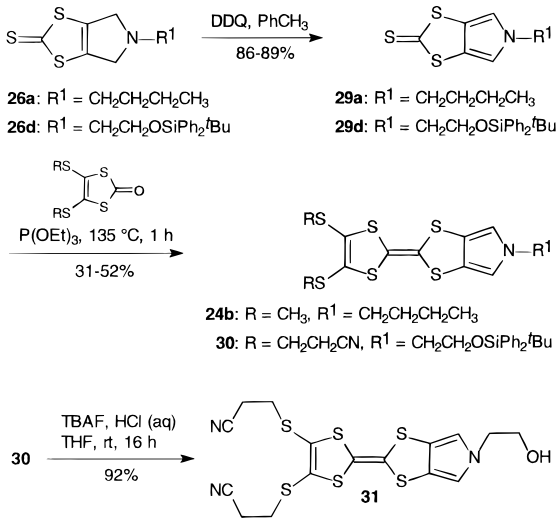


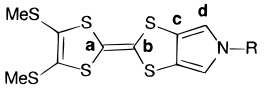
Table 1. Oxidation Potentials $E_{1/2}^1$ and $E_{1/2}^2$ of Pyrrolo-TTF Derivatives 7, 18, 19a,b, 22a−c, 23a,b, 24a−c, and 25 Determined by Cyclic Voltammetry[a,b]

compd	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)	ΔE_p (V)
TTF (**1**)	0.34	0.73	0.39
5	0.33	0.74	0.41
7	0.38	0.72	0.34
18[c]	0.55	0.96	0.41
19a	0.36	0.70	0.34
19b	0.36	0.70	0.34
22a	0.60	0.87	0.27
22b	0.59	0.86	0.27
22c	0.66	0.95	0.29
23a	0.44	0.75	0.31
23b	0.44	0.75	0.31
24a	0.42	0.74	0.32
24b	0.42	0.73	0.31
24c	0.42	0.73	0.31
25	0.62	0.90	0.28
32	0.42	0.76	0.34

[a] Conditions: Ag/AgCl electrode, Pt electrode, 20 °C, Bu_4NPF_6 (0.1 M in CH_3CN), scan rate 0.1 Vs^{-1}, [compound] 10^{-3} M. [b] The oxidation potentials for parent TTF (**1**), bis(2,5-dimethylpyrrolo-[3,4-*d*])tetrathiafulvalene (**5**),[9] and 4,6-dimethyl-2-[4,5-bis(methylthio)-1,3-dithiole-2-yliden]-(1,3)-dithiolo[4,5-*c*]pyrrole (**32**) (i.e., α,α′-dimethyl substituted analogue of **22a**)[29] were measured under identical conditions for comparison. [c] [**18**] ≪ 10^{-3} M, on account of the low solubility in CH_3CN.

DFT calculated first oxidation potentials are summarized in Table 1.[27,28] The CVs of all compounds revealed two pairs of reversible redox waves, indicating good stability of the corresponding radical cation ($D^{\bullet+}$) and dication (D^{2+}). Compound **7** showed a higher first half-wave oxidation potential $E_{1/2}^1$ (50 mV) than its α,α′,α″,α‴-tetramethylated analogue **5**. This effect was also observed for **23a** and its α,α′-bismethylated analogue **32** (20 mV) on account of the electron-donating effect of the α-methyl groups.

Table 2. ^{1}H NMR Chemical Shifts for Pyrrole α-Protons and Selected ^{13}C NMR Chemical Shifts (in ppm) for *N*-Substituted Asymmetrical Monopyrrolo-TTFs 22a, 23a, and 24a[a]



R	fulvene C_a=C	fulvene C=C_b	dithiole =C_c−C=	pyrrole C_d	H_α
Ts	112.52	117.73	126.14	112.84	7.40
H	107.27	121.95	117.16	110.88	6.81
Me	107.24	121.34	116.77	114.66	6.78

[a] Spectra were recorded in DMSO-d_6 (25 °C) at 300 and 75 MHz for protons and carbons, respectively.

The first-half wave oxidation potential $E_{1/2}^1$ of **7** is higher (40 mV) than that of TTF (**1**), indicating that annelation of two pyrrolo units to the TTF framework results in a decrease of the electron-donating ability. The *N*-tosylated pyrrolo-TTFs (i.e., **18** and **22a**,**b**) showed the highest oxidation potentials (both $E_{1/2}^1$ and $E_{1/2}^2$) in both the bis(pyrrolo)-TTF series and the monopyrrolo-TTF series, whereas the *N*-alkylated pyrrolo-TTFs (i.e., **19a**,**b** and **24a**−**c**) revealed the lowest oxidation potentials (both $E_{1/2}^1$ and $E_{1/2}^2$), due to the inductive effect exhibited from the tosyl groups and alkyl groups, respectively.

NMR Spectroscopy. An interesting feature of the monopyrrolo-TTFs is found in their ^{13}C chemical shifs, which are summarized in Table 2 together with the ^{1}H chemical shifts.

As expected, the tosyl group has a strong influence on the chemical shift of the pyrrole protons. The most remarkable fact, however, is that the tosyl group is able to shift most of the ^{13}C resonances in **22a**. Especially for the fulvene C_a=C, which is located six bonds away from the tosyl group, a significant change in the chemical shift is observed, indicating a pronounced extension of the π-surface in monopyrrolo-TTFs.

Highest Occupied Molecular Orbitals. To shed more light on the extension of the π-surface in pyrrolo-TTFs, the characters of the highest occupied molecular orbital (HOMO) of **7** and **23a** were calculated using the semiempirical PM3 method.[30] Figure 3 (top) shows the electron distribution of **7**, and it is noteworthy that approximately 21% of the HOMO density is located on the outer two pyrrole rings, similar to that of BEDT-TTF (**2**) where the outer sulfur atoms have relatively large HOMO densities with the same phase as the inner sulfur atoms.[31]

For the asymmetrical monopyrrolo-TTF **23a**, approximately 13% of the HOMO density is located on the outer pyrrole ring (Figure 3, bottom), clearly demonstrating an extension of the π-surface in pyrrolo-TTFs.

X-ray Crystallography. To study the effect of *N*-substitution at the bond lengths in pyrrolo-TTFs, X-ray crystal structure determinations were performed at the

(27) The first oxidation potentials were calculated from the energy difference between D and $D^{\bullet+}$ with the B3LYP/6-31G(d) method and the PCM solvent model, using PM3-optimized geometries.

(28) Gaussian 98 (Revision A.5): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Nudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Comperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(29) Lomholt, C.; Nielsen, M. B.; Becher, J. Unpublished results.

(30) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, 221−264.

(31) Mori, T.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627−633.

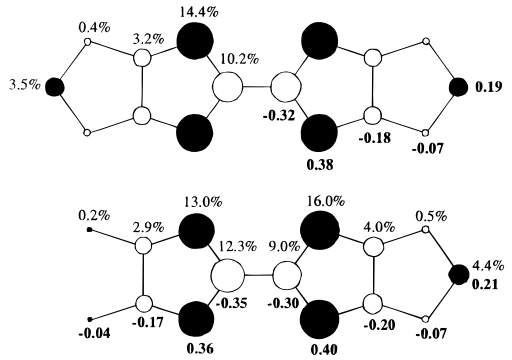


Figure 3. HOMO orbitals of **7** (top) and **23a** (bottom): lightface numbers = HOMO electron density, boldface numbers = HOMO coefficients.

asymmetrical monopyrrolo-TTFs **22b** and **24b**.[32] Single crystals of **22b** and **24b** were obtained by recrystallization from acetone/cyclohexane and dichloromethane/hexane, respectively. The bond lengths in the structure of **22b** differ little from those of **24b**. The only significant difference is the length of the formal double bond C3−C4 which is 1.348(4) Å in **22b**, whereas the corresponding value in **24b** is 1.30(1) Å (Figure 4). This observation may indicate a more extended π-electron system in the former compound. This assumption is corroborated by the fact that the pyrrolo-TTF part of **22b** is close to planar as opposed to the bent structure of **24b**. The central TTF plane (S1, S2, S5, S6, C1, and C2) in **22b** makes a dihedral angle of 2.8° with the pyrrole outer plane (S1, S6, N1, C5, C6, C7, and C8) and a dihedral angle of 4.9° with the outer plane (S2, S3, S4, S5, C3, and C4). The corresponding angles in **24b** are 17.6° and 19.3°, respectively.

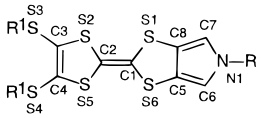


Figure 4. Crystallographic atom numbering of **22b** and **24b**.

Charge-Transfer Complex. A combination of equimolar amounts of the new donor **7** and TCNQ in acetonitrile gave a crystalline charge-transfer complex, which was shown to be a 1:1 complex by elemental analysis. The conductivity of **7**·TCNQ on a single crystal was measured at room temperature, using the four probe method, and was relatively high, 0.02 S cm^{-1}.

Electrochemistry of Asymmetrical *N*-Alkylated Monopyrrolo/Monodihydropyrrolotetrathiafulvalenes. As expected, the dihydropyrrolo-TTFs **27a**,**d** and **28** and the pyrrolo-TTFs **24b**, **30**, and **31** display different physical properties. In particular with regard to solubility and affinity toward silica gel. To shed more light on the differences between dihydropyrrolo-TTFs and pyrrolo-TTFs, their electrochemical properties were investigated by cyclic voltammetry. Solution oxidation potentials obtained from cyclic voltammograms (CVs) are summarized in Table 3.

The pyrrolo-TTFs have lower oxidation potentials (both $E_{1/2}{}^1$ and $E_{1/2}{}^2$) compared to the dihydropyrrolo-TTFs. This indicates that annelation of tetrathiafulvalene to an electron rich aromatic pyrrole ring produces a stronger donor system compared to annelation of a nonaromatic dihydropyrrole system.

Table 3. Oxidation Potentials $E_{1/2}{}^1$ and $E_{1/2}{}^2$ of Asymmetrical Monopyrrolo/Dihydropyrrolo-TTF Derivatives 27a,b,d, 28, 24b, 30, and 31 Determined by Cyclic Voltammetry[a]

compd	$E_{1/2}{}^1$ (V)	$E_{1/2}{}^2$ (V)	ΔE_p (V)
27a	0.50	0.92	0.42
27b	0.56	0.96	0.40
27d	0.56	0.96	0.40
28	0.58[b]	0.96[b]	0.38
24b	0.44	0.87	0.33
30	0.54	0.95	0.41
31	0.54[c]	0.92[c]	0.38

[a] Conditions: Ag/AgCl electrode, Pt electrode, 20 °C, Bu_4NPF_6 (0.1 M in CH_2Cl_2), scan rate 0.1 Vs^{-1}, [compound] 10^{-3} M. [b] Irreversible. [c] Quasi-reversible.

Theorectical Calculations. The energy for removing one electron was calculated at the B3LYP density functional level with the 6-31G(d) basis set, using PM3-optimized geometries.[33] Solvent effects were modeled with the IEFPCM method,[34] which is a continuum solvent model employing a molecular shaped cavity. As seen from the results in Table 4 this method is capable of reproducing trends in the first oxidation potential quite well, both between different compounds in the same solvent, and changes between solvents.

Table 4. Comparison of Oxidation Potentials $E_{1/2}{}^1$ and $E_{1/2}{}^2$ for Selected Pyrrolo/Dihydropyrrolo-TTF Derivatives in CH_3CN or CH_2Cl_2, Respectively, Determined by Cyclic Voltammetry[a]

	CH_3CN			CH_2Cl_2		
compd	$E_{1/2}{}^1$ (V)	$E_{1/2}{}^2$ (V)	$E_{ox}{}^1$(DFT) (eV)	$E_{1/2}{}^1$ (V)	$E_{1/2}{}^2$ (V)	$E_{ox}{}^1$(DFT) (eV)
19a	0.36	0.70	4.49	0.36	0.86	4.57
19b	0.36	0.70		0.35	0.86	
22a	0.60	0.87	4.82	0.64	1.01	4.93
22b	0.59	0.86		0.62	1.00	
22c	0.66	0.95	4.91	0.73	1.10	5.03
23a	0.44	0.75	4.65	0.46	0.92	4.74
23b	0.44	0.75		0.48	0.93	
24a	0.42	0.74	4.61	0.43	0.87	4.70
24b	0.42	0.73		0.44	0.87	
24c	0.42	0.73	4.60	0.44	0.87	4.69
25	0.62	0.90		0.67	1.04	
27a	0.44[b]	0.74[b]	4.64	0.50	0.92	4.75
28	0.50[c]	0.81[c]	4.74	0.58[c]	0.96[c]	4.90
31	0.48[d]	0.80	4.70	0.54[d]	0.92[d]	4.82

[a] Conditions: Ag/AgCl electrode, Pt electrode, 20 °C, Bu_4NPF_6 (0.1 M in CH_3CN or CH_2Cl_2), scan rate 0.1 Vs^{-1}, [compound] 10^{-3} M. [b] [**27a**] $\ll 10^{-3}$ M, on account of the low solubility in CH_3CN. [c] Irreversible. [d] Quasi-reversible.

Conclusions

In conclusion, we have described a short and efficient synthetic route to the potentially useful symmetric bis(pyrrolo)-TTF **7** and the asymmetric monopyrrolo-TTFs **23a**,**b** and demonstrated that the new pyrrole synthesis for construction of α,α′-unsubstituted pyrrolo-annelated heterocycles is useful for 1,3-dithiole-2-thione. This route may be extended to other fused pyrroles as well.

(32) The X-ray data and molecular structures for compounds **22b** and **24b** are included as Supporting Information.

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Furthermore, we have developed an efficient synthesis of the asymmetric monopyrrolo-TTF **22c** and demonstrated that it is promising as a new building block for supramolecular and macrocyclic chemistry.

The pyrrolo-annelated tetrathiafulvalenes have highly extented π-surfaces, which strongly influence the physical properties of this class of heteocycles in both the solid state and in solution.

Investigations in the direction of tetrathiafulvalene-containing polypyrroles and porphyrin[35] systems are currently in progress.

Experimental Section

All reactions were carried out under an atmosphere of dry N_2 unless otherwise stated. THF was distilled from Na/benzophenone immediately prior to use; toluene was also purified by this procedure when high purity was needed. MeOH was distilled from Mg. DMF and CH_3CN were allowed to stand over molecular sieves (4 Å) for at least 3 days before use. Triethyl phosphite was purified by distillation and stored over molecular sieves (3 Å). All reagents were standard grade and used as received, except sodium tosylamide,[14d] 2-(tetrahydropyran-2-oxy)ethylamine,[26] 4,5-bis(hydroxymethyl)-1,3-dithiole-2-thione (**13**),[18] 4,5-bis(methylthio)-1,3-dithiole-2-thione,[16b,36] 4,5-bis(2-pentylthio)-1,3-dithiole-2-thione,[16b] 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione,[16a] 4,5-bis(methylthio)-1,3-dithiol-2-one,[37] and 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one,[16a] which were prepared according to the literature.

Analytical thin layer chromatography (TLC) was performed on Merck DC-Alufolien Kiselgel 60 F_{254} 0.2 mm thickness precoated TLC plates, while column chromatography was performed using Merck Kiselgel 60 (0.040−0.063 mm, 230−400 mesh AST0000M). Melting points (mp) are uncorrected. ^{1}H NMR spectra were recorded at 300 and 250 MHz, respectively. ^{13}C NMR spectra were recorded at 75 or 63 MHz using broad band decoupling. Cyclic voltammetry (CV) was carried out using CH_2Cl_2 or CH_3CN as solvent employing Bu_4NPF_6 (0.10 M) as supporting electrolyte, with a sweep rate of 0.100 V s^{-1}. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl.

4,5-Bis(bromomethyl)-1,3-dithiole-2-thione (14). A solution of **13** (4.85 g, 25.0 mmol) in THF (150 mL) was cooled on an ice bath before phosphorus tribromide (4.7 mL, 13.6 g, 50.4 mmol) was added, and the yellow solution was stirred for 30 min at 0 °C, whereupon the reaction mixture was stirred overnight at room temperature. The reaction mixture was concentrated in vacuo to a yellow oil, and carbon tetrachloride (100 mL) was added to precipitate the product, after which the mixture was left in a freezer for 2 h. The product was collected by filtration and washed with cold carbon tetrachloride to give 6.40 g (80%) of pure **14** as yellow needles: mp 125.5−126 °C dec (lit.[19] mp 124−126 °C). The combined filtrate was subsequently washed with 2 M HCl, saturated aqueous $NaHCO_3$ solution and H_2O. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to a yellow oil, which was dissolved in CH_2Cl_2 (20 mL) and filtered through a short column (4.5 cm silica gel, 10 cm Ø, CH_2Cl_2). The broad yellow band ($R_f = 0.8$) was collected and concentrated to give a yellow powder, which was recrystallized from CH_2Cl_2/petroleum ether (bp 60−80 °C) to give additional 0.90 g (11%) of **14** as fine yellow needles: mp 126−126.5 °C dec; ^{1}H NMR ($CDCl_3$) δ 4.33 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 20.1, 139.5, 208.3.

4,6-Dihydro-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (15a). Method 1. A solution of **14** (3.20 g, 10.0 mmol) in anhyd DMF (10 mL) was added dropwise over a period of 20 min to a suspension of TsNHNa (4.00 g, 20.7 mmol) in anhyd CH_3CN (100 mL) at 80 °C. The brown reaction mixture was stirred for further 5 min, whereupon the hot mixture was filtered through Celite (1 cm) and the filter washed with DMF. The filtrates were combined and allowed to cool to room temperature giving a yellow precipitate, which was collected by filtration and washed with CH_3CN to give 0.81 g (25%) of pure **15a** as yellow needles. The mother liquid was subsequently concentrated in vacuo and the brown residue was purified by column chromatography (silica gel, CH_2Cl_2, R_f = 0.4) to give additional 2.10 g (64%) of pure **15a** as yellow needles. Recrystallization from toluene/cyclohexane gave **15a** as fine yellow needles: mp 234 °C dec.

Method 2. A solution of **14** (4.81 g, 15.0 mmol) in anhyd DMF (75 mL) was added in one portion to a solution of TsNHNa (2.90 g, 15.0 mmol) in anhyd DMF (200 mL) at 80 °C, whereupon the orange brown reaction mixture was stirred for 1 h at 80 °C. Additional TsNHNa (2.90 g, 15.0 mmol) was added in one portion, leaving a dark brown reaction mixture. After the mixture was stirred for 1 h at 80 °C and cooled to room temperature, the solvent was removed in vacuo. The brown residue was dissolved in CH_2Cl_2 (500 mL), washed with H_2O (3 × 200 mL). The combined aqueous phases were extracted with CH_2Cl_2 (2 × 100 mL) and the combined organic phases were dried ($MgSO_4$). Concentration in vacuo gave a yellow brown solid, which was suspended in CH_2Cl_2 (75 mL) and purified by column chromatography (silica gel, CH_2Cl_2, R_f = 0.4) to give 3.00 g (61%) of **15a** as analytically pure yellow needles. Recrystallization from toluene/cyclohexane gave **15a** as fine yellow needles: mp 234 °C dec; ^{1}H NMR (DMSO-d_6) δ 2.40 (s, 3H), 4.47 (s, 4H), 7.46 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 21.0, 53.3, 127.6, 130.3, 133.1, 136.4, 144.4, 218.7; MS (EI) m/z 329 (M^+, 35), 173 (M^+ − HTs, 100); IR (KBr) ν 1343 (SO_2), 1158 (SO_2), 1055 (C═S) cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_2S_4$: C, 43.75; H, 3.37; N, 4.25; S, 38.92. Found: C, 43.91; H, 3.26; N, 4.24; S, 38.93.

4,6-Dihydro-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrol-2-one (15b). Mercuric acetate (5.49 g, 17.2 mmol) was added in one portion to a suspension of **15a** (3.00 g, 9.11 mmol) in a mixture of $CHCl_3$ (160 mL) and glacial acetic acid (16 mL) causing the initially yellow solution to change to white within 2 min. The resulting white suspension was stirred for 4 h at room temperature, whereupon the white precipitate was filtered using Celite (1.0 cm) and washed thoroughly with CH_2Cl_2. The combined organic phase was washed with saturated aqueous $NaHCO_3$ solution, H_2O and dried ($MgSO_4$). Evaporation of the solvent in vacuo gave 2.82 g (99%) of **15b** as an analytically pure off-white solid. Recrystallization from toluene/cyclohexane gave **15b** as fine off-white needles: mp 174−174.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H), 4.49 (s, 4H), 7.36 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.5, 53.7, 123.3, 127.6, 130.2, 133.5, 144.6, 193.9; MS (EI) m/z 313 (M^+, 14), 158 (M^+ − Ts, 58), 157 (M^+ − HTs, 100); IR (KBr) ν 1687 (C═O), 1343 (SO_2), 1160 (SO_2) cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_3S_3$: C, 45.99; H, 3.54; N, 4.47; S, 30.69. Found: C, 45.89; H, 3.49; N, 4.39; S, 30.79.

General Procedure for DDQ Oxidation of 15a and 15b. A mixture of **15a** or **15b** and 2.2 equiv of DDQ in chlorobenzene was refluxed until all starting material was consumed. After cooling to room temperature, the solvent was removed in vacuo and the brown residue was purified by column chromatography (silica gel, CH_2Cl_2/cyclohexane 1:1 or CH_2Cl_2) to give **16a** or **16b** as analytically pure compounds.

***N*-Tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (16a). 15a** (0.164 g, 0.50 mmol), chlorobenzene (10 mL), and reflux for 16 h: R_f = 0.3 (CH_2Cl_2/cyclohexane 1:1); yield 0.123 g (75%); yellow needles; mp 215−215.5 °C dec (CH_2Cl_2/cyclohexane); ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 7.16 (s, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.6, 110.6, 127.3, 128.8, 130.5, 135.0, 146.3, 218.8; MS (EI) m/z 327 (M^+, 72), 155 (Ts^+, 76), 91 (100); IR (KBr) ν 1372 (SO_2), 1174 (SO_2), 1049 (C═S) cm^{-1}. Anal. Calcd for $C_{12}H_9NO_2S_4$: C, 44.02; H, 2.77; N, 4.28; S, 39.16. Found: C, 44.16; H, 2.67; N, 4.28; S, 39.07.

(35) See, for example: Ramondenc, Y.; Schwenninger, R.; Phan, T.; Gruber, K.; Kratky, C.; Kräutler, B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 889−891.

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***N*-Tosyl-(1,3)-dithiolo[4,5-*c*]pyrrol-2-one (16b). 16a** (2.88 g, 9.19 mmol), chlorobenzene (120 mL), and reflux for 2 h: R_f = 0.5 (CH_2Cl_2); yield 2.71 g (95%); white powder; mp 178.5−179 °C (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H), 7.22 (s, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.6, 112.9, 119.5, 127.2, 130.4, 135.2, 146.1, 193.9; MS (EI) m/z 311 (M^+, 52), 283 ($M^+ - CO$, 23), 155 (Ts^+, 81), 91 (100); IR (KBr) ν 1716 (CO), 1369 (SO_2), 1171 (SO_2) cm^{-1}. Anal. Calcd for $C_{12}H_9NO_3S_3$: C, 46.29; H, 2.91; N, 4.50; S, 30.89. Found: C, 46.38; H, 2.81; N, 4.56; S, 30.85.

(1,3)-Dithiolo[4,5-*c*]pyrrole-2-thione (17). Compound **16a** (0.28 g, 0.82 mmol) was dissolved in anhyd THF−MeOH (1:1 v/v, 20 mL) and degassed (N_2, 15 min) before sodium methoxide (30% in MeOH, 0.80 mL, 0.23 g, 4.20 mmol) was added in one portion. The yellow solution was stirred for 60 min at room temperature, leaving a yellow orange solution. H_2O was added and pH adjusted (pH = 7) by addition of 4 M HCl. The yellow precipitate was filtered, whereupon the slight yellow filtrate was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo to give a yellow red residue. The yellow needles and the yellow red residue were combined and purified by column chromatography (silica gel, CH_2Cl_2/cyclohexane 9:1, R_f = 0.2) to give 0.12 g (84%) of pure **17** as yellow needles. Recrystallization from CH_2Cl_2/petroleum ether (bp 60−80 °C) gave **17** as fine yellow needles: mp 178−178.5 °C. The product is unstable under ambient conditions and darkens after a few days; ^{1}H NMR (DMSO-d_6) δ 7.14 (d, J = 2.6 Hz, 2H), 12.05 (bs, 1H); ^{13}C NMR (DMSO-d_6) δ 110.9, 121.4, 220.7; MS (EI) m/z 173 (M^+, 100); IR (KBr) ν 1055 (C=S) cm^{-1}. Anal. Calcd for $C_5H_3NS_4$: C, 34.66; H, 1.75; N, 8.08; S, 55.51. Found: C, 34.86; H, 1.93; N, 7.98; S, 55.23.

Bis(*N*-tosylpyrrolo[3,4-*d*])tetrathiafulvalene (18). Compound **16b** (1.03 g, 3.31 mmol) was suspended in distilled $P(OEt)_3$ (50 mL) and the suspension was heated to 120 °C, causing dissolution within 5 min, leaving a yellow reaction mixture. After approximately 15 min, a yellow precipitate was formed. The yellow suspension was stirred for 5 h at 120 °C, cooled to room temperature and addition of MeOH (50 mL) yielded a yellow solid which was filtered and washed with MeOH to give 0.82 g (84%) of **18** as analytically pure yellow needles: mp > 250 °C; ^{1}H NMR (DMSO-d_6) δ 2.38 (s, 6H), 7.38 (s, 4H), 7.45 (d, J = 8.4 Hz, 4H), 7.81 (d, J = 8.4 Hz, 4H); MS (EI) m/z 590 (M^+, 46), 435 ($M^+ - Ts$, 84), 280 ($M^+ - 2 \times Ts$, 100); IR (KBr) ν 1369 (SO_2), 1173 (SO_2) cm^{-1}. Anal. Calcd for $C_{24}H_{18}N_2O_4S_6$: C, 48.79; H, 3.07; N, 4.74; S, 32.56: Found: C, 48.64; H, 2.96; N, 4.74; S, 32.77.

Bis(pyrrolo[3,4-*d*])tetrathiafulvalene (7). A suspension of **18** (0.65 g, 1.10 mmol) in anhyd THF-MeOH (1:1 v/v, 90 mL) was degassed (N_2, 15 min) before sodium methoxide (30% in MeOH, 6.3 mL, 1.8 g, 33 mmol) was added in one portion. The yellow suspension was refluxed for 30 min, leaving a yellow solution, and cooled to room temperature. The reaction mixture was concentrated to approximately 30 mL, whereupon H_2O (150 mL) was added. The yellow precipitate was filtered, washed with H_2O and dried in vacuo to give 0.31 g (quant.) of **7** as an analytically pure yellow powder: mp 215−220 °C (dec without melting). Highly purified **7** can be obtained by column chromatography (Al_2O_3, deactivated with 4% H_2O, THF/MeOH 50:1): ^{1}H NMR (DMSO-d_6) δ 6.78 (d, J = 2.1 Hz, 4H), 11.08 (bs, 2H); ^{13}C NMR (DMSO-d_6) δ 110.6, 117.3, 119.5; MS (EI) m/z 282 (M^+, 100). Anal. Calcd for $C_{10}H_6N_2S_4$: C, 42.53; H, 2.14; N, 9.92; S, 45.41. Found: C, 42.47; H, 2.15; N, 9.66; S, 45.28.

General Procedure for *N*-Alkylation of 7. Compound **7** (0.052 g, 0.184 mmol) was dissolved in anhyd DMF (5 mL), cooled to 0 °C and degassed (N_2, 15 min) before the alkylating reagent was added to the yellow solution. Hexane washed sodium hydride (0.032 g, 1.33 mmol) was added in one portion, whereupon the resulting orange yellow reaction mixture was stirred for 1 h at 0 °C. Brine (20 mL) was added careful and the yellow precipitate was filtered, washed with H_2O, MeOH and dried in vacuo. The resulting yellow solid was purified by column chromatography (silica gel) to give **19a** or **19b** as analytically pure compounds.

Bis(*N*-methylpyrrolo[3,4-*d*])tetrathiafulvalene (19a). Alkylation using iodomethane (0.12 mL, 0.27 g, 1.90 mmol): R_f = 0.7 (CH_2Cl_2); yield 0.047 g (82%); yellow solid; mp 257−258 °C dec (toluene/petroleum ether (bp 60−80 °C)); ^{1}H NMR (DMSO-d_6) δ 3.60 (s, 6H), 6.75 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 36.8, 114.4, 116.9, 118.9; MS (EI) m/z 310 (M^+, 100). Anal. Calcd for $C_{12}H_{10}N_2S_4$: C, 46.42; H, 3.25; N, 9.02; S, 41.31. Found: C, 46.14; H, 3.39; N, 8.93; S, 41.02.

Bis(*N*-butylpyrrolo[3,4-*d*])tetrathiafulvalene (19b). Alkylation using butyl bromide (0.61 mL of a 0.90 M solution in DMF, 0.55 mmol): R_f = 0.4 (CH_2Cl_2/cyclohexane 1:1); yield 0.060 g (83%); yellow solid; mp 190.5−191 °C (toluene/petroleum ether (bp 60−80 °C)); ^{1}H NMR (DMSO-d_6) δ 0.87 (t, J = 7.2 Hz, 6H), 1.22 (sextet, J = 7.2 Hz, 4H), 1.64 (quintet, J = 7.2 Hz, 4H), 3.84 (t, J = 7.2 Hz, 4H), 6.81 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 13.9, 19.1, 32.9, 49.6, 113.4, 116.7, 119.1; MS (EI) m/z 394 (M^+, 100), 337 ($M^+ - {}^n$Bu, 4). Anal. Calcd for $C_{18}H_{22}N_2S_4$: C, 54.79; H, 5.62; N, 7.10; S, 32.50. Found: C, 54.91; H, 5.66; N, 7.15; S, 32.45.

Bis(2,5-dihydro-*N*-tosylpyrrolo[3,4-*d*])tetrathiafulvalene (20). A solution of **15b** (0.155 g, 0.49 mmol) in distilled $P(OEt)_3$ was heated at 120 °C for 2 h. After cooling to room temperature the resulting orange precipitate was collected by filtration, washed with MeOH and dried. Recrystallization from DMF gave 0.052 g (35%) of **20** as orange micro crystals: mp 272 °C (dec without melting); MS (EI) m/z 594 (M^+, 20), 438 ($M^+ - HTs$, 18), 282 ($M^+ - 2 \times HTs$, 14); IR (KBr) ν 1344 (SO_2), 1162 (SO_2) cm^{-1}. Anal. Calcd for $C_{24}H_{22}N_2O_4S_6$: C, 48.46; H, 3.73; N, 4.71. Found: C, 47.98; H, 3.46; N, 4.41.

2-[4,5-Bis(methylthio)-1,3-dithiole-2-ylidene]-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]-pyrrole 22a. Method 1. Compound **16b** (0.49 g, 1.57 mmol) and 4,5-bis(methylthio)-1,3-dithiole-2-thione (0.36 g, 1.59 mmol) were suspended in distilled $P(OEt)_3$ (15 mL) and heated to 130 °C (during heating the two solids dissolved leaving a red solution). After 5−10 min, a yellow precipitate was formed and the suspension was stirred for additional 20 min at 130 °C, whereupon 4,5-bis(methylthio)-1,3-dithiole-2-thione (0.36 g, 1.59 mmol) was added in one portion. The red reaction mixture was stirred for 3 h at 130 °C, cooled to room temperature and addition of MeOH (40 mL) yielded a yellow solid which was filtered and washed with MeOH. The yellow powder was purified by column chromatography (silica gel, CH_2Cl_2/cyclohexane 1:1, R_f = 0.3) to give a yellow orange semisolid, which was redissolved in CH_2Cl_2/MeOH (1:1 v/v, 80 mL) and concentrated to approximately half of its volume to precipitate the product. The yellow crystals were collected by filtration, washed with MeOH and dried in vacuo to give 0.44 g (57%) of **22a** as analytically pure yellow needles: mp 160−160.5 °C (CH_2Cl_2/MeOH); ^{1}H NMR (DMSO-d_6) δ 2.38 (s, 3H), 2.42 (s, 6H), 7.40 (s, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 18.4, 21.1, 112.5, 112.8, 117.7, 126.1, 126.2, 127.0, 130.6, 134.6, 146.0; MS (EI) m/z 489 (M^+, 86), 334 ($M^+ - Ts$, 100); IR (KBr) ν 1373 (SO_2), 1172 (SO_2) cm^{-1}. Anal. Calcd for $C_{17}H_{15}NO_2S_7$: C, 41.69; H, 3.09; N, 2.86; S, 45.83. Found: C, 41.85; H, 2.93; N, 2.90; S, 45.97.

2-[4,5-Bis(pentylthio)-1,3-dithiole-2-ylidene]-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]-pyrrole 22b. Compound **16b** (1.74 g, 5.59 mmol) and 4,5-bis(pentylthio)-1,3-dithiole-2-thione (1.50 g, 4.43 mmol) were suspended in distilled $P(OEt)_3$ (20 mL) and heated to 130 °C (during heating the two solids dissolved leaving a red solution and after 5−10 min a yellow precipitate was formed). Two additional portions of 4,5-bis(pentylthio)-1,3-dithiole-2-thione (0.90 g, 2.66 mmol) were added after 10 and 20 min, respectively. The red reaction mixture was stirred for 5 h at 130 °C and cooled to room temperature, and addition of MeOH (150 mL) yielded a yellow solid, which was filtered and washed with MeOH. The yellow solid was redissolved in CH_2Cl_2/MeOH (1:1 v/v, 100 mL) and concentrated to approximately half of its volume to precipitate the crude product, which was purified by column chromatography (silica gel, toluene, R_f = 0.5) to give 2.33 g (69%) of pure **22b** as yellow microcrystals. Recrystallization from acetone/cyclohexane gave yellow needles of **22b** suitable for X-ray analysis: mp 79−81 °C; ^{1}H NMR (DMSO-d_6) δ 0.84 (t, J = 7.0 Hz, 6H), 1.20−1.40

(m, 8H), 1.54 (quintet, $J = 7.0$ Hz, 4H), 2.37 (s, 3H), 2.82 (t, $J = 7.0$ Hz, 4H), 7.33 (s, 2H), 7.41 (d, $J = 6.8$ Hz, 2H), 7.79 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 13.7, 21.1, 21.6, 29.0, 30.00, 35.6, 112.5, 112.7, 117.2, 126.1, 126.8, 126.9, 130.3, 134.8, 145.7; MS (EI) m/z 601 (M^+, 83), 446 ($M^+ - Ts$, 100); IR (KBr) ν 1372 (SO_2), 1166 (SO_2) cm^{-1}. Anal. Calcd for $C_{25}H_{31}NO_2S_7$: C, 49.88; H, 5.19; N, 2.33; S, 37.29. Found: C, 49.95; H, 5.22; N, 2.38; S, 37.41.

2-[4,5-Bis(2-cyanoethylthio)-1,3-dithiole-2-ylidene]-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole 22c. Compound **16b** (3.00 g, 9.63 mmol) and 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione (2.93 g, 9.63 mmol) were suspended in distilled $P(OEt)_3$ (100 mL) and heated to 130 °C (during heating the two solids dissolved leaving a red solution and after 10−15 min a yellow orange precipitate was formed). Two additional portions of 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione (á 1.47 g, 4.82 mmol) were added after 10 and 20 min, respectively. The red reaction mixture was stirred for 1 h at 130 °C, cooled to room temperature and addition of MeOH (100 mL) yielded an orange solid, which was filtered and washed with MeOH. The orange powder was purified by column chromatography (silica gel, CH_2Cl_2, $R_f = 0.2$) to give 3.51 g (64%) of pure **22c** as an orange solid. Recrystallization from CH_2Cl_2/petroleum ether (bp 60−80 °C) gave **22c** as orange needles: mp 177−178 °C; ^{1}H NMR (DMSO-d_6) δ 2.38 (s, 3H), 2.86 (t, $J = 6.6$ Hz, 4H), 3.14 (t, $J = 6.6$ Hz, 4H), 7.39 (s, 2H), 7.46 (d, $J = 8.6$ Hz, 2H), 7.82 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 18.1, 21.0, 30.8, 112.0, 112.7, 118.1, 118.8, 125.9, 126.7, 127.2, 130.4, 134.4, 145.8; MS (EI) m/z 567 (M^+, 2); IR (KBr) ν 2251 (CN), 1375 (SO_2), 1172 (SO_2) cm^{-1}. Anal. Calcd for $C_{21}H_{17}N_3O_2S_7$: C, 44.42; H, 3.02; N, 7.40; S, 39.53. Found: C, 44.53; H, 2.98; N, 7.27; S, 39.63.

General Procedure for Detosylation of 22a and 22b. A solution of **22a** or **22b** in anhyd THF−MeOH (1:1 v/v) was degassed (N_2, 15 min) before NaOMe (30% solution in MeOH, 15 equiv) was added in one portion. The yellow solution was refluxed for 20 min, and after cooling to room temperature purification was performed as described below.

2-[4,5-Bis(methylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-*c*]pyrrole (23a). 22a (0.37 g, 0.76 mmol) and THF−MeOH (1:1 v/v, 50 mL). Removal of the solvent gave a yellow residue, which was dissolved in CH_2Cl_2 (60 mL), washed with H_2O, and dried ($MgSO_4$). Concentration in vacuo gave a yellow orange solid, which was purified by column chromatography (silica gel, CH_2Cl_2, $R_f = 0.3$) to give 0.24 g (95%) of **23a** as an analytically pure yellow orange solid: mp 143.5−144 °C dec; ^{1}H NMR (DMSO-d_6) δ 2.44 (s, 6H), 6.81 (d, $J = 2.9$ Hz, 2H), 11.14 (bs, 1H); ^{13}C NMR (DMSO-d_6) δ 18.4, 107.3, 110.9, 117.2, 122.0, 126.2; MS (EI) m/z 335 (M^+, 100), 320 ($M^+ - CH_3$, 24). Anal. Calcd for $C_{10}H_9NS_6$: C, 35.80; H, 2.70; N, 4.17; S, 57.33. Found: C, 35.91; H, 2.68; N, 4.15; S, 57.15.

2-[4,5-Bis(pentylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-*c*]pyrrole (23b). 22b (2.69 g, 4.47 mmol) and THF−MeOH (1:1 v/v, 100 mL). Removal of the solvent gave a yellow residue, which was dissolved in CH_2Cl_2 (150 mL), washed with H_2O and brine, and dried ($MgSO_4$). Concentration in vacuo gave a yellow orange solid, which was purified by column chromatography (silica gel, CH_2Cl_2, $R_f = 0.6$) to give 1.77 g (88%) of **23b** as a dark oil, which upon standing solidifed giving **23b** as analytically pure yellow crystals: mp 62−63 °C; ^{1}H NMR (DMSO-d_6) δ 0.86 (t, $J = 7.0$ Hz, 6H), 1.20−1.50 (m, 8H), 1.57 (quintet, $J = 7.0$ Hz, 4H), 2.85 (t, $J = 7.0$ Hz, 4H), 6.81 (d, $J = 2.3$ Hz, 2H), 11.13 (bs, 1H); ^{13}C NMR (DMSO-d_6) δ 13.7, 21.5, 28.8, 29.8, 35.2, 107.3, 110.6, 117.0, 121.5, 126.6; MS (EI) m/z 447 (M^+, 100). Anal. Calcd for $C_{18}H_{25}NS_6$: C, 48.28; H, 5.63; N, 3.13; S, 42.96. Found: C, 48.48; H, 5.57; N, 3.24; S, 42.84.

General Procedure for *N*-Alkylation of 23a. Compound **23a** (20.2 mg, 0.060 mmol) was dissolved in anhyd DMF (3 mL) and degassed (N_2, 15 min) before hexane washed sodium hydride (10 mg, 0.42 mmol) was added in one portion. The mixture was stirred for 15 min at room temperature, causing the initially yellow solution to become orange, whereupon the alkylating reagent was added in one portion, causing a color change to yellow. The reaction mixture was stirred for 1 h at room temperature, followed by careful addition of brine (20 mL). The yellow suspension was extracted with CH_2Cl_2, after which the yellow organic phase was washed with brine and H_2O. After drying ($MgSO_4$) and evaporation of the solvent, the resulting yellow oil was purified by column chromatography (silica gel, CH_2Cl_2 or CH_2Cl_2/cyclohexane 1:4) to give pure **24a**−**c** as yellow solids.

***N*-Methyl-2-[4,5-bis(methylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-*c*]pyrrole (24a).** Alkylation using iodomethane (0.06 mL, 0.14 g, 0.96 mmol): $R_f = 0.6$ (CH_2Cl_2); yield 19.5 mg (93%); yellow orange solid; mp 101−102 °C (CH_2Cl_2); ^{1}H NMR (DMSO-d_6) δ 2.43 (s, 6H), 3.60 (s, 3H), 6.78 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 18.4, 36.9, 107.2, 114.7, 116.8, 121.3, 126.2; MS (EI) m/z 349 (M^+, 100), 334 ($M^+ - CH_3$, 21). Anal. Calcd for $C_{11}H_{11}NS_6$: C, 37.79; H, 3.17; N, 4.01. Found: C, 37.34; H, 3.28; N, 4.24

***N*-Butyl-2-[4,5-bis(methylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-*c*]pyrrole (24b). Method 1.** Alkylation using butyl bromide (0.10 mL of a 0.90 M solution in DMF, 0.090 mmol): $R_f = 0.8$ (CH_2Cl_2); yield 21.0 mg (89%). Recrystallization from CH_2Cl_2/petroleum ether (bp 60−80 °C) gave **24b** as yellow plates suitable for X-ray analysis: mp 105.5−106 °C; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.30 (sextet, $J = 7.3$ Hz, 2H), 1.70 (quintet, $J = 7.3$ Hz, 2H), 2.42 (s, 6H), 3.81 (t, $J = 7.3$ Hz, 2H), 6.45 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5, 19.1, 19.6, 33.4, 50.5, 110.2, 112.5, 118.5, 121.3, 127.3; MS (EI) m/z 391 (M^+, 100), 376 ($M^+ - CH_3$, 20). Anal. Calcd for $C_{14}H_{17}NS_6$: C, 42.93; H, 4.37; N, 3.58; S, 49.11. Found: C, 43.03; H, 4.34; N, 3.69; S, 48.99.

***N*-Benzyl-2-[4,5-bis(methylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-*c*]pyrrole (24c).** Like **24a**,**b**, except that the reaction was performed on a larger scale. Compound **23a** (70.0 mg, 0.21 mmol), DMF (10 mL) and NaH (50 mg, 2.1 mmol). Alkylation using benzyl bromide (0.25 mL, 0.36 g, 2.10 mmol): $R_f = 0.25$ (CH_2Cl_2/cyclohexane 1:4); yield 80.0 mg (90%). Recrystallization from CH_2Cl_2/petroleum ether (bp 60−80 °C) gave **24c** as yellow needles: mp 133−134 °C; ^{1}H NMR (DMSO-d_6) δ 2.43 (s, 6H), 5.07 (s, 2H), 6.88 (s, 2H), 7.27 (m, 5H); ^{13}C NMR (DMSO-d_6) δ 18.4, 53.3, 107.7, 113.9, 117.3, 121.0, 126.0, 127.2, 127.6, 128.6, 138.2; MS (EI) m/z 425 (M^+, 76), 410 ($M^+ - CH_3$, 11). Anal. Calcd for $C_{17}H_{15}NS_6$: C, 47.97; H, 3.55; N, 3.29; S, 45.19. Found: C, 48.09; H, 3.52; N, 3.21; S, 45.23.

Potential of 22c as a Building Block for Supramolecular Chemistry. 2-[4-(2-Cyanoethylthio)-5-methylthio-1,3-dithiole-2-ylidene]-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole (25). A solution of **22c** (0.100 g, 0.18 mmol) in anhyd THF (10 mL) was degassed (N_2, 15 min) before a solution of $CsOH\cdot H_2O$ (0.032 g, 0.19 mmol) in anhyd MeOH (1 mL) was added dropwise via a syringe over a period of 1 h. The mixture was stirred for 15 min, whereupon MeI (0.52 mL, excess) was added in one portion. After stirring for further 30 min and removal of the solvent, the yellow residue was purified by column chromatography (silica gel, CH_2Cl_2/cyclohexane 2:1, $R_f = 0.35$) to give 0.089 g (96%) of **25** as an analytically pure yellow solid: mp 186.5−187 °C (CH_2Cl_2/cyclohexane); ^{1}H NMR (DMSO-d_6) δ 2.39 (s, 3H), 2.47 (s, 3H), 2.83 (t, $J = 6.6$ Hz, 2H), 3.10 (t, $J = 6.6$ Hz, 2H), 7.39 (s, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 18.0, 18.4, 21.0, 30.7, 112.2, 112.6, 117.6, 118.7, 120.6, 125.8, 125.8, 126.7, 130.3, 132.5, 134.3, 145.7 two lines overlapping; MS (EI) m/z 528 (M^+, 40), 373 ($M^+ - Ts$, 71); IR (KBr) ν 2251 (CN), 1372 (SO_2), 1172 (SO_2) cm^{-1}. Anal. Calcd for $C_{19}H_{16}N_2O_2S_7$: C, 43.16; H, 3.05; N, 5.29; S, 42.45. Found: C, 43.21; H, 3.03; N, 5.20; S, 42.54.

2-[4,5-Bis(methylthio)-1,3-dithiole-2-ylidene]-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole 22a. Method 2. A solution of **25** (0.050 g, 0.095 mmol) in anhyd THF (10 mL) was degassed (N_2, 15 min) before a solution of $CsOH\cdot H_2O$ (0.017 g, 0.10 mmol) in anhyd MeOH (1 mL) was added dropwise via a syringe over a period of 1 h. The mixture was stirred for 15 min, whereupon MeI (0.10 mL, excess) was added in one portion. After stirring for further 30 min and removal of the solvent the yellow residue was purified by column chromatography (silica gel, CH_2Cl_2/cyclohexane 1:1, $R_f = 0.3$) to give

0.044 g (95%) of pure **22a** as a yellow solid: mp 157−158 °C (CH_2Cl_2/cyclohexane).

Method 3. A solution of **22c** (0.20 g, 0.35 mmol) in anhyd THF (15 mL) was degassed (N_2, 15 min) before a solution of $CsOH·H_2O$ (0.062 g, 0.37 mmol) in anhyd MeOH (1 mL) was added dropwise via a syringe over a period of 1 h. The mixture was stirred for 15 min, whereupon MeI (0.44 mL, excess) was added in one portion. After stirring for further 45 min the solvent and excess of MeI were removed in vacuo. The yellow residue was redissolved in THF (15 mL) and degassed (N_2, 15 min) before a solution of $CsOH·H_2O$ (0.062 g, 0.37 mmol) in anhyd MeOH (1 mL) was added dropwise via a syringe over a period of 1 h. MeI (0.44 mL, excess) was added in one portion and after removal of the solvent the yellow residue was purified by column chromatography (silica gel, CH_2Cl_2/cyclohexane 1:1, R_f = 0.3) to give 0.16 g (93%) of pure **22a** as a yellow solid: mp 158−159 °C (CH_2Cl_2/cyclohexane). The spectroscopic data for **22a** obtained by methods 2 and 3 were identical to those reported by method 1.

Ring Closure Reaction Between 14 and Primary Amines. *N*-Butyl-4,6-dihydro-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (26a). Butylamine (0.73 g, 9.98 mmol) was added in one portion to a refluxing mixture of **14** (3.20 g, 10.0 mmol) and cesium carbonate (13 g, 40 mmol) in THF−CH_3CN (300 mL,1:2 v/v), whereupon the mixture was refluxed for 45 min. After the mixture was cooled to room temperature, the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (300 mL), washed with H_2O, and dried ($MgSO_4$). The organic phase was concentrated in vacuo and the crude product purified by column chromatography (silica gel, first CH_2Cl_2 then CH_2Cl_2/EtOAc 10:1, R_f = 0.4) to give 1.83 g (79%) of pure **26a** as a yellow oil, which upon cooling solidified. Recrystallization from hexane gave **26a** as yellow micro crystals: mp 105.5−106 °C; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3H), 1.39 (sextet, J = 7.2 Hz, 2H), 1.50 (quintet, J = 7.2 Hz, 2H), 2.74 (t, J = 7.2 Hz, 2H), 3.85 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 13.9, 20.3, 30.8, 56.0, 57.4, 138.6, 217.6; MS (EI) m/z 231 (M^+, 42); IR (KBr) ν 1055 (C=S) cm^{-1}. Anal. Calcd for $C_9H_{13}NS_3$: C, 46.72; H, 5.66; N, 6.05. Found: C, 46.87; H, 5.58; N, 5.95.

4,6-Dihydro-*N*-[2-(tetrahydropyran-2-oxy)ethyl]-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (26b). 2-(Tetrahydropyran-2-oxy)ethylamine (2.91 g, 20.0 mmol) was added in one portion to a refluxing mixture of **14** (6.40 g, 20.0 mmol) and cesium carbonate (26 g, 80 mmol) in THF−CH_3CN (600 mL,1:2 v/v), whereupon the mixture was refluxed for 1 h. After cooling to room temperature, the solvent was removed in vacuo and the yellow residue was dissolved in CH_2Cl_2 (400 mL), washed with H_2O and dried (Na_2SO_4). Concentration in vacuo gave a brown oil, which was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc 2:1, R_f = 0.3) to give 4.44 g (73%) of **26b** as an analytically pure light brown oil: ^{1}H NMR ($CDCl_3$) δ 1.50−1.80 (m, 6H), 3.03 (t, J = 5.5 Hz, 2H), 3.50−3.60 (m, 2H), 3.86−3.93 (m, 2H), 3.97 (s, 4H), 4.60 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 19.5, 25.2, 30.5, 55.5, 57.9, 62.4, 66.4, 99.1, 138.7, 217.7; MS (EI) m/z 303 (M^+, 17); IR (neat) ν 1057 (C=S) cm^{-1}. Anal. Calcd for $C_{12}H_{17}NO_2S_3$: C, 47.50; H, 5.65; N, 4.62. Found: C, 47.67; H, 5.57; N, 4.59.

4,6-Dihydro-*N*-(2-hydroxyethyl)-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (26c). To a well stirred solution of **26b** (4.44 g, 14.63 mmol) in acetone-MeOH (300 mL, 2:1 v/v) was added a 2 M HCl solution (20 mL) and the yellow reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo (T < 30 °C) and the yellow oily residue was treated with saturated aqueous $NaHCO_3$ solution (150 mL) to precipitate the product, which was collected by filtration, washed with H_2O and dried in vacuo to give 2.50 g (78%) of pure **26c** as a yellow powder. Extraction of the filtrate with EtOAc followed by drying of the combined organic phases (Na_2SO_4) and concentration in vacuo gave 0.64 g (20%) of pure **26c** as a yellow powder. Recrystallization from toluene/cyclohexane gave **26c** as yellow needles: mp 101.5−102 °C; ^{1}H NMR ($CDCl_3$) δ 2.38 (bs, 1H), 2.98 (t, J = 5.2 Hz, 2H), 3.69 (t, J = 5.2 Hz, 2H), 3.94 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 57.6, 58.0, 60.1, 138.3, 217.6; MS (EI) m/z 219 (M^+, 91); IR (KBr) ν 3154 (OH), 1055 (C=S) cm^{-1}. Anal. Calcd for $C_7H_9NOS_3$: C, 38.83; H, 4.14; N, 6.39. Found: C, 38.55; H, 4.27; N, 6.31.

***N*-(2-*tert*-Butyldiphenylsiloxyethyl)-4,6-dihydro-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (26d). Method 1.** To a solution of **26c** (0.44 g, 2.00 mmol) in anhyd DMF (20 mL) was first added *tert*-butyldiphenylchlorosilane (0.60 mL, 0.63 g, 2.30 mmol) in one portion followed by imidazole (1.50 g, 22.0 mmol). The yellow solution was stirred overnight at room temperature, whereupon the solvent was evaporated in vacuo. The brown oily residue was dissolved in CH_2Cl_2 (150 mL), washed with H_2O and dried ($MgSO_4$), after which the solvent was evaporated. The resulting yellowish brown residue was purified by column chromatography (silica gel, CH_2Cl_2, R_f = 0.2) to give 0.74 g (81%) of **26d** as a dark yellow oil. Leaving the product in a vacuum overnight afforded **26d** as an analytically pure yellow solid: mp 87−88.5 °C.

Method 2. 2-Aminoethanol (0.60 mL, 0.87 g, 14.2 mmol) was added in one portion to a refluxing mixture of **14** (3.20 g, 10.0 mmol) and cesium carbonate (13 g, 40 mmol) in THF−CH_3CN (300 mL,1:2 v/v), whereupon the mixture was refluxed for 30 min. After cooling to room temperature, the solvent was removed in vacuo. The yellowish brown residue was dissolved in EtOAc (400 mL) and washed with H_2O. The aqueous phase was extracted with EtOAc (3 × 150 mL) and the combined organic phases were dried (Na_2SO_4). Concentration in vacuo gave a yellow solid, which was redissolved in anhyd DMF (100 mL) and *tert*-butyldiphenylchlorosilane (3.00 mL, 3.17 g, 11.5 mmol) was added in one portion followed by imidazole (8.0 g, 118 mmol). The orange solution was stirred for 45 min, whereupon the solvent was evaporated in vacuo. The brown oily residue was dissolved in CH_2Cl_2 (300 mL), washed with H_2O and dried ($MgSO_4$). Concentration in vacuo gave a brown residue which was purified by column chromatography (silica gel, CH_2Cl_2, R_f = 0.2) to give 1.95 g (43%) of **26d** as a dark yellow oil. Leaving the product in a vacuum overnight afforded **26d** as an analytically pure yellow solid: mp 87.5−89 °C; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 9H), 2.94 (t, J = 5.6 Hz, 2H), 3.80 (t, J = 5.6 Hz, 2H), 3.87 (s, 4H), 7.41 (m, 6H), 7.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.0, 26.7, 57.8, 58.0, 63.3, 127.8, 129.8, 133.5, 135.6, 138.7, 217.8; MS (EI) m/z 457 (M^+, 3), 400 ($M^+ - {}^t$Bu, 40); IR (KBr) ν 1059 (C=S) cm^{-1}. Anal. Calcd for $C_{23}H_{27}NOS_3Si$: C, 60.35; H, 5.95; N, 3.06. Found: C, 60.13; H, 5.99; N, 3.04.

***N*-Butyl-4,6-dihydro-2-[4,5-bis(2-methylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-*c*]pyrrole (27a).** A mixture of **26a** (0.46 g, 1.99 mmol) and 4,5-bis(methylthio)-1,3-dithiol-2-one (0.63 g, 3.00 mmol) in neat $P(OEt)_3$ (10 mL) was refluxed for 30 min, whereupon additional 4,5-bis(methylthio)-1,3-dithiol-2-one (0.63 g, 3.00 mmol) was added in one portion and the red mixture was refluxed for further 1.5 h. After the mixture was cooled to room temperature, excess $P(OEt)_3$ was evaporated in vacuo and the red residue was purified by column chromatography (silica gel, EtOAc/hexane 1:10, R_f = 0.5) to give 0.27 g (34%) of pure **27a** as orange crystals. Recrystallization from hexane afforded **27a** as orange-rod like cystals: mp 78−79 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3H), 1.36 (sextet, J = 7.2 Hz, 2H), 1.47 (quintet, J = 7.2 Hz, 2H), 2.42 (s, 6H), 2.70 (t, J = 7.2 Hz, 2H), 3.62 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 19.2, 20.3, 30.9, 56.5, 57.3, 108.2, 120.4, 127.4, 129.6; FAB (EI) m/z 393 (M^+, 100). Anal. Calcd for $C_{14}H_{19}NS_6$: C, 42.71; H, 4.86; N, 3.56. Found: C, 42.48; H, 4.49; N, 3.52.

2-[4,5-Bis(2-cyanoethylthio)-1,3-dithiole-2-ylidene]-4,6-dihydro-*N*-[2-(tetrahydropyran-2-oxy)ethyl]-(1,3)-dithiolo-[4,5-*c*]pyrrole (27b). A mixture of **26b** (0.45 g, 1.48 mmol) and 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (1.06 g, 3.67 mmol) in $P(OMe)_3$ (10 mL) and toluene was refluxed for 30 min, whereupon additional 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (0.70 g, 2.43 mmol) was added in one portion and the orange red mixture was refluxed for further 2 h. Upon cooling MeOH (40 mL) was added and the orange solid that precipitated (tetrakis(2-cyanoethylthio)TTF) was collected by filtration. The filtrate was concentrated in vacuo and the orange red residue was purified by column chromatography (silica gel, CH_2Cl_2/CH_3CN 4:1, R_f = 0.3) giving an orange powder, which

was recrystallized from toluene/petroleum ether (bp 60−80 °C) to give 0.25 g (31%) of **27b** as fine orange crystals: mp 117−118 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.50−1.80 (m, 6H), 2.74 (t, J = 7.0 Hz, 4H), 2.98 (t, J = 5.7 Hz, 2H), 3.09 (t, J = 7.0 Hz, 4H), 3.49−3.55 (m, 2H), 3.74 (s, 4H), 3.84−3.89 (m, 2H), 4.62 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.7, 19.5, 25.3, 30.5, 31.1, 56.0, 57.8, 62.4, 66.5, 99.1, 105.4, 117.5, 124.1, 128.1, 129.7; MS (FAB) m/z 543 (M^+, 100); IR (KBr) ν 2250 (CN) cm^{-1}. Anal. Calcd for $C_{21}H_{25}N_3O_2S_6$: C, 46.38; H, 4.63; N, 7.73. Found: C, 46.34; H, 4.60; N, 7.65.

***N*-(2-*tert*-Butyldiphenylsiloxyethyl)-2-[4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-ylidene]-4,6-dihydro-(1,3)-dithiolo-[4,5-*c*]pyrrole (27d).** Compound **26d** (0.64 g, 1.40 mmol) and 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (0.40 g, 1.40 mmol) were suspended in distilled $P(OEt)_3$ (30 mL) and heated to 135 °C (during heating the two solids dissolved and an orange precipitate of tetrakis(2-cyanoethylthio)TTF was formed). Then 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (0.40 g, 1.40 mmol) was added in one portion and the orange red suspension was stirred for 30 min at 135 °C, followed by an addition of 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (0.40 g, 1.40 mmol). The orange red suspension was stirred for further 30 min at 135 °C and cooled to room temperature. Addition of MeOH (20 mL) yielded an orange solid, which was filtered and washed with MeOH. The combined filtrate was concentrated in vacuo and the resulting orange red oil was purified by column chromatography (silica gel, CH_2Cl_2/EtOAC 19:1, R_f = 0.3) to give 0.36 g (37%) of **27d** as an orange oil. The product is sufficiently pure (NMR and TLC) for further reaction, but can be purified further by column chromatography (silica gel, CH_2Cl_2/EtOAC 19:1, R_f = 0.3) to give 0.33 g (34%) of **27d** as an analytically pure orange oil: ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 9H), 2.73 (t, J = 7.1 Hz, 4H), 2.91 (t, J = 5.8 Hz, 2H), 3.08 (t, J = 7.1 Hz, 4H), 3.68 (s, 4H), 3.76 (t, J = 5.8 Hz, 2H), 7.40 (m, 6H), 7.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 18.7, 18.9, 26.7, 31.1, 57.8, 58.2, 63.2, 105.4, 117.5, 124.0, 127.7, 128.0, 129.7, 129.7, 133.4, 135.6; MS (FAB) m/z 697 (M^+, 100); IR (neat) ν 2250 (CN) cm^{-1}. Anal. Calcd for $C_{32}H_{35}N_3OS_6Si$: C, 55.06; H, 5.05; N, 6.02. Found: C, 55.27; H, 5.18; N, 5.90.

2-[4,5-Bis(2-cyanoethylthio)-1,3-dithiole-2-ylidene]-4,6-dihydro-*N*-(2-hydroxyethyl)-(1,3)-dithiolo[4,5-*c*]pyrrole (28). Method 1. To a solution of **27b** (0.50 g, 0.92 mmol) in acetone-MeOH (80 mL, 2:1 v/v) was added a 2M HCl solution (6 mL) and the orange solution was stirred overnight at room temperature, whereupon a saturated aqueous $NaHCO_3$ solution (50 mL) was added and the mixture was concentrated in vacuo to give an orange precipitate, which was collected by filtration, washed with H_2O and dried in vacuo. Recrystallization from EtOH gave 0.35 g (83%) of **28** as fine orange needles: mp 152−153 °C dec.

Method 2. A solution of 4 M HCl (0.07 mL, 0.28 mmol) was via a syringe added to a solution of **27d** (0.18 g, 0.26 mmol) in THF (10 mL) in one portion, whereupon TBAF (0.38 mL of a 1.0 M solution in THF, 0.38 mmol) was added dropwise to the orange red mixture. The reaction mixture was stirred at room temperature for 24 h, followed by addition of TBAF (0.38 mL of a 1.0 M solution in THF, 0.38 mmol) and stirred for further 16 h, after which saturated aqueous $NaHCO_3$ solution (25 mL) was added to precipitate the product, which was collected by filtration, washed with H_2O and dried in vacuo. Recrystallization from 2-propanol gave 0.063 g (54%) of **28** as an orange powder: mp 146−148 °C; ^{1}H NMR (DMSO-d_6) δ 2.74 (t, J = 6.0 Hz, 2H), 2.87 (t, J = 6.6 Hz, 4H), 3.15 (t, J = 6.6 Hz, 4H), 3.46 (m, 2H), 3.64 (s, 4H), 4.53 (t, J = 5.3 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 18.2, 30.8, 57.3, 58.3, 59.9, 105.9, 119.0, 121.2, 127.7, 129.7; MS (FAB) m/z 459 (M^+, 100); IR (KBr) ν 2251 (CN) cm^{-1}. Anal. Calcd for $C_{16}H_{17}N_3OS_6$: C, 41.81; H, 3.73; N, 9.14. Found: C, 41.70; H, 3.84; N, 8.85.

***N*-Butyl-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (29a).** A mixture of **26a** (1.15 g, 4.97 mmol) and DDQ (1.25 g, 5.51 mmol) in anhyd toluene (50 mL) was refluxed for 1 h. After cooling to room temperature, the precipitate was removed by filtration, and the filtrate was washed with 10% aqueous NaOH solution and dried ($MgSO_4$). The toluene solution was filtered through a pad of silica gel (3 cm), and concentration of the filtrate gave a dark brown oil, which was purified by column chromatography (silica gel, CH_2Cl_2, R_f = 0.7) to give 1.01 g (89%) of **29a** as an analytically pure dark brown oil, which solidified upon cooling: mp 40−41 °C; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3H), 1.32 (sextet, J = 7.2 Hz, 2H), 1.78 (quintet, J = 7.2 Hz, 2H), 3.97 (t, J = 7.2 Hz, 2H), 6.70 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5, 19.7, 33.4, 51.0, 111.7, 122.6, 219.5; MS (EI) m/z 229 (M^+, 100); IR (neat) ν 1047 (C=S) cm^{-1}. Anal. Calcd for $C_9H_{11}NS_3$: C, 47.13; H, 4.83; N, 6.11. Found: C, 47.18; H, 4.81; N, 6.08.

***N*-(2-*tert*-Butyldiphenylsiloxyethyl)-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (29d).** A mixture of **26d** (0.13 g, 0.28 mmol) and DDQ (0.13 g, 0.57 mmol) in anhyd toluene (15 mL) was stirred for 15 min at room temperature, whereupon the solvent was removed in vacuo. The dark red residue was purified by column chromatography (silica gel, CH_2Cl_2, R_f = 0.6) to give 0.11 g (86%) of **29d** as a brownish yellow oil. Leaving the product in a vacuum overnight afforded **29d** as an analytically pure yellow solid: mp 77.5−79 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 3.86 (t, J = 5.0 Hz, 2H), 4.06 (t, J = 5.0 Hz, 2H), 6.68 (s, 2H), 7.32−7.50 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 18.9, 26.6, 53.4, 63.8, 112.4, 123.0, 127.9, 130.0, 132.7, 135.5, 219.8; MS(EI) m/z 455 (M^+, 11), 398 ($M^+ - {}^t$Bu, 100); IR (KBr) ν 1040 (C=S) cm^{-1}. Anal. Calcd for $C_{23}H_{25}NOS_3Si$: C, 60.62; H, 5.53; N, 3.07; S, 21.11. Found: C, 60.47; H, 5.47; N, 3.13; S, 21.20.

***N*-Butyl-2-[4,5-bis(2-methylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-*c*]pyrrole (24b). Method 2.** A mixture of **29a** (1.37 g, 5.97 mmol) and 4,5-bis(methylthio)-1,3-dithiol-2-one (1.88 g, 8.94 mmol) in neat $P(OEt)_3$ (30 mL) was refluxed for 30 min, whereupon additional 4,5-bis(methylthio)-1,3-dithiol-2-one (1.88 g, 8.94 mmol) was added in one portion and the red mixture was refluxed for further 1 h. After cooling to room temperature, excess $P(OEt)_3$ was evaporated in vacuo and the red residue was purified by column chromatography (silica gel, EtOAc/hexane 1:10, R_f = 0.40) to give 1.30 g (56%) of **24b** as orange crystals. The complete separation of **24b** from tetrakis(methylthio)TTF may require two or three runs of column chromatography. Recrystallization from CH_2Cl_2/hexane afforded orange plates of **24b** suitable for X-ray analysis: mp 107−108 °C. The spectroscopic data for **24b** obtained by Method 2 were identical to those reported by Method 1.

***N*-(2-*tert*-Butyldiphenylsiloxyethyl)-2-[4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-*c*]pyrrole (30).** A mixture of **29d** (0.34 g, 0.75 mmol) and 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (0.22 g, 0.76 mmol) in distilled $P(OEt)_3$ (20 mL) was heated to 135 °C (during heating the two solids dissolved and an orange precipitate of tetrakis(2-cyanoethylthio)TTF was formed). Then 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (0.22 g, 0.76 mmol) was added in one portion and the orange red suspension was stirred for 30 min at 135 °C, followed by addition 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (0.22 g, 0.76 mmol). The orange red suspension was stirred for further 30 min at 135 °C and cooled to room temperature. Addition of MeOH (30 mL) yielded an orange solid, which was filtered and washed with MeOH. The combined filtrate was concentrated in vacuo and the resulting dark red oil was purified by column chromatography (silica gel, CH_2Cl_2, R_f = 0.25) to give 0.16 g (31%) of **30** as an orange oil. The product is sufficiently pure (NMR and TLC) for further reactions, but can be purified further by column chromatography to give **30** as an orange oil containing a small amount of CH_2Cl_2: ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 2.74 (t, J = 7.1 Hz, 4H), 3.09 (t, J = 7.1 Hz, 4H), 3.80 (t, J = 5.1 Hz, 2H), 3.93 (t, J = 5.1 Hz, 2H), 6.48 (s, 2H), 7.33−7.52 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 18.7, 19.0, 26.6, 31.2, 53.0, 64.0, 106.6, 113.2, 117.5, 118.5, 124.8, 127.8, 127.9, 129.9, 132.9, 135.6; MS(EI) m/z 695 (M^+, 55); IR (neat) ν 2250 (CN) cm^{-1}. Anal. Calcd for $C_{32}H_{33}N_3OS_6Si$: C, 55.22; H, 4.78; N, 6.04; S, 27.63 and $C_{32}H_{33}N_3OS_6Si\cdot 0.7CH_2Cl_2$: C, 51.98; H, 4.59; N, 5.56; S, 25.46. Found: C, 51.93; H, 4.57; N, 5.59; S, 25.90.

2-[4,5-Bis(2-cyanoethylthio)-1,3-dithiole-2-ylidene]-*N*-(2-hydroxyethyl)-(1,3)-dithiolo[4,5-*c*]pyrrole (31). Compound **30** (0.066 g, 0.095 mmol) was dissolved in anhyd THF (5 mL) and a 4 M HCl solution (0.05 mL, 0.20 mmol) was added

to the orange solution in one portion, followed by addition of TBAF (0.14 mL of a 1.0 M solution in THF, 0.14 mmol). The orange solution was stirred at room temperature for 45 min, whereupon additional TBAF (0.16 mL of a 1.0 M solution in THF, 0.16 mmol) was added. The reaction mixture was stirred for further 15 h and the solvent was evaporated in vacuo. The resulting orange oil was dissolved in EtOAc (40 mL), washed with H_2O, and dried (Na_2SO_4). Concentration in vacuo gave an orange solid, which was purified by column chromatography (silica gel, EtOAc, $R_f = 0.4$) to give 0.040 g (92%) of **31** as an analytically pure orange solid. Recrystallization from toluene/petroleum ether (bp 60−80 °C) gave **31** as an orange powder: mp 130−131 °C; ^{1}H NMR (DMSO-d_6) δ 2.88 (t, $J = 6.7$ Hz, 4H), 3.15 (t, $J = 6.7$ Hz, 4H), 3.60 (t, $J = 5.1$ Hz, 2H), 3.89 (t, $J = 5.1$ Hz, 2H), 4.89 (bs, 1H), 6.84 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 18.1, 30.7, 52.6, 61.1, 106.8, 114.0, 116.5, 118.9, 121.8, 127.3; MS(EI) m/z 457 (M^+, 6); IR (KBr) ν 2250 (CN) cm^{-1}. Anal. Calcd for $C_{16}H_{15}N_3OS_6$: C, 41.99; H, 3.30; N, 9.18; S, 42.03. Found: C, 41.88; H, 3.18; N, 9.02; S, 41.87.

Complex of Donor 7 with TCNQ. A hot solution of **7** (1 equiv) in CH_3CN was added to a hot solution of TCNQ (1 equiv) in CH_3CN. The resulting green solution was allowed to cool to room temperature and the crystals that precipitated was collected by filtration to give **7**·TCNQ as black plates: mp 220 °C (dec without melting); IR (KBr) 2208 (CN), 2197 (CN) cm^{-1}. Anal. Calcd for $C_{22}H_{10}N_6S_4$: C, 54.30; H, 2.07; N, 17.27. Found: C, 53.70; H, 2.23; N, 16.60.

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Supporting Information Available: X-ray crystal structures, crystal data, data collection details, and refinement parameters for **22b** and **24b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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