

Synthesis and Characterization of Tetrathiafulvalene-Substituted Di- and Tetraethynylethenes with *p*-Nitrophenyl Acceptors

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Novel di- and tetraethynylethene (DEE and TEE) compounds functionalized with tetrathiafulvalene (TTF) donor groups and *p*-nitrophenyl acceptor groups were synthesized by palladium-catalyzed cross-coupling reactions under various conditions. The molecules are strong chromophores and were investigated for their optical properties. Placement of two TTFs and two *p*-nitrophenyls about a central TEE core provides a molecule with a high third-order optical nonlinearity. The molecules experience reversible oxidations of the TTF units, and the optical properties of the oxidized species were elucidated by spectroelectrochemistry. The degree of quinoid character of the *p*-nitrophenyl in the molecules was determined by X-ray crystallography.

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Introduction

Tetrathiafulvalene (TTF) is a good electron donor that is oxidized reversibly in two steps, hereby gaining heteroaromaticity,¹ and it has for this reason found wide applications in both materials and supramolecular chemistry.² In recent years, several nonlinear optical (NLO) investigations on TTF donor acceptor dyads have been undertaken, pioneered by Martín and co-workers,³ while the third-order NLO properties of chromophores incorporating the parent TTF unit have been less explored.⁴ A variety of dimeric TTFs have been reported in which two TTF units are linked by a conjugated spacer that may convey an intramolecular interaction between the two TTFs. For example, extensive conjugation in an ethynediyl-bridged TTF dimer is apparent from its UV-vis absorption spectrum as it is not merely a superposition of the spectra of two isolated TTFs.⁵ We became interested in separating two TTF donor units by larger acetylenic scaffolds, such as the tetraethynylethene (TEE) unit. It was previously shown by Diederich, Günter, and co-workers⁶ that donor-acceptor aryl-substituted TEEs exhibit remarkable third-order NLO properties owing to the coplanarity of the aryl groups. Here we describe the synthesis of new chromophores incorporating TTF as donor unit and *p*-nitrophenyl as acceptor unit about acetylenic cores, such as TEE or

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diethynylethene (DEE). The optical properties as well as electrochemical and spectroelectrochemical properties are compared to scaffolds incorporating dithiafulvene (DTF, i.e., TTF "half-unit") as donor unit, *cis/trans*-1 and TEE 2.⁷ These previously investigated DTF compounds unfortunately suffered from irreversible electrochemical oxidations. As eventually we want to combine the inherent TTF redox properties with the scaffolding power of acetylenic modules,⁸ we found it attractive to substitute the DTF donor groups with "intact" TTFs. The syntheses rely on modifications of the Sonogashira palladium-catalyzed coupling reaction⁹ between aryl/vinylic halides and terminal alkynes and on ready access to the *p*-nitrophenyl-based vinylic bromide building blocks *trans*-3, 4, and 5 recently developed by us (Chart 1).⁷

Results and Discussion

Synthesis. The vinylic bromide *trans*- 3^7 was treated with ethynyltetrathiafulvalene 6^5 in a Sonogashira cross-coupling reaction to give *trans*-7 in good yield (Scheme 1). To prepare the corresponding cis compound, the dibromide 4^7 was converted to *cis*-3 in a stereoselective hydrogenolysis¹⁰ using Bu₃SnH and cat. [Pd(PPh₃)₄] (Scheme 2). This compound was subsequently subjected to a Sonogashira cross-coupling reaction with 6, which furnished *cis*-7. The alternative one-pot reaction (4 to *cis*-7) gave a lower yield compared to that of the stepwise

SCHEME 1. Synthesis of Donor-Acceptor trans-DEE







process. Although the two stereoisomers have nonidentical proton chemical shift values, a verification of the proposed stereochemistry was not possible based only on the ¹H NMR

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SCHEME 3. Synthesis of Donor-Acceptor TEE



spectra. Yet, the IR spectrum of *trans*-7 showed a strong absorption at 933 cm⁻¹ which was not present in the spectrum of *cis*-7. This band was assigned to a C–H out-of-plane twisting mode characteristic of a trans substituted ethene. Conclusive evidence for the isomer designations was obtained from an X-ray crystal structure of *trans*-7 (vide infra).

Since the solubility of the previously reported DTF-functionalized TEE 2 in organic solvents was rather low,⁷ we decided to incorporate hexyl substituents at the TTF units in the analogous TTF-functionalized TEE. The synthesis is revealed in Scheme 3. Monolithiation of the known 4,5-dihexylTTF 8¹¹ was accomplished using LDA in THF at -78 °C and subsequent trapping with 1,2-diiodoethane afforded 9 in 78% yield. Next, a Sonogashira cross-coupling reaction with trimethylsilylacetylene gave 10 in 62% yield. This relatively low yield was due to a competing deiodination reaction producing 4,5-dihexylTTF in almost 30% (isolated yield). This side reaction has been reported previously and seems to be more pronounced for electron-rich electrophiles.^{11,12} Desilylation provided the terminal alkyne 11. Attempted coupling of dibromide 5 with 11 using the [Pd(PPh₃)₂Cl₂]/CuI catalyst system failed to provide the target donor-acceptor compound 12. Many cross-couplings are enhanced by using bulky, electron-rich phosphines,¹³ and SCHEME 4. Synthesis of TTF-TEE

(i-Pr)₃Si



Si(i-Pr)

hence we decided to use the catalyst system, $[Pd(PhCN)_2Cl_2]/t$ -Bu₃P/CuI, developed by Hundertmark et al.,¹⁴ which allows coupling of aryl bromides with a wide variety of terminal acetylenes at rt. By using this catalyst system in combination with ultrasonification at 30 °C for 5 h we obtained the TTF-substituted TEE **12** in a yield of 31%. Substituting $[Pd(PhCN)_2-Cl_2]/t$ -Bu₃P with the commercially available $[Pd(t-Bu_3P)_2]$ improved the yield to 40% and reduced the reaction time to 30 min employing ultrasound conditions. Promotion of the Sonogashira cross-coupling reaction using ultrasound has attracted considerable interest in recent years.^{7,15} In particular, we have found this method useful for Sonogashira reactions that produce compounds of limited stability and that hence would not tolerate conditions of conventional or microwave heating.⁷

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Finally, a cross-coupling reaction was performed between the vinylic dibromide 13^{16} and the alkyne 6 (Scheme 4), which furnished TTF-TEE 14 lacking the acceptor substituents. The rather low yield of this 2-fold coupling reaction may in part be ascribed to the lower reactivity of the vinylic dibromide in the absence of the electron-withdrawing *p*-nitrophenyl groups.

X-ray Crystallographic Analysis. Single crystals of *cis*-**3** were obtained by slow evaporation of a CH_2Cl_2 /heptane solution at rt. The structure obtained by X-ray crystallographic analysis is shown in Figure 1a. Unfortunately, we did not manage to obtain crystals of *cis*-**7** that were suitable for X-ray analysis. However, crystals of *trans*-**7** suitable for X-ray crystallographic analyses were grown by slow evaporation of a CDCl₃ solution at rt. The X-ray crystal structure of *trans*-**7** confirms the postulated isomer designation (Figure 1b).

All the atoms of *trans*-7 are nearly coplanar, except that the central double bond is twisted ca. 23° in respect to the plane of the rest of the molecule. The crystal packing diagram (Figure

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FIGURE 1. Ortep-style plots of the X-ray crystal structures of cis-3 (a) and trans-7 (b) (generated using the program Platon¹⁷).



FIGURE 2. Crystal packing of *trans*-7 (generated using the program PyMol¹⁸).



FIGURE 3. Definition of bond lengths for calculation of quinoid character (δr).

2) shows a short contact between one of the vinyl hydrogen atoms and an oxygen atom of the nitro group of a neighbor molecule (2.56 Å). Molecules of *trans*-7 form pseudodimers, in which the molecules stack with an antiparallel molecular dipole orientation and an intermolecular distance of 3.64 Å.

The bond length alternation in the ground-state of the p-nitrophenyl ring can be expressed by the quinoid character of the ring defined as in Figure 3.¹⁹

Interestingly, no change in quinoid character was found upon replacing the DTF-donor (*trans*-1, $\delta r = 0.011$ Å) with the stronger electron donor TTF (*trans*-7, $\delta r = 0.011$ Å). For CHART 2



comparison, the same quinoid character was found for the *p*-nitrophenyl ring of *p*-NO₂C₄H₆C \equiv CC₆H₄NH₂ ($\delta r = 0.011$ Å). Compound **15**,²⁰ with a single triple bond between the DTF-unit and the *p*-nitrophenyl ring, exhibits a δr value of 0.027 Å, indicating a larger contribution of the quinoid structure in the ground-state compared with the other molecules (Chart 2).

Electronic Absorption Spectroscopy. UV–vis absorption data for the new compounds *cis*-7, *trans*-7, 12, and 14 are collected in Table 1 together with literature data for *cis*-1, *trans*-1, and $2.^{7b}$

The longest-wavelength absorption for TTF-TEE 12 extends beyond 850 nm and is significantly red-shifted relative to that of cis-7 and trans-7 (Figure 4). This decrease in the HOMO-LUMO gap is ascribed to the more extended conjugated TEE system compared with the DEE system. The strongest absorption band in trans-7 exhibits approximately twice the molar absorptivity than that of the corresponding absorption band of *cis*-7; a trend that was also observed for *cis*-1 and *trans*-1.^{7b} A large red-shift of the longest-wavelength absorption is seen when comparing the TTF-substituted compounds cis-7, trans-7 and 12 with the corresponding DTF-substituted compounds *cis*-1, trans-1, and 2. These red-shifts are explained by the stronger donor character of TTF compared to that of DTF, and hence a higher energy HOMO, which decreases the HOMO-LUMO gap. Interestingly, the CT absorption bands in the TTF compounds have much smaller molar absorptivities compared to the absorption bands at higher energy. This is in contrast with the finding from the DTF-substituted compounds, for which the CT bands exhibit roughly the same molar absorptivity as

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TABLE 1. UV-vis Absorption Maxima (λ_{max}) and Molar Absorptivities (ϵ) in CHCl₃^{*a*}

	-		- · · ·			
compd	$\lambda_{\max} \text{ [nm]} (\epsilon \text{ [M}^{-1} \text{ cm}^{-1} \text{]})$					
cis-7 trans-7 12 14 cis-1 ^b	303 (27700) 300 (sh, 51600) 301 (32900) 305 (sh, 16800)	325 (sh, 24600) 336 (61500) 322 (33200) 330 (20600)	362 (sh, 17400) 349 (42300) 433 (30800) 364 (25100) 423 (12600)	497 (br, 2700) 490 (br, 5900) 661 (br, 8400) 377 (24800)	520 (br, 6100)	
$trans-1^b$ 2^b	305 (sh, 10800) 305 (sh, 16400) 301 (29900)	325 (19300) 327 (34600)	423 (12000) 424 (29800) 343 (sh, 33400)	381 (23000)	491 (35400)	525 (sh, 29000)

^{*a*} sh = shoulder; br = broad. ^{*b*} Reference 7b.



FIGURE 4. UV-vis spectra of acetylenic TTF chromophores in CHCl₃.

the higher energy transitions. It is also noteworthy that compound **14** devoid of the *p*-nitrophenyl acceptor groups exhibits a significant CT absorption band, albeit blue-shifted relative to that of **12**. This observation agrees with previous findings that the TEE core is by itself a good electron acceptor.²¹ Thus, tetrakis(trimethylsilylethynyl)ethene (**16**) is reduced at -1.96 V vs Fc⁺/Fc.²¹

Nonlinear Optical Properties. The third-order optical polarizability of 12 was determined by measuring the third-order susceptibility of a solution of the compound in chloroform at various concentrations. We used Degenerate Four Wave Mixing with 1-ps long pulses at a wavelength of $\lambda = 1500$ nm. The rotational average of the third-order polarizability of 12 was found to be $\gamma_{rot} = 9 \pm 3 \times 10^{-48} \text{ m}^5 \text{V}^{-2}$. This value can be compared to related TEE molecules incorporating instead anilino donor groups,⁶ which were measured by third-harmonic generation from a wavelength of 1.9 μ m. The best molecule (17) was found to have a third-order polarizability $\gamma_{\rm rot} = 14.8$ \pm 0.7 \times 10^{-48} m^5 V^{-2}, while TEE 18 incorporating the same *p*-nitrophenyl acceptor groups as **12** was found to have $\gamma_{\rm rot} =$ $11.6 \pm 0.6 \times 10^{-48} \text{ m}^5 \text{V}^{-2}$ (Chart 3).^{6d} Thus, compound 12 exhibits NLO properties that resemble those of related arylated TEEs,^{6b} and the high γ -value indicates that larger acetylenic TEE-TTF scaffolds are worthwhile to pursue in the future. As TTF is a particularly useful π -donor molecule for intermolecular host-guest systems based on donor-acceptor interactions,^{2b} larger supramolecular assemblies based on such scaffolds are also interesting targets. In addition, it should be noted that the three reversible redox states of TTF (0, +1, +2) makes it a particularly attractive unit in redox-controlled NLO devices. Indeed, compound 12 exhibits reversible electrochemistry (vide infra) in contrast to the previously investigated TEE-extended **TTF 2**.

Electrochemistry. Cyclic voltammetry (CV) data show that the novel TTF compounds *cis/trans*-7, 10, and 12 experience



TABLE 2. Cyclic Voltammetry Data Measured in $CH_2Cl_2 + 0.15 \text{ M}$ $Bu_4NPF_6^a$

Compd	E_{1}^{0} [V] ^b	$E^{0}_{2} [V]^{b}$
cis-7	+0.13	+0.61
trans-7	+0.01	+0.52
10	-0.07	+0.45
12	0.00	+0.48
14	+0.04	$+0.45^{\circ}$
19	+0.02	+0.55

^{*a*} All potentials versus Fc⁺/Fc. ^{*b*} $E^0 = (E_{\rm pc} + E_{\rm pa})/2$, where $E_{\rm pc}$ and $E_{\rm pa}$ are the cathodic and anodic peak potentials, respectively. Index 1 and 2 refers to the first and second reversible oxidation steps, respectively. ^{*c*} Cathodic peak is enhanced, presumably owing to adsorption.

two well-resolved reversible oxidations in CH₂Cl₂ (Table 2, Figure 5). For compound 14 some adsorption of the oxidized species seems to occur at the electrode as judged from the appearance of the CV. For both 12 and 14, each oxidation step is ascribed to two electrons and hence the two TTFs act as independent redox centers. The first oxidation of 14 is anodically shifted relative to the TTF reference compound 19, while the second oxidation step occurs more readily. Both oxidation steps for cis-7 are anodically shifted relative to those of trans-7. In cis-7 the electron-withdrawing p-nitrophenyl-substituent is forced closer in space to the TTF moiety than in trans-7, and this interaction may possibly account for the more difficult oxidation of cis-7 relative to that of trans-7. The redox potentials of the parent ethynylTTF 19 are very similar to those of trans-7, which seems to indicate that the through-bond interaction alone of the donor and acceptor is not enough to alter the oxidation potentials (Chart 4). This conclusion is in agreement with the small ground-state quinoid character ascertained by X-ray crystallography as well as by frontier orbital calculations (vide infra).

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FIGURE 5. Cyclic voltammograms measured in $CH_2Cl_2 + 0.15$ M Bu_4NPF_6 . All potentials vs Fc⁺/Fc.

CHART 4



Owing to the electron-donating effect of the hexyl substituents both oxidation steps of 10 are lowered by ca. 0.1 V relative to those of 19. The oxidation steps for TEE 12 are anodically shifted relative to those of the corresponding ethynylTTF 10. Spectroelectrochemistry of TEE 12 is shown in Figure 6. For the first oxidation step (electrolysis at +0.10 V versus Fc⁺/Fc), absorption bands at $\lambda_{max} = 438$ and 678 nm are observed and attributed to the dication 12^{2+} . These evolving absorption bands are assigned to intrinsic absorptions of the two TTF radical cations. The spectral evolution shows isosbestic points (not shown), which suggest that disproportionation does not take place; that is, mixed oxidative states are not observed. The second oxidation (electrolysis at +0.58 V versus Fc⁺/Fc), generating the tetracation 12^{4+} , is accompanied by a decrease in the 678-nm absorption, while a broad absorption around 550 nm appears. For comparison, the parent TTF radical cation exhibits absorptions at 430 and 580 nm, while the dication absorbs at 390 nm.²² The lowest energy absorption maxima are collected in Table 3 together with spectroelectrochemical data of cis/trans-7. The extended conjugation results in significantly red-shifted absorption maxima of the oxidized species of the acetylenic TTF scaffolds relative to those of the parent TTF.



FIGURE 6. UV–vis spectroelectrochemistry of **12** in CH_2Cl_2 (+ 0.15 M Bu₄NPF₆). Electrolysis at +0.10 V vs Fc⁺/Fc generates **12**²⁺, and electrolysis at +0.58 V vs Fc⁺/Fc generates **12**⁴⁺.

TABLE 3. Low-Energy Absorption Maxima (λ_{max}) of Oxidized Species in CH₂Cl₂ (+0.15 M Bu₄NPF₆)^{*a*}

Compd	λ_{\max} [nm]
$[cis-7]^+$ $[cis-7]^+$ $[trans-7]^+$ $[trans-7]^{2+}$ 12^{2+}	426, 618 550 (br) ^b 409, 626 528 (br) 438, 678
12^{4+} TTF $^{+c}$ TTF $^{2+c}$	550 (br) 430, 580 390

 a br = broad. b Spectral evolution did not show fully isosbestic behavior for this oxidation process. c Reference 22.

Computational Study. Compound **12** devoid of the hexyl substituents was subjected to a computational study at the B3LYP/6–31G(d) level using the Gaussian03 program package.²³ The optimized structure deviates slightly from planarity. The frontier orbitals are shown in Figure 7. Both the HOMO-1 and HOMO are located almost entirely at the TTF units, while the LUMO and LUMO+1 include both the nitrophenyl groups and the central TEE spacer and in the case of the LUMO also a part of the TTFs. The location of the HOMO at the donor groups agrees well with the relatively small change in electrochemical properties induced by the TEE unit and contrasts the appearance of the HOMO of **2** that was found previously to include both the DTFs and the TEE spacer.^{7b}

Conclusions

Palladium-catalyzed cross-coupling reactions have allowed the synthesis of DEE/TEE-TTFs incorporating *p*-nitrophenyl acceptor groups. These chromophores exhibit charge-transfer absorptions that are red-shifted relative to those of previously investigated DEE/TEE-DTFs. TEE compound 12 incorporating two geminal TTF groups and two geminal p-nitrophenyl groups exhibits a high third-order optical nonlinearity that is comparable to that of related arylated TEEs, which makes it an attractive candidate for future device fabrication. It is noteworthy that this compound exhibits two reversible two-electron oxidations. These reversible redox properties were not experienced by the previously investigated TEE-DTF 2 incorporating two DTFs instead of two TTFs. The π -electrons of the DTF units in 2 are considerably delocalized onto the TEE unit; this delocalization does not seem to be as significant for the π -electrons of the TTF units in 12 (and neither for those in *cis/trans-7*) as judged from both cyclic voltammetry data and the appearance of the HOMO and HOMO-1. The optical properties of the cationic species were investigated in detail by spectroelectrochemistry,

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FIGURE 7. Frontier orbitals of 12 (devoid of the hexyl substituents) (B3LYP/6-31G(d)).

which revealed significantly red-shifted absorption maxima of the oxidized species relative to those of the parent TTF. All in all, the incorporation of TTF rather than DTF is an important structural modification, and larger acetylenic scaffolds based on TEE-TTFs are attractive targets to pursue in the future.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of Ar or N₂ by applying a positive pressure of the protecting gas. Deactivation of silica was done by stirring the silica with Et₃N/heptane 1:9, packing the column and finally flushing with heptane. ¹³C NMR data were calibrated using δ (CDCl₃) = 77.0 ppm and δ (CD₂Cl₂) = 54.0 ppm.

Nonlinear Optics. The third-order susceptibility of compound **12** dissolved in chloroform was determined by degenerate four wave mixing (DFWM) at a wavelength of 1500 nm and using a 1-kHz pulsed laser (pulse duration 1 ps). The DFWM signal for varying concentrations of the solution was measured along with an identical cuvette of chloroform for reference, and the signals where calibrated using a fused silica reference with a third-order susceptibility of $1.9 \times 10^{-22} \text{ m}^2 \text{V}^{-2}$.

Electrochemistry and UV–Vis Absorption Spectroscopy. Cyclic voltammetry was measured using a platinum working electrode and a Pt wire counter electrode. All potentials are expressed relative to that of Fc⁺/Fc and were measured in CH₂Cl₂ with 0.15 M Bu₄NPF₆ as supporting electrolyte; scan rate 0.1 V s⁻¹. All measured potentials are uncorrected for ohmic drop. Spectroelectrochemical experiments were performed in a 1-mm absorption cuvette (Quartz), the counter electrode was separated from the solution by a glass frit, and a Pt grid (mesh 400) was used as working electrode. Setting the potential at ca. 0.1 V more oxidative value than the peak potentials found from cyclic voltammetry, the UV/vis spectra of the neutral and cationic species were recorded on a UV–vis spectrophotometer. The same spectrophotometer was used to determine the molar absorptivities of the neutral species (1-cm path length cuvette).

trans-4-[6-(4-Nitrophenyl)hex-3-ene-1,5-diynyl]tetrathiafulvalene (trans-7). To a solution of the bromide trans-3 (43 mg, 0.17 mmol) in argon-degassed toluene (1.5 mL) was added $[Pd(PPh_3)_4]$ (10 mg, 8.6 μ mol), and the mixture was stirred at rt for 0.5 h. Then i-Pr₂NH (0.3 mL) was added followed by the terminal alkyne 6 (42 mg, 0.18 mmol) in degassed THF (1 mL). The reaction mixture was degassed with argon for a few minutes, whereupon CuI (7 mg, 37 μ mol) was added. After stirring for 3 h at rt, the mixture was filtered through a short plug of silica (SiO_2 , CH₂Cl₂). Column chromatography (SiO₂, CH₂Cl₂/cyclohexane, 1:3) afforded trans-7 (56 mg, 82%) as a red solid. mp 207-209 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.25$ (s, 1 H), 6.26 (s, 1 H), 6.33 (s, 1 H), 6.34 (s, 1 H), 6.57 (s, 1 H), 7.58 (d, 8.8 Hz, 2 H), 8.20 (d, 8.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ = 87.2, 91.8, 92.7, 93.6, 107.5, 113.9, 115.5, 118.8, 119.1, 120.6, 121.5, 123.7, 126.5, 129.5, 132.3, 147.2. IR (KBr): $\tilde{\nu} = 3436$ (br), 3073 (w), 2167 (m), 1595 (m), 1583 (m), 1510 (vs), 1489 (w), 1339 (vs), 1309 (m), 1285 (w), 1254 (w), 1224 (w), 1173 (w), 1109 (m), 933 (s), 853 (s), 829 (w), 797 (w), 777(m), 748 (m), 686 (w), 649 (m) cm⁻¹. MS(FAB): $m/z = 399 [M^+]$. HR-MS(FAB): $m/z = 398.9518 [M^+]$ (calcd for C₁₈H₉NO₂S₄: 398.9516).

cis-1-Bromo-4-(4-nitrophenyl)but-1-en-3-yne (cis-3). To a solution of the dibromide 4 (415 mg, 1.25 mmol) in toluene (10 mL) cooled to 0 °C was added [Pd(PPh₃)₄] (72 mg, 0.063 mmol) followed by Bu₃SnH (0.35 mL, 1.3 mmol), and the mixture was stirred at 0 °C for 2.5 h. Heptane (75 mL) was added and the organic phase washed with H_2O (2 × 50 mL), dried (MgSO₄), concentrated in vacuo, and removal of volatile stannane byproducts was effected by oil pump vacuum (ca. 0.1 mmHg) overnight. Column chromatography (SiO₂, EtOAc/heptane 1:19) afforded cis-3 (184 mg, 58%) as an off-white solid. mp 87-88 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.55$ (d, 7.6 Hz, 1 H), 6.78 (d, 7.6 Hz, 1 H), 7.63 (d, 9.1 Hz, 2 H), 8.19 (d, 9.1 Hz, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ = 90.0, 94.6, 115.0, 120.4, 123.6, 129.5, 132.4, 147.3. IR (KBr): v = 3436 (br), 3081 (m), 2200 (w), 1636 (w), 1595 (s), 1576 (m), 1513 (vs), 1490 (m), 1338 (vs), 1319 (s), 1285 (m), 1171 (w), 1107 (s), 980 (w), 853 (vs), 772 (w), 749 (m), 730 (s), 685 (m), 578 (m), 521 (m) cm⁻¹. MS(GC): m/z (%) = 251 [M⁺, 100%], 253 (98%). HR-MS(FAB): m/z = 251.9675 [M + H⁺] (calcd for C₁₀H₇NO₂Br: 251.9660).

cis-4-[6-(4-Nitrophenyl)hex-3-ene-1,5-diynyl]tetrathiafulvalene (cis-7). To an argon-degassed solution of cis-3 (25 mg, 99 μ mol), 6 (35 mg, 153 μ mol) and i-Pr₂NH (0.1 mL) in toluene (2 mL) were added [Pd(t-Bu₃P)₂] (3.5 mg, 7 µmol) and CuI (1.9 mg, 10 μ mol) and the mixture was stirred at rt for 2 h. Then, the reaction mixture was filtered through a short plug of silica (SiO₂, CH₂Cl₂/ cyclohexane 1:1). Column chromatography (SiO₂, CHCl₂/heptane, 1:2) afforded cis-7 (29 mg, 73%) as a red solid. mp 147-148 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.16$ (s, 2 H), 6.40 (s, 1 H), 6.41 (s, 1 H), 6.64 (s, 1 H), 7.74 (d, 8.8 Hz, 2 H), 8.29 (d, 8.8 Hz, 2H). ¹³C NMR (75 MHz, CD₂Cl₂): $\delta = 89.6, 92.0, 92.1, 96.5, 107.7,$ 114.7, 116.0, 119.5, 119.7, 120.2, 120.9, 124.2, 127.1, 130.1, 133.2, 147.9. IR (KBr): $\tilde{\nu} = 3436$ (br), 3073 (m), 2925, (w), 2169 (m), 1592 (s), 1510 (vs), 1489 (w), 1338 (vs), 1308 (w), 1286 (w), 1275 (w), 1255 (vw), 1228 (w), 1169 (w), 1107 (m), 1087 (m), 894 (w), 853 (s), 822 (w), 797 (m), 779(w), 747 (s), 685 (w), 660 (m), 644 (m), 513 (w) cm⁻¹. MS(FAB): m/z = 399 [M⁺]. HR-MS(FAB): $m/z = 398.9527 [M^+]$ (calcd for C₁₈H₉NO₂S₄: 398.9516). Anal. calcd for C₁₈H₉NO₂S₄: C, 54.11; H, 2.27; N, 3.51. Found: C, 53.84; H, 2.20; N, 3.36.

4,5-Dihexyl-4'-iodotetrathiafulvalene (9). To a solution of 4,5dihexylTTF 8 (534 mg, 1.43 mmol) in THF (25 mL) cooled to -78 °C was added freshly prepared LDA (2.64 mL, 0.65 м in THF, 1.72 mmol) dropwise and the mixture was stirred for 2 h at low temperature. Freshly purified 1,2-diiodoethane (484 g, 1.72 mmol) was added in one portion and the mixture stirred for 1 h and then warmed to 0 °C, quenched by addition of saturated, aqueous Na₂S₂O₃ (2 mL) and concentrated in vacuo. Et₂O (100 mL) was added and the organic layer washed with H_2O (2 × 100 mL), dried (MgSO₄) and concentrated in vacuo. Column chromatography (deactivated SiO₂, Et₂O/pentane 2:98) afforded 9 as an orange oil (558 mg, 78%). ¹H NMR (300 MHz, CDCl₃): $\delta = 0.88$ (t, 6.6 Hz, 6 H), 1.2-1.4 (m, 12 H), 1.42-1.51 (m, 4 H), 2.33 (t, 7.9 Hz, 4 H), 6.38 (s, 1 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 14.0, 22.5,$ 28.7 (two overlapping), 29.6, 31.5, 63.9, 109.1, 112.0, 124.3, 128.7 (x 2). MS(FAB): m/z = 498 [M⁺]. HR-MS(EI): m/z = 498.0032 $[M^+]$ (calcd for C₁₈H₂₇IS₄: 498.0040).

4,5-Dihexyl-4'-(trimethylsilylethynyl)tetrathiafulvalene (10). A solution of iodide **9** (219 mg, 0.439 mmol) in Et₃N (5 mL) was degassed vigorously with argon, whereupon trimethylsilyl-

acetylene (93 μ L, 0.64 mmol), [Pd(PPh₃)₂Cl₂] (15 mg, 21 μ mol) and CuI (8 mg, 42 μ mol mmol) were added. The reaction mixture was stirred for 2 h at rt and then heptane (50 mL) was added. The reaction mixture was filtered, and the filtrate washed with H₂O (2 × 50 mL), dried (MgSO₄) and concentrated in vacuo. Column chromatography (deactivated SiO₂, heptane) afforded **10** as an orange oil (128 mg, 62%). ¹H NMR (300 MHz, CDCl₃): $\delta = 0.19$ (s, 9 H), 0.88 (t, 6.6 Hz, 6 H), 1.2–1.4 (m, 12 H), 1.41–1.52 (m, 4 H), 2.33 (t, 7.9 Hz, 4 H), 6.48 (s, 1 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = -0.4$, 14.0, 22.5, 28.7 (two overlapping), 29.6, 31.5, 95.2, 99.5, 106.4, 112.1, 116.0, 125.8, 128.5, 128.8. MS(FAB): *m/z* = 468 [M⁺]. HR-MS(FAB): *m/z* = 468.1474 [M⁺] (calcd for C₂₃H₃₆S₄Si: 468.1469).

4-Ethynyl-4',5'-dihexyltetrathiafulvalene (11). To a solution of **10** (128 mg, 0.273 mmol) in THF (15 mL) and MeOH (3 mL) was added K₂CO₃ (40 mg, 0.289 mmol) and the mixture was stirred for 30 min at rt. Heptane (50 mL) was added and the organic phase was washed with H₂O (25 mL) and brine (25 mL), dried (MgSO₄) and concentrated in vacuo to give the terminal alkyne **11** (107 mg, 99%) as an orange, instable oil. ¹H NMR (300 MHz, CDCl₃): δ = 0.89 (t, 6.6 Hz, 6 H), 1.2–1.4 (m, 12 H), 1.41–1.54 (m, 4 H), 2.33 (t, 7.9 Hz, 4 H), 3.21 (s, 1 H), 6.56 (s, 1 H). MS(GC): *m*/*z* = 396 [M⁺].

4-[6-(4-Nitrophenyl)-4-(4-nitrophenylethynyl)-3-(tetrathiafulvalenylethynyl)hex-3-ene-1,5-diynyl]tetrathiafulvalene (12). To a solution of dibromide **5** (25 mg, 53 μ mol) and **11** (70 mg, 176 μ mol) in argon-degassed toluene/THF (1:1, 1 mL) and *i*-Pr₂NH (40 μ L) were added [Pd(*t*-Bu₃P)₂] (2.3 mg, 4.5 μ mol) and CuI (1 mg, 5 μ mol) and the mixture was subjected to ultrasonification at rt for 30 min. Then, the reaction mixture was filtered through a short plug of neutral alumina (CH₂Cl₂/cyclohexane 1:1) and concentrated to the point of precipitation. The crude product was filtered and washed with cyclohexane to afford **12** (23 mg, 40%) as a dark green solid. mp >250 °C (dec). ¹H NMR (300 MHz, CDCl₃): δ = 0.89 (t, 6.2 Hz, 12 H), 1.2–1.4 (m, 24 H), 1.4–1.6 (m, 8 H), 2.37 (m, 8 H), 6.73 (s, 2 H), 7.79 (d, 8.8 Hz, 4 H), 8.28 (d, 8.8 Hz, 4 H). ¹³C NMR (75 MHz, CDCl₃): δ = 14.0, 22.6, 28.8, 29.7 (×2), 31.5, 90.7, 91.0, 92.3, 98.1, 104.7, 114.6, 114.9, 115.5, 118.3, 123.8, 128.7 (x 2), 129.0, 129.1, 132.9, 147.7. IR (KBr): $\tilde{\nu} = 3450$ (br), 3096 (w), 2955, (s), 2925 (s), 2854 (s), 2167 (s), 1591 (s), 1519 (vs), 1459 (m), 1439 (m), 1372 (w), 1341 (vs), 1287 (w), 1265 (w), 1173 (w), 1105 (m), 959 (w), 852 (s), 835 (m), 779(m), 748 (s), 686 (m) 529 (w) cm⁻¹. MS(FAB): *m/z* = 1106 [M⁺]. Anal. calcd for C₅₈H₆₂N₂O₄S₈: C, 62.89; H, 5.64; N, 2.53. Found: C, 62.76; H, 5.68; N, 2.47.

4-[6-(4-Triisopropylsilyl)-4-(4-triisopropylsilylethynyl)-3-(tetrathiafulvalenylethynyl)hex-3-ene-1,5-diynyl]tetrathiafulvalene (14). To a solution of dibromide 13 (100 mg, 0.183 mmol) and terminal alkyne 6 (117 mg, 0.512 mmol) in argon-degassed toluene/THF (1:1, 6 mL) and *i*-Pr₂NH (72 μ L) were added [Pd(*t*-Bu₃P)₂] (13 mg, 26 μ mol) and CuI (9.8 mg, 51 μ mol). After stirring for 24 h, the reaction mixture was filtered through a short plug of silica (SiO₂, CH₂Cl₂/heptane 1:1) and concentrated. The residue was subjected to column chromatography (SiO₂, EtOAc/heptane 1:6) to afford 14 (37.5 mg, 24%) as a dark violet solid. mp 240–241 °C (dec). ¹H NMR (300 MHz, CDCl₃): δ = 1.12 (m, 42 H), 6.32/ 6.33 (2*s*, 4 H), 6.58 (s, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ = 11.2, 18.7, 89.6, 90.2, 103.5, 104.3, 107.8, 113.6, 114.9, 115.5, 118.5, 118.7, 119.2, 126.9. HR-MS(ES): *m*/*z* = 840.1041 [M⁺] (calcd. for C₄₀H₄₈S₈Si₂: 840.1060).

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Supporting Information Available: NMR spectra of all new compounds, X-ray crystallographic data for *cis*-**3** and *trans*-**7** (cif files), and atom coordinates and energies obtained from computational study on compound **12** (without hexyl substituents). This material is available free of charge via the Internet at http://pubs.acs.org.

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