# Acetylenic Tetrathiafulvalene Scaffolds – Intramolecular Charge-Transfer Molecules

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Two tetrathiafulvalene-functionalized acetylenic scaffolds were synthesized by *Glaser–Hay* and *Sonogashira* coupling reactions; the one scaffold was based on a central dehydroannulene core and the other on a tetraethynylethene core. Peripheral propyl groups on the tetrathiafulvalenes ascertained solubility. The compounds are strong donor–acceptor chromophores and exhibit characteristic charge-transfer absorptions according to UV/VIS absorption spectroscopy. Furthermore, the redox properties were investigated by cyclic and differential-pulse voltammetries. The experiments allow for a direct comparison between the acceptor strengths of the two acetylenic cores, and the conclusions are supported by electron-affinity calculations.

**Introduction.** – Dehydroannulenes and tetraethynylethylenes are acetylenic scaffolds with excellent electron-acceptor properties [1]. Dehydroannulenes such as 1,3,5,7,9,13,15-hexadehydro[18]annulene (HDA; *Fig. 1*), first prepared by *Sondheimer* and co-workers [2], are fully conjugated macrocyclic systems and have been studied extensively to enhance the understanding of aromaticity and, in general, $\pi$-conjugation in unsaturated macrocyclic systems [3]. The unsubstituted dehydroannulenes are unstable and extremely sensitive towards $O_2$ [2c][2d] rendering investigations of their properties difficult. Therefore, *Diederich* and co-workers [4] prepared stable perethynylated derivatives using tetraethynylethylene (TEE; *Fig. 1*) as a building block. Substitution with *N,N*-dialkyl-*p*-anilino donor groups resulted in strong and red-shifted intramolecular charge-transfer transitions [5]. Donor–acceptor substitution of tetraethynylethene itself has also furnished a variety of chromophores of which several were shown to exhibit interesting third-order nonlinear optical properties [6].

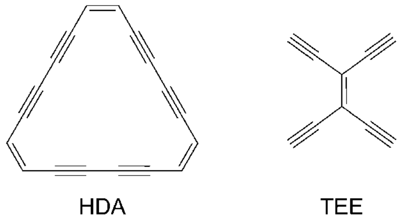
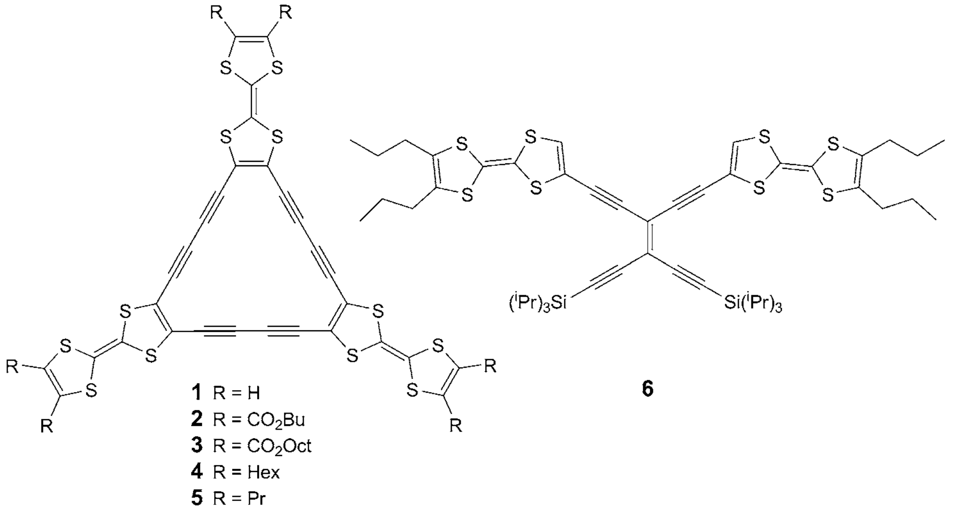


Fig. 1. *Acetylenic scaffolds: 1,3,5,7,9,13,15-hexadehydro[18]annulene* (HDA) *and tetraethynylethene* (TEE)

Owing to the electron-acceptor strengths of dehydroannulenes and TEEs, we have in recent years been interested in combining these molecules with the good electron donor tetrathiafulvalene (TTF) in order to gain new donor–acceptor chromophores. TTF can be reversibly oxidized in two steps, first generating the radical cation and second the dication, and has for this reason been explored considerably in supramolecular chemistry, molecular electronics, and materials science [7].

*Rubin* and co-workers [8] suggested in 1998 tris(tetrathiafulvaleno)dodecadehydro[18]annulene **1** as an attractive molecule for conductive charge-transfer salts (*Fig. 2*). Almost ten years after this proposal, derivatives were synthesized by *Iyoda* and co-workers [9], with peripheral ester groups (**2** and **3**), and by *Diederich*, *Nielsen*, and co-workers [10], with peripheral hexyl groups (**4**). Common for compounds **2**, **3**, and **4** were their excellent solubility, which, at the same time, prevented crystallization. For this reason, we became interested to investigate the possibility for achieving soluble macrocycles incorporating smaller alkyl groups, such as the Pr-substituted dehydroannulene **5**. Furthermore, we were interested in comparing the properties of this chromophore with the TEE scaffold **6** containing the same Pr-substituted TTF donors. A similar TEE scaffold incorporating TTFs with no peripheral substituents had previously been prepared, but in rather low yield [11].

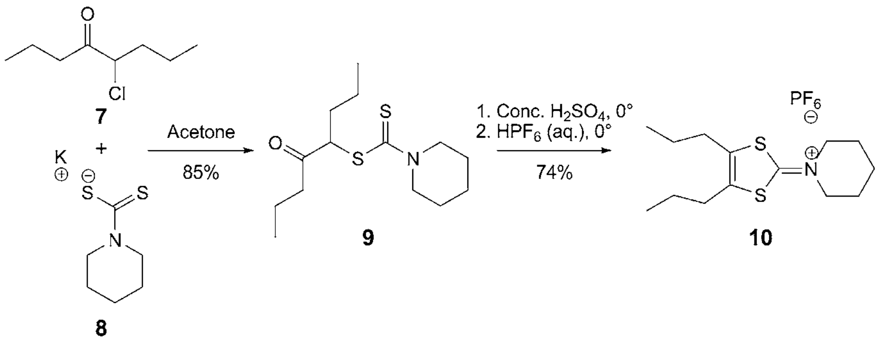


**1** R = H
**2** R = $CO_2Bu$
**3** R = $CO_2Oct$
**4** R = Hex
**5** R = Pr

**6**

Fig. 2. *Tetrathiafulvalene-functionalized HDA and TEE*

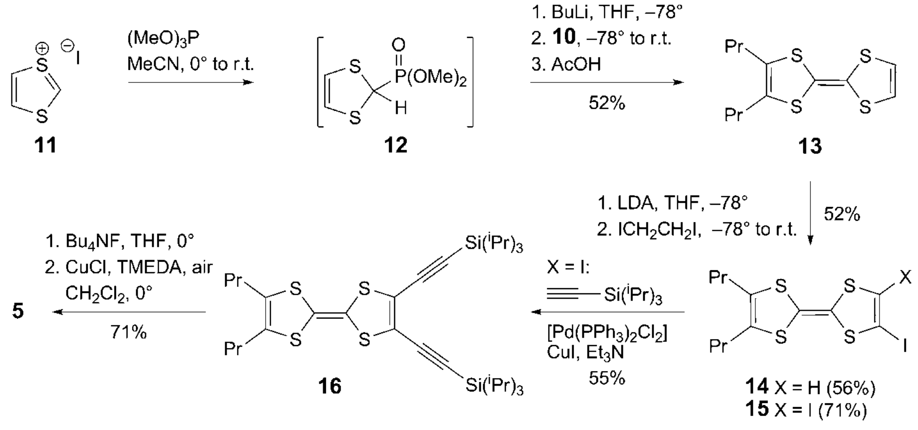
**Results and Discussion.** – *Synthesis.* First, a TTF derivative, in which one of the dithiol rings is substituted with Pr substituents, was prepared. The synthesis of unsymmetrically substituted TTFs is conveniently accomplished by *Horner–Wadsworth–Emmons* condensation between an iminium ion and a phosphonate ester, forming the central fulvalene bond in the final step [12]. The iminium half-unit was synthesized according to *Scheme 1*. Thus, 5-chlorooctan-4-one (**7**) was treated with potassium piperidine-1-carbodithioate (**8**) to furnish compound **9**. Ring-closing, Scheme 1



followed by dehydration, was accomplished by using concentrated $H_2SO_4$, and subsequent ion exchange provided the hexafluorophosphate salt **10**.

The known phosphonate **12** [13] was prepared by treating 1,3-dithiolium iodide **11** with $(MeO)_3P$ (*Scheme 2*). The crude product was deprotonated with BuLi and then treated with the electrophile **10**. After addition of AcOH in a deamination step, TTF **13** was obtained. Deprotonation of **13** by lithium diisopropylamide (LDA) gave mono- or dilithiated TTF, depending on the number of mol.-equiv. used. Treatment of either of these with 1,2-diiodoethane furnished TTFs **14** or **15**, respectively. The diiodo-TTF **15** was subjected to a *Sonogashira* cross-coupling reaction [14] with (triisopropylsilyl)-acetylene, which gave the dialkynylated TTF **16**. Desilylation of **16** by addition of $Bu_4NF$, followed by an oxidative *Hay* coupling reaction [15], gave the strongly violet-colored macrocycle **5**. The high yield (71%) of **5**, even higher than that previously obtained for **4** (47%) [10], signals the strong preference for cyclization of exactly three units. This preference for the [18]dehydroannulene ring size is likely explained by the fact that formation of other macrocycles would require unfavorable internal bond angles. Gratifyingly, macrocycle **5** exhibited excellent solubility in chlorinated solvents,

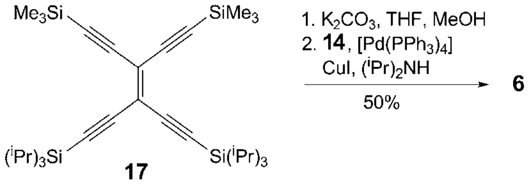
Scheme 2



which allowed studies on its optical and electrochemical properties. Several attempts of crystallization failed, however, indicating that the substituents may have to be even further reduced to reach this goal.

Our next objective was to functionalize the planar TEE core with two TTF units, containing Pr substituents on the terminal dithiol rings. Selective desilylation of the geminally substituted TEE **17** [16], followed by a double *Sonogashira* cross-coupling reaction with the monoiodo-TTF **14**, gave the TEE-TTF conjugate **6** as a dark purple solid (*Scheme 3*). Purification of **6** turned out rather difficult on account of the inherent acid sensitivity of the TTF moieties, which is likely amplified by the weakly electron-donating Pr substituents. For this reason, flash column chromatography was performed on silica neutralized with $Et_3N$. Dry column vacuum chromatography (DCVC) with neutralized silica could also be utilized as a purification method if performed under $N_2$ to avoid oxidation of the TTF moieties by air.

*Scheme 3*



*UV/VIS Spectroscopy.* Both **5** and **6** are purple compounds, which seem to indicate that they are both strong donor–acceptor chromophores. The UV/VIS absorption spectra of these compounds are shown in *Fig. 3*. The HDA-TTF **5** exhibited absorption properties similar to those of **4** [10] and is characterized by a broad charge-transfer absorption at *ca.* 525 nm with a broad shoulder at *ca.* 625 nm extending to *ca.* 800 nm

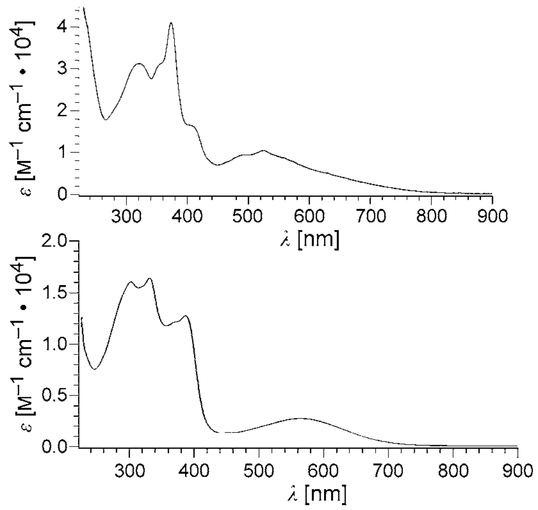


Fig. 3. *UV/VIS Spectra of* **5** (top) *and* **6** (bottom) *in* $CH_2Cl_2$

(1.55 eV). In comparison, the longest-wavelength absorption of the parent HDA is at 405 nm (reported as a shoulder) in cyclohexane [2d], while the longest-wavelength absorption of the parent TTF is at 450 nm (very weak) in hexane [17]. TEE-TTF **6** exhibited a broad charge-transfer absorption at *ca.* 565 nm extending to *ca.* 720 nm (1.72 eV), but with significantly lower molar absorptivities as compared to **5** (*Fig. 3*). In comparison, the longest-wavelength absorption maximum of the TEE precursor **17** was previously determined as 351 nm in MeOH [16].

The strong donor–acceptor character of the low-energy absorptions of TTF-fused dehydroannulenes were previously substantiated by HOMO and LUMO calculations, which revealed that the degenerate HOMO and HOMO-1 are situated at the TTF units, while the degenerate LUMO and LUMO + 1 are located on the cyclic core [10]. We decided to also calculate the frontier orbitals of TEE-TTF **6** (excluding the Pr groups), and the results are shown in *Fig. 4*. As for the TTF-dehydroannulene, the degenerate HOMO and HOMO-1 are almost exclusively located on the TTF moieties, while the LUMO is on the central acetylenic core. The calculations were performed at the B3PW91/6-31 + G** level using the Gaussian03 program package [18].

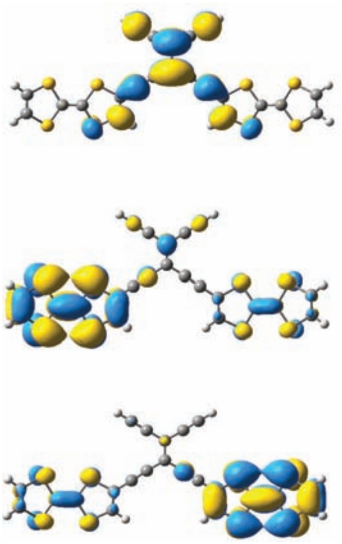


Fig. 4. *From top to bottom: LUMO, HOMO, and HOMO-1* (degenerate) *of TEE-TTF* **6** (without the Pr substituents)

*Cyclic Voltammetry.* Cyclic voltammetry (CV) of **5** revealed two reversible oxidations (*Fig. 5* and *Table*). The same behavior was previously observed for **4** [10]. However, the first oxidation wave of **5** was rather broad, and, by differential-pulse voltammetry (DPV), a shoulder to the first peak was discovered. This shoulder supports the previous claim that each of the two waves in the cyclic voltammogram involves more than one electron. Thus, each wave most likely involves three electrons corresponding to the generation of first three TTF radical cations and next three TTF dications. After the second oxidation, the molecule should then have an overall charge of six. In addition, compound **5** exhibited an irreversible reduction. The CV of TEE-

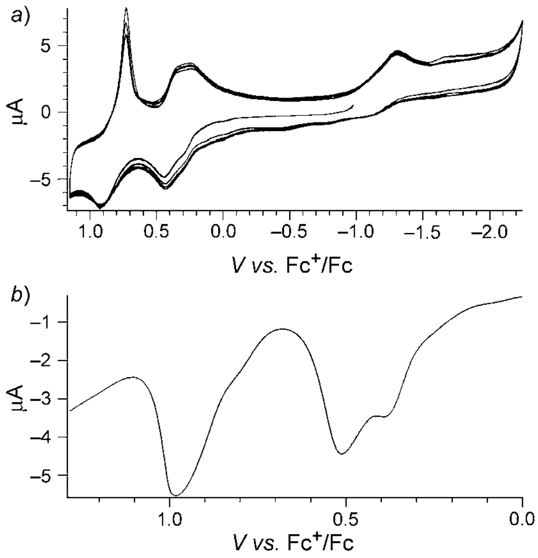


Fig. 5. a) *Cyclic voltammogram of* **5** *in* $CH_2Cl_2 + 0.1$M $Bu_4NPF_6$. b) *Differential-pulse voltammogram showing the oxidations of* **5** *in* $CH_2Cl_2 + 0.1$M $Bu_4NPF_6$. Potentials *vs.* $Fc^+/Fc$.

Table. *Cyclic and Differential Pulse-Voltammetry Data Measured in* $CH_2Cl_2 + 0.2$M $Bu_4NPF_6$ *for* **14** *and* **4**, *and in* $CH_2Cl_2 + 0.1$M $Bu_4NPF_6$ *for* **5** *and* **6**. All potentials *vs.* $Fc^+/Fc$. Working electrode, glassy carbon; counter electrode, Pt; reference electrode, $Ag/Ag^+$.

| Compound | CV[a]) | | DPV |
|---|---|---|---|
| | $E^{\text{o}}$[b]) [V] | $E_p$[c]) [V] | $E$ [V] |
| **14** | +0.00 | | |
| | +0.52 | | |
| **5** | +0.34 | | +0.39 |
| | | | +0.51 |
| | +0.82 | | +0.98 |
| | | – 1.31 | |
| **4**[d]) | +0.20 | | |
| | +0.64 | | |
| | +1.20 | | |
| | | – 1.40 | |
| | | – 1.70 | |
| **6** | +0.19 | | |
| | +0.73 | | |
| | – 1.45 | | |

[a]) Scan rate 0.1 V $s^{-1}$. [b]) $E^{\text{o}} = (E_{pc} + E_{pa})/2$, where $E_{pc}$ and $E_{pa}$ correspond to the cathodic and anodic peak potentials, respectively. [c]) Peak potential $E_p$ for irreversible electron transfer. [d]) From [10].

TTF **6** showed two reversible two-electron oxidations and one reversible reduction (*Fig. 6*). A small splitting of the first oxidation peak was, however, observed by DPV. From the data, the following electrochemical HOMO-LUMO gaps are estimated:

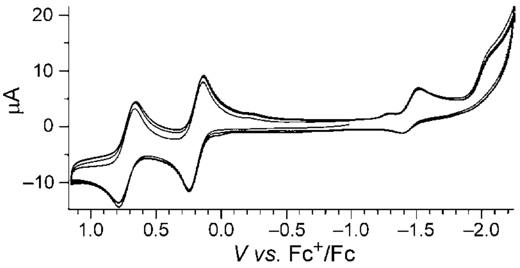


Fig. 6. *Cyclic voltammogram of* **6** *in* $CH_2Cl_2 + 0.1M\ Bu_4NPF_6$. Potentials *vs.* $Fc^+/Fc$.

1.60 eV (**4**), 1.65 eV (**5**), and 1.69 eV (**6**; by subtracting in each case the first cathodic reduction peak potential from the first half-wave potential of oxidation). Thus, the TEE-TTF has a slightly higher HOMO-LUMO gap than the HDA-TTFs, which is also reflected in the relative position of the charge-transfer absorptions (*vide supra*). This difference is likely the result of an enhanced acceptor strength of the dehydroannulene core relative to the TEE core. Indeed, calculations (B3PW91/6-311 + + G**//B3PW91/6-31 + G**) on the parent cores without TTF moieties (*cf.*, *Fig. 1*) provide vertical electron affinities of 0.86 (TEE) and 1.39 eV (HDA).

**Conclusions.** – In conclusion, donor–acceptor chromophores with central acetylenic cores and peripheral TTF donors were prepared by metal-catalyzed coupling reactions. The identical substitution of the TTF units allows direct comparison of the electronic properties of these compounds as determined by UV/VIS spectroscopy and electrochemistry. The experiments reveal that the HOMO–LUMO gap is slightly smaller for the TTF-dehydroannulene than for the TEE-TTF, but both compounds exhibit charge-transfer absorptions that extend to the near-IR. Despite less efficient electron delocalization *via* cross-conjugation in the TEE core, it has, according to calculations, an electron affinity that is only *ca.* 0.5 eV lower than that of the linearly conjugated and in addition larger hexadehydroannulene core. The low energy charge-transfer absorptions of both the TTF-dehydroannulene and TEE-TTF scaffolds support a relatively weak coupling between the donor and acceptor units (TTFs and acetylenic core, resp.) in accordance to frontier orbital calculations. This interpretation is in line with our previous studies on chromophores with donor and acceptor units that are either strongly or weakly coupled *via* a conjugated bridge [19]. In general, a low energy of a charge-transfer transition can result from two opposing conjugation effects: *i*) by an increase in the HOMO energy of the donor and a decrease in the LUMO energy of the acceptor as a result of extended conjugation of each of these individual units, and *ii*) by a poor mixing of the HOMO of the donor unit and the LUMO of the acceptor unit in the donor–acceptor chromophore *via* the conjugated bridge (*i.e.*, inefficient conjugation between the donor and acceptor units). We are currently targeting derivatives with less flexible substituent groups in the quest for compounds that can be crystallized in both the neutral and charged states.

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## Experimental Part

*General.* Chemicals were purchased from *Aldrich* and *Merck*, and used as received. Dry solvents were obtained from a Solvent Purification System, *Innovative Technology, Inc.* (dry THF was in some cases distilled from Na/benzophenone). All reactions were performed under Ar if not otherwise stated. *Hay* catalyst refers to a freshly prepared soln. of CuCl (100 mg, 1.0 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; 0.15 ml, 1.0 mmol) in $CH_2Cl_2$ (25 ml). Neutralization of $SiO_2$ was accomplished by flushing the column with 10% $Et_3N$ in heptane or $CH_2Cl_2$, followed by washing with either heptane or $CH_2Cl_2$. TLC was carried out using aluminum sheets pre-coated with silica gel *60F* (*Merck 5554*); the plates were inspected under UV light. $^1$H-NMR (300 MHz) and $^{13}$C-NMR (75 MHz) spectra: *Varian* instrument, using the residual solvent as the internal standard; all chemical shifts are quoted on the $\delta$ scale [ppm], and all coupling constants ($J$) are expressed in Hz. ESI-MS: *Micromass Q-TOF* spectrometer; FAB-MS: *Jeol JMS-HX 110* tandem mass spectrometer; MALDI-MS: *Bruker Daltonix Autoflex* time-of-flight apparatus or a *Bruker Daltonics UltraFlex II* apparatus. Microanalyses were performed at the Department of Chemistry, University of Copenhagen.

*5-Oxooctan-4-yl Piperidine-1-carbodithioate* (**9**). To a soln. of **7** (3.51 g, 21.6 mmol) in acetone (100 ml), *potassium piperidine-1-carbodithioate* (**8**; 4.6 g, 23.1 mmol) was added, and the mixture was stirred at r.t. for 3 h. The solvent was removed *in vacuo*, and $Et_2O$ (200 ml) was added. The resulting mixture was washed with $H_2O$ (3 × 100 ml); the $H_2O$ phase was extracted with $Et_2O$ (100 ml), and the combined org. phases were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to provide **9** (5.29 g, 85%). Colorless oil. An anal. pure sample was obtained by column chromatography (CC; $SiO_2$; heptane/AcOEt 9:1). $^1$H-NMR (300 MHz, $CDCl_3$): 4.99 (*t*, $J = 7.1$, 1 H); 4.30, 4.22 (2 br. *s*, 2 H); 3.91 (br. *s*, 2 H); 2.45–2.83 (*m*, 2 H); 1.58–2.03 (*m*, 10 H); 1.30–1.53 (*m*, 2 H); 0.87–1.02 (*m*, 6 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 208.1; 194.2; 59.7; 53.6; 51.8; 43.6; 32.6; 26.2; 25.6; 24.4; 20.7; 17.4; 14.1; 13.9. FAB-MS: 288 ($[M+H]^+$). Anal. calc. for $C_{14}H_{25}NOS_2$ (287.48): C 58.49, H 8.77, N 4.87; found C 58.38, H 8.93, N 4.76.

*1-(4,5-Dipropyl-1,3-dithiol-2-ylidene)piperidinium Hexafluorophosphate* (**10**). Compound **9** (2.79 g, 9.72 mmol) was dissolved during 30 min in an ice-cold soln. of conc. $H_2SO_4$ (12 ml). The mixture was allowed to reach r.t. and then stirred for 4 h, then it was poured slowly into ice-cold $H_2O$ (50 ml) containing $HPF_6$ (2.38 g, 60 wt-% in $H_2O$, 9.72 mmol). The resulting precipitate was filtered, washed with $H_2O$ (2 × 10 ml), and then dissolved in $CH_2Cl_2$ (100 ml). The mixture was washed with $H_2O$ (50 ml), sat. aq. $NaHCO_3$ (50 ml), and $H_2O$ (50 ml); then it was dried ($MgSO_4$), filtered, and concentrated *in vacuo* to a volume of *ca.* 20 ml. The product was precipitated by addition of $Et_2O$ (50 ml), filtered, and washed with $Et_2O$ (10 ml), providing **10** (2.70 g, 74%). White crystals. M.p. 77–78°. $^1$H-NMR (300 MHz, $CDCl_3$): 3.78 (*t*, $J = 5.7$, 4 H); 2.63 (*t*, $J = 7.6$, 4 H); 1.82–1.98 (*m*, 4 H); 1.72–1.82 (*m*, 2 H); 1.54–1.72 (*m*, 4 H); 0.98 (*t*, $J = 7.3$, 6 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 184.8; 134.0; 56.6; 30.4; 25.0; 23.7; 21.5; 13.5. ESI-MS: 270 ($[M - PF_6]^+$), 685 ($[2M - PF_6]^+$). Anal. calc. for $C_{14}H_{24}F_6NPS_2$ (415.10): C 40.47, H 5.82, N 3.37; found C 40.52, H 5.74, N 3.31.

*2-(1,3-Dithiol-2-ylidene)-4,5-dipropyl-1,3-dithiole* (**13**). A suspension of **11** (3.68 g, 16.01 mmol) in dry MeCN (80 ml) was cooled to 0°, whereupon $(MeO)_3P$ (2.08 ml, 17.6 mmol) was added dropwise. The soln. was allowed to reach r.t. and was then stirred for 0.5 h. The mixture was then concentrated *in vacuo*, and the crude phosphonate ester **12** was dissolved in dry THF (40 ml), and the mixture was cooled to −78°. BuLi (10.0 ml, 2.5M in hexanes, 16.0 mmol) was added, resulting in a milky white color of the mixture. After stirring for 10 min, **10** (7.99 g, 19.2 mmol) in dry THF (7 ml) was added in one portion. The mixture was stirred for 15 min at −78°, then allowed to reach r.t., and stirred for another 45 min. Then, AcOH (8 ml) was added, and stirring was continued for an additional 3 h. The mixture was then concentrated *in vacuo* to a dark green oil. $Et_2O$ (70 ml) was added, and the org. phase was twice washed with $NaHCO_3$ (50 ml) and $H_2O$ (50 ml). CC ($SiO_2$; hexane/AcOEt 94:6) afforded **13** (2.40 g, 52%). Orange oil. $^1$H-NMR (300 MHz, $CDCl_3$): 6.27 (*s*, 2 H); 2.34 (*t*, $J = 7.5$, 4 H); 1.38–1.69 (*m*, 4 H); 0.93 (*t*,

$J = 7.3$, 6 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 129.0; 119.4; 109.4; 108.6; 31.0; 23.3; 13.9. HR-MALDI-MS: 288.0129 ($M^+$, $C_{12}H_{16}S_4^+$; calc. 288.0135). Anal. calc. for $C_{12}H_{16}S_4$ (288.52): C 49.96, H 5.59; found C 50.32, H 5.49.

*2-(4-Iodo-1,3-dithiol-2-ylidene)-4,5-dipropyl-1,3-dithiole* (**14**). To a soln. of **13** (233.8 mg, 0.8104 mmol) in dry THF (12 ml) at − 78° was added freshly prepared LDA (2.71 ml, 0.72M in THF, 1.94 mmol) dropwise, and the mixture was stirred for 2 h at low temp. 1,2-Diiodoethane (553.0 mg, 1.96 mmol) was added in one portion, and the mixture was stirred for an additional 1 h at low temp. The mixture was then allowed to heat to 0° and was stirred for an additional h, and the reaction was quenched with sat. aq. $Na_2S_2O_3$ (2 ml). The mixture was concentrated *in vacuo*, and $Et_2O$ (100 ml) was added. The org. phase was washed with $H_2O$ (3 × 100 ml), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. CC (neutralized $SiO_2$; $Et_2O$/Pentane 15 : 85) afforded **14** (372.1 mg, 56%). Orange oil. $^1$H-NMR (300 MHz, $CDCl_3$): 6.39 (*s*, 1 H); 2.33 (*t*, $J = 7.5$, 6 H); 1.54 (*sext.*, $J = 7.5$, 6 H); 0.94 (*t*, $J = 7.5$, 9 H). $^{13}$C-NMR (50 MHz, $CDCl_3$): 128.9; 124.6; 119.3; 109.5; 64.2; 31.3; 23.6; 14.2 (missing signals due to overlap). HR-MALDI-MS: 413.9100 ($M^+$, $C_{12}H_{15}IS_4^+$; calc. 413.9101).

*2-(4,5-Diiodo-1,3-dithiol-2-ylidene)-4,5-dipropyl-1,3-dithiole* (**15**). $^iPr_2NH$ (0.85 ml, 6.0 mmol) was dissolved in dry THF (10 ml) and cooled to 0°. Then, BuLi (2.36 ml, 2.5M in hexane, 5.90 mmol) was added. The resulting soln. of LDA was added to a soln. of **13** (567 mg, 1.97 mmol) in THF (35 ml) cooled to − 78°. After stirring for 2 h at − 78°, 1,2-diiodoethane (1.67 g, 5.92 mmol) was added. The mixture was stirred for 1 h at − 78°, then allowed to reach r.t., and stirred for another 2 h. Sat. aq. $Na_2S_2O_3$ (100 ml) was added, and the mixture was extracted with $Et_2O$ (100 ml + 2 × 70 ml). The combined org. phases were washed with $H_2O$ (70 ml), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. CC (neutralized $SiO_2$; heptane/AcOEt 99 : 1) afforded **15** (759 mg, 71%). Red solid. M.p. *ca.* 65° (dec.). $^1$H-NMR (300 MHz, $CDCl_3$): 2.33 (*t*, $J = 7.3$, 4 H); 1.42 – 1.63 (*m*, 4 H); 0.93 (*t*, $J = 7.3$, 6 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 128.8; 124.5; 115.3; 111.0; 30.8; 23.2; 13.8. FAB-MS: 539 ($M^+$). Anal. calc. for $C_{12}H_{14}I_2S_4$ (540.31): C 26.68, H 2.61; found C 26.62, H 2.67.

*{[2-(4,5-Dipropyl-1,3-dithiol-2-ylidene)-1,3-dithiole-4,5-diyl]diethyne-2,1-diyl}bis[tri(propan-2-yl)silane]* (**16**). To an Ar-flushed soln. of **15** (600 mg, 1.11 mmol) and (triisopropylsilyl)acetylene (0.62 ml, 2.78 mmol) in $Et_3N$ (50 ml), $[Pd(PPh_3)_2Cl_2]$ (150 mg, 0.213 mmol), and CuI (42.0 mg, 0.222 mmol) were added. The mixture was stirred at r.t. under Ar for 48 h, filtered through a plug of $SiO_2$ (heptane), and concentrated *in vacuo*. CC (neutralized $SiO_2$; heptane) gave **16** (397 mg, 55%). Red oil. $^1$H-NMR (300 MHz, $CDCl_3$): 2.32 (*t*, $J = 7.5$, 4 H); 1.39 – 1.63 (*m*, 4 H); 1.00 – 1.15 (*m*, 42 H); 0.92 (*t*, $J = 7.3$, 6 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 128.8; 121.5; 114.9; 104.0; 102.7; 96.9; 30.9; 23.2; 18.8; 13.8; 11.4. MALDI-MS: 648 ($M^+$). Anal. calc. for $C_{34}H_{56}S_4Si_2$ (649.24): C 62.90, H 8.69; found C 62.68, H 8.85.

*2,9,16-Tris(4,5-dipropyl-1,3-dithiol-2-ylidene)-4,5,6,7,11,12,13,14,18,19,20,21-dodecadehydrocyclooctadeca[1,18-*d*:12,13-*d'*:6,7-*d''*]tris[1,3]dithiole* (**5**). To a soln. of **16** (250 mg, 0.386 mmol) in THF (20 ml) cooled to 0°, $Bu_4NF$ (0.78 ml, 1M in wet THF, 0.78 mmol) was added, and the dark red soln. was stirred for 10 min. The mixture was filtered through a plug of $Al_2O_3$ (heptane/$CH_2Cl_2$ 1 : 1). Most of the solvent was removed under reduced pressure to give the desilylated dialkyne as a dark red oil, which was dissolved in $CH_2Cl_2$ (40 ml) and cooled to 0°. *Hay* catalyst (7 ml) was added, and the mixture was stirred at 0° in a flask open to the air for 1 h. The mixture was filtered through a plug of $Al_2O_3$ (heptane/$CH_2Cl_2$ 1 : 1) and concentrated *in vacuo*. CC (neutralized $SiO_2$; heptane/$CH_2Cl_2$ 1 : 1) afforded **5** (91.7 mg, 71%). Dark purple solid. M.p.: decomp. $^1$H-NMR (300 MHz, $CDCl_3$): 2.36 (*t*, $J = 7.5$, 12 H); 1.40 – 1.68 (*m*, 12 H); 0.95 (*t*, $J = 7.3$, 18 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 128.8; 125.3; 118.9; 102.1; 85.2; 79.7; 30.9; 23.2; 13.8. MALDI-MS: 1002 ($M^+$). Anal. calc. for $C_{66}H_{78}S_{12}$ (1256.11): C 63.11, H 6.26, S 30.63; found C 63.37, H 6.14, S 30.41.

*TEE-TTF* (= *(6-[2-(4,5-Dipropyl-1,3-dithiol-2-ylidene)-1,3-dithiol-4-yl]-4-{[2-(4,5-dipropyl-1,3-dithiol-2-ylidene)-1,3-dithiol-4-yl]ethynyl}-3-{[tri(propan-2-yl)silyl]ethynyl}hex-3-ene-1,5-diyn-1-yl)[tri(propan-2-yl)]silane*; **6**). Compound **17** (88.9 mg, 0.15 mmol) in THF (2 ml) was added to a soln. of $K_2CO_3$ (92.8 mg, 0.67 mmol) in MeOH (10 ml), and the mixture stirred at r.t. for 20 min. Then, the soln. was filtered through a short plug of $SiO_2$ ($CH_2Cl_2$). $^iPr_2NH$ (3 ml) was added to the org. phase, before it was concentrated *in vacuo* until only $^iPr_2NH$ was left. Additional $^iPr_2NH$ (5 ml) was added, and the soln. was flushed vigorously with a stream of Ar on an ultrasound bath for 30 min. Then, $[Pd(PPh_3)_4]$ (8.8 mg, 0.0076 mmol) and CuI (4.2 mg, 0.022 mmol), and finally a soln. of **14** in Ar-flushed $^iPr_2NH$ (2 ml), which caused the soln. to turn dark purple, were added. After stirring at r.t. for 1 h, heptane (20 ml) was added, and the mixture was filtered through a plug of neutralized $SiO_2$ ($CH_2Cl_2$) and concentrated *in vacuo* to a dark purple solid. CC (neutralized $SiO_2$; heptane/AcOEt 96:4) gave **6** (75.3 mg, 50%). Dark purple, non-crystalline solid. $^1$H-NMR (300 MHz, $CD_2Cl_2$): 6.61 (*s*, 2 H); 2.35 (*t*, *J* = 7.2, 8 H); 1.54 (*sext.*, *J* = 7.2, 8 H); 1.12 (*m*, 42 H); 0.94 (*t*, *J* = 7.2, 12 H). $^{13}$C-NMR (75 MHz, $CD_2Cl_2$): 129.1; 128.7; 127.8; 118.3; 115.3; 115.1; 113.2; 105.8; 104.5; 103.6; 90.2; 90.0; 31.1; 23.7; 19.0; 13.9; 11.8. HR-MALDI-MS: 1008.296 ($M^+$; $C_{52}H_{72}S_8Si_2^+$; calc. 1008.294).

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