Novel Extended Tetrathiafulvalenes Based on Acetylenic Spacers: Synthesis and Electronic Properties

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Dedicated to Professor J. Fraser Stoddart on the occasion of his 60th birthday

Abstract: A selection of mono- and diacetylenic dithiafulvalenes was synthesized and employed for the construction of extended tetrathiafulvalenes (TTFs) with hexa-2,4-diyne-1,6-diylidene or deca-2,4,6,8-tetrayne-1,10-diylidene spacers between the two 1,3-dithiole rings. By stepwise acetylenic scaffolding using (*E*)-1,2-diethynylethene (DEE) building blocks, an extended TTF containing a total of 18 C(sp) and C(sp^2) atoms in the spacer was prepared. The versatility of the acetylenic dithiafulvene modules was also established by the efficient synthesis of a thiophene-spaced TTF, employing a palladium-catalyzed cross-coupling reaction. The developed synthetic protocols allow functionalization of the extended TTFs in three general ways: with 1) peripheral substituents on the fulvalene cores, 2) alkynyl moieties laterally appended to the spacer, and 3) cobalt clusters involving acetylenic moieties. Strong chromophoric properties of the extended TTFs were revealed by linear and nonlinear optical spectroscopies. Extensive electrochemical studies and calculations on these compounds are also reported, as well as X-ray crystallographic analyses.

Keywords: alkynes • conjugation • electrochemistry • nonlinear optics • tetrathiafulvalene

Introduction

Tetrathiafulvalene (TTF) and derivatives such as **1** (see Scheme 1) are reversible, two-electron donors that have been intensively studied for almost three decades, mainly with the aim of developing low-temperature organic superconductors, but also as important redox-active units in supramolecular chemistry.[1] Combined with the three reversible redox states of TTF, the engineering of switchable nonlinear optical (NLO) materials is also of major focus. Martín and coworkers[2] reported in 1997 the first second-order NLO materials containing the TTF unit as the donor moiety in extended donor–acceptor π systems. A great diversity of structural variations of the parent TTF system has been carried out, in particular by insertion of π-conjugated spacers between the two 1,3-dithiole units.[3] Thus, a considerable number of olefinic and aromatic spacers have been introduced with the aim to tune the redox properties of the π-electron system.[4] However, numerous studies on materials for quadratic nonlinear optics have revealed that the efficient electron transmission and high second-order nonlinearities exhibited by alkene-spaced compounds are counterbalanced by a lack of thermal stability.[5] To overcome this problem, substantial effort has been devoted to the insertion of heteroaromatic

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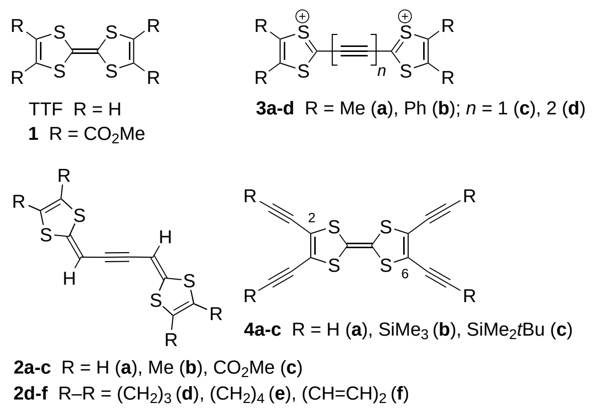
rings into the olefinic spacer, while at the same time increasing the electron-donor strength of the system.[6]

Recent advances in acetylenic scaffolding[7] motivated us to develop efficient synthetic strategies for the preparation of extended TTFs containing acetylenic spacers with lengths up to several nanometers, that is, an alternative way of extending the conjugation. In contrast to the many literature examples of alkene-spaced TTFs, only two types of acetylene-spaced TTFs are known, namely **2a–f**[8] and **3a–d**[9] (Scheme 1). The first derivatives of 1,4-bis(1,3-dithiol-2-ylidene)but-2-yne (**2a**) were prepared by Gorgues and co-workers.[8] Compounds **3a–d** were only isolated as the dications, since the cumulenic neutral forms are unstable. The peralkynylated TTFs **4a–c** represent another family of modules for acetylenic scaffolding and were reported by Rubin and co-workers.[10] Yamamoto and Shimizu prepared polymers by cross-coupling of 2,6-diethynylated TTFs,[11] whereas Shimada and co-workers[12] carried out polymerization in the solid state of a TTF-substituted diacetylene, yielding a poly(diacetylene) with laterally appended TTF moieties.



Scheme 1. Acetylenic derivatives of TTF known in the literature.[8–10]

Here, we report the synthesis and the structural and electronic properties of a large series of novel extended TTFs containing varying numbers of acetylene units in the spacer, as well as laterally appended alkynyl moieties offering the possibility for additional one- and two-dimensional scaffolding (Figure 1).[13] The physical properties of poly(triacetylene) (PTA) oligomers and polymers,[14] derived from (*E*)-1,2-diethynylethene (DEE) monomeric repeat units, (Scheme 2) have been found to strongly depend on the presence of aromatic groups, either laterally appended, or positioned within the linearly π-conjugated backbone or as end-caps.[14, 15] Therefore, we have introduced dithiafulvene units ("half-TTF") as new end-caps into short PTA oligomers which can be viewed either as dithiafulvene end-capped oligomers or as PTA-spaced TTFs.

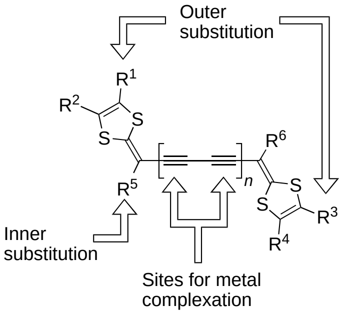
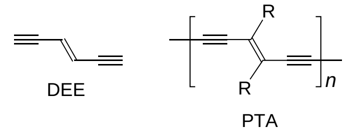


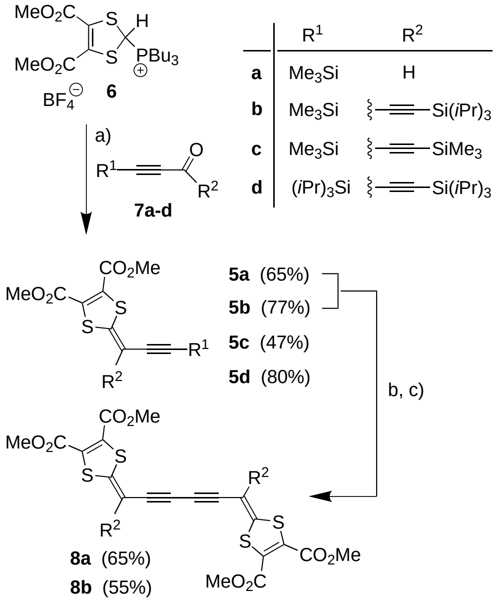
Figure 1. Three general positions are available for functionalization in acetylene-extended TTFs.



Scheme 2. (*E*)-1,2-Diethynylethene (DEE) is the monomeric repeat unit in poly(triacetylene)s (PTAs).[14]

Results and Discussion

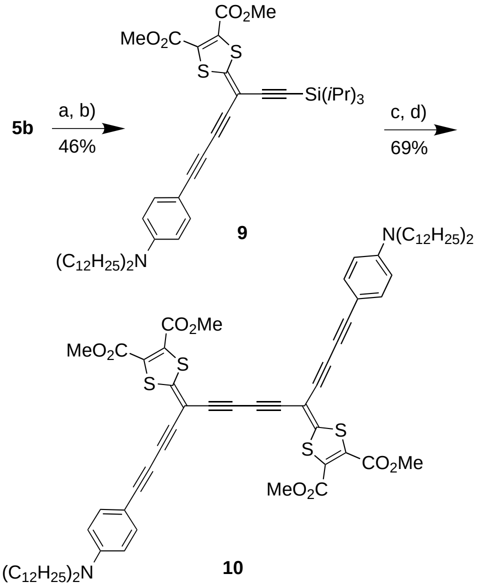
Synthesis: First, a selection of silyl-protected mono- and diacetylenic dithiafulvenes (**5a–d**) was prepared by Wittig reaction between the readily available phosphonium salt **6**[16] and aldehydes **7a–d**[17] (Scheme 3). Desilylation of **5a** using K_2CO_3 in MeOH/THF followed by oxidative Hay coupling gave the extended TTF **8a** in good yield. Similarly, the differentially protected dialkynyl derivative **5b** was selectively mono-deprotected with K_2CO_3 and subsequently homo-coupled to afford **8b**. These acetylenic analogues of TTF were stable when isolated after chromatographic workup. Yet, we found that they were somewhat unstable under the Hay conditions, and that the reaction time should be no longer



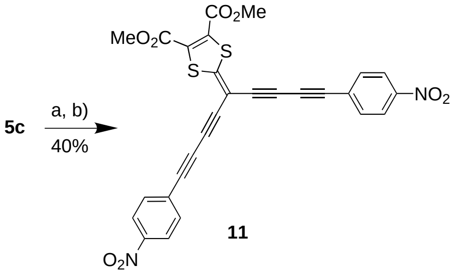
Scheme 3. Synthesis of mono- and diacetylenic dithiafulvenes and extended TTFs. a) BuLi, THF, −78 °C. b) K_2CO_3, MeOH/THF. c) CuCl, TMEDA, air, CH_2Cl_2. TMEDA = *N,N,N',N'*-tetramethylethylenediamine.

than 15–20 min. Indeed, the yield of **8a** was improved from 36%[13] to 65% when decreasing the reaction time from 20 to 15 min.

Next, we incorporated electron-donating anilino substituents by reacting **5b**, after mono-deprotection, with an excess of 4-ethynyl-(*N,N*-didodecylamino)benzene (4.5 equiv) under oxidative conditions, providing **9** (Scheme 4). The Si(*i*Pr)$_3$ group was subsequently removed with Bu$_4$NF, and another Hay coupling gave the extended TTF **10** with laterally appended anilino groups. Both SiMe$_3$ groups of **5c** were readily removed by Bu$_4$NF, and the two terminal alkynes were then cross-coupled with an excess of (4-nitrophenyl)acetylene (5.7 equiv) under Hay conditions, affording the acceptor-substituted derivative **11** (Scheme 5).

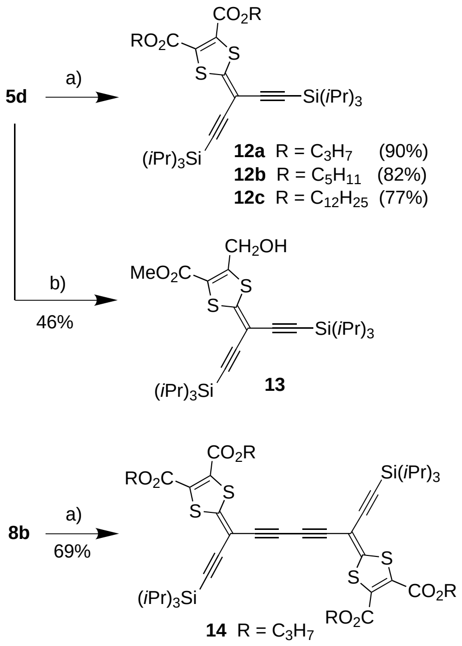


Scheme 4. Synthesis of the extended TTF **10** with laterally appended anilino groups. a) K$_2$CO$_3$, MeOH/THF. b) 4-Ethynyl-(*N,N*-didodecylamino)benzene (4.5 equiv), CuCl, TMEDA, air, CH$_2$Cl$_2$. c) Bu$_4$NF, THF/H$_2$O. d) CuCl, TMEDA, air, CH$_2$Cl$_2$.



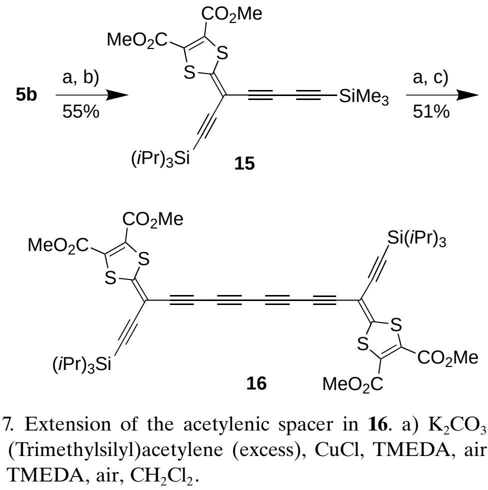
Scheme 5. Introduction of electron-withdrawing groups in **11**. a) Bu$_4$NF, THF/H$_2$O. b) (4-Nitrophenyl)acetylene (5.7 equiv), CuCl, TMEDA, air, CH$_2$Cl$_2$.

For a possible incorporation of the new dithiafulvene building blocks into larger systems, it was advantageous to improve their solubility by changing the nature of the ester groups. Whereas acid-catalyzed transesterification attempts proved unsuccessful owing to decomposition, base-catalyzed transesterification of **5d**, employing K$_2$CO$_3$ as base, gave high yields of the propyl, pentyl, and dodecyl derivatives **12a–c**, respectively (Scheme 6). Moreover, one ester group in **5d** could be selectively reduced to the alcohol with NaBH$_4$, activated by LiCl,[18] affording the unsymmetrically substituted dithiafulvene **13**. Conveniently, the transesterification can also be carried out at the stage of the extended TTF. Thus, when **8b** was treated with K$_2$CO$_3$ and 1-propanol, the tetrapropyl ester **14** resulted.



Scheme 6. Reactions at the ester groups attached to the dithiafulvene cores of **5d** and **8b**: base-catalyzed transesterification and mono-reduction. a) K$_2$CO$_3$, ROH/THF. b) NaBH$_4$, LiCl, THF/MeOH, 15 °C.

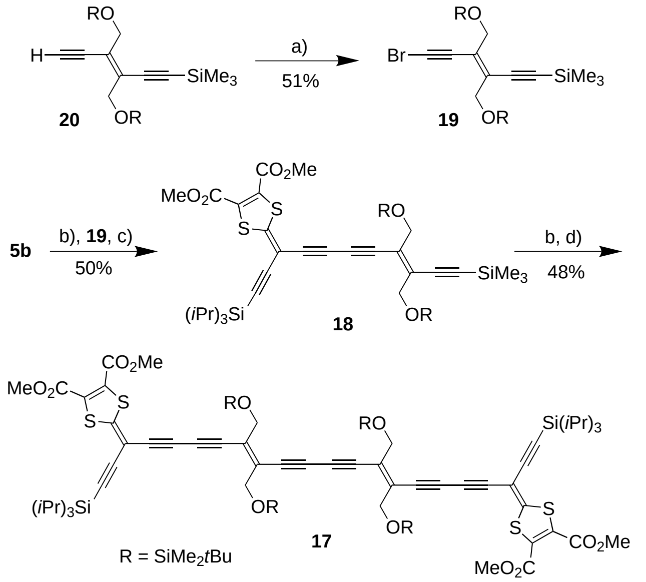
To study the influence of spacer length on the stability of the extended TTF, two more acetylenes were incorporated (Scheme 7). Mono-deprotection of **5b**, followed by heterocoupling with (trimethylsilyl)acetylene (large excess) gave **15**



Scheme 7. Extension of the acetylenic spacer in **16**. a) K$_2$CO$_3$, MeOH/THF. b) (Trimethylsilyl)acetylene (excess), CuCl, TMEDA, air, CH$_2$Cl$_2$. c) CuCl, TMEDA, air, CH$_2$Cl$_2$.

that was subsequently mono-deprotected again. Gratifyingly, the resulting terminal buta-1,3-diyne was quite stable and could be readily homocoupled to give the long extended TTF **16** in remarkably good yield (51%). It is noteworthy that **16**, with its octa-1,3,5,7-tetraynediyl spacer, is very stable; indeed, no decomposition was visible during chromatographic workup.

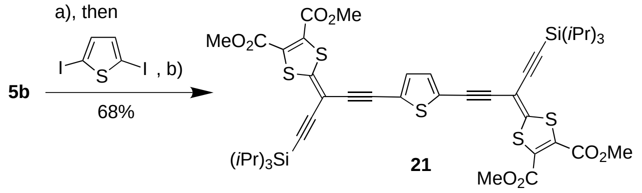
It is evident, however, that when oxidative heterocouplings—requiring a large excess of one component—to more expensive compounds than (trimethylsilyl)acetylene are to be performed, other protocols have to be chosen. The versatility offered by dithiafulvene building block **5b** was first demonstrated in the synthesis of the long extended TTF **17**, containing two (*E*)-1,2-diethynylethene (DEE) units as spacer (Scheme 8). The half-unit **18** was prepared by a modified Cadiot–Chodkiewicz cross-coupling, employing the conditions of Cai and Vasella,[19] between deprotected **5b** and bromide **19**. This bromide was obtained from bromination of mono-deprotected DEE **20**, prepared according to a standard protocol.[14] Unfortunately, purification by column chromatography of **18** from unreacted, deprotected **5b** (used in small excess) was very tedious. To overcome this problem, Hay catalyst was added to the crude reaction product just before chromatographic workup, hereby converting deprotected **5b** into the more polar TTF **8b** and allowing easy chromatographic separation from **18**. Deprotection of **18**, followed by Hay coupling afforded **17**, which contains 18 acyclic C(sp) and C(sp^2) atoms in the spacer.[20]



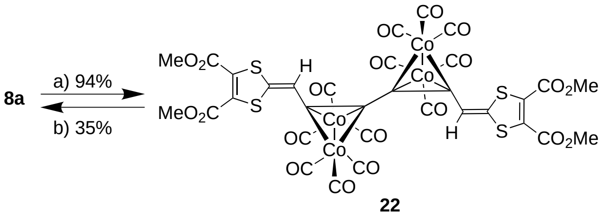
Scheme 8. Synthesis of the extended TTF **17** with a dimeric DEE spacer. a) BuLi, Br_2, THF, −78 °C. b) K_2CO_3, MeOH/THF. c) $[Pd_2(dba)_3]$, LiI, PMP, CuI, benzene. d) CuCl, TMEDA, air, CH_2Cl_2. dba = dibenzylideneacetone; PMP = 1,2,2,6,6-pentamethylpiperidine.

The monomeric building block **5b** was also without difficulty cross-coupled to heteroaromatic halides under Sonogashira conditions.[21] Thus, palladium-catalyzed cross-coupling to 2,5-diiodothiophene provided in high yield the extended TTF **21** containing an electron-rich thiophene ring in the spacer (Scheme 9).

A large number of TTF derivatives with the ability to complex metal ions are described in the literature. Thus, crown ether-annellated TTFs act as redox-responsive sensor molecules for alkali metal ions as well as for Ag^+, Pb^{2+}, Sr^{2+}, and Ba^{2+}.[22] Moreover, the TTF chromophore has been exploited as redox-active unit for discriminating Cu^+, Ag^+, and Li^+ in phenanthroline-based precatenate complexes.[23] The new series of extended TTFs offers the possibility for cobalt complexation at the acetylene spacer[24a] between the two dithiafulvene rings. Thus, when **8a** was treated with $[Co_2(CO)_8]$, the very robust tetrakis-cobalt complex **22** was obtained in near-quantitative yield (Scheme 10). This strongly colored complex (dark green in solution, red-brown as a solid) was purified by column chromatography (SiO_2, CH_2Cl_2) without any apparent decomposition. The complexation induces a significant downfield shift of the fulvene proton from $\delta = 5.53$ ppm in **8a** to $\delta = 6.63$ ppm in **22**. Moreover, there are marked differences in the ^{13}C NMR resonances (Table 1). Thus, the resonances of the spacer C atoms that are part of the cobalt clusters in **22** shift upfield by $\delta = 5.3$ ppm and $\delta = 7.8$ ppm relative to the corresponding alkyne C atoms in **8a**. Significant shifts were also experienced by the ^{13}C NMR resonances of the dithiafulvene moieties, one moving upfield by $\delta = 15.8$ ppm and the other downfield by $\delta = 6.1$ ppm. In addition to these spectroscopic changes, cobalt complexation changes the electrochemical properties of **22** relative to those of **8a** (vide infra). Removal of the $[Co_2(CO)_6]$ clusters was only partly successful employing trimethylamine oxide,[24b] regenerating the alkyne-spaced TTF **8a** in 35% after chromatographic workup. The remaining material seems to be lost by decomposition under the reaction conditions.



Scheme 9. Synthesis of thiophene-spaced TTF **21**. a) K_2CO_3, MeOH/THF. b) $[Pd(PPh_3)_4]$, CuI, Et_2NH/THF.



Scheme 10. Synthesis of tetrakis-cobalt complex **22**. a) $[Co_2(CO)_8]$, THF. b) Me_3NO, THF.

Table 1. Selected ^{13}C NMR (50 or 75 MHz, CDCl$_3$, 298 K) resonances of fulvene and alkyne C atoms.

Compound	C (alkyne) δ [ppm]						C (fulvene) δ [ppm]	
5a					101.6	105.4	93.5	146.6
5d					100.2	101.8	90.0	152.9
8a	82.9	84.0					91.9	149.5
8b	81.3	82.5			100.3	101.6	88.0	157.3
15	71.9	83.0	87.4[a]	95.5	100.2	101.6	87.5[a]	157.5
16	66.1	72.6	74.5	83.8	99.5	102.6	86.8	159.0
22	88.2	91.8					107.7	143.4

[a] The signal at 87.4 ppm may instead be a fulvene resonance and the one at 87.5 ppm an alkyne resonance.

X-ray crystallography: Single crystals of **8a** and **22** were grown by slow diffusion of hexane into CH$_2$Cl$_2$ solutions and used for X-ray crystal structure analyses (Figure 2 Figure 3, respectively). The structure of **8a** reveals that the two fulvene double bonds adopt the s-*trans* conformation with respect to the connecting buta-1,3-diynediyl moiety. The two dithiafulvene units are not in the same plane but rotated about the central linear diacetylene core with a torsional angle C1-C14-C19-C20 of −138.6°. Upon cobalt complexation, forming **22**, the complexing alkyne bond lengths increase from 1.197 Å (C15–C16 in **8a**) to 1.358 Å (C3–C4 in **22**), and the central single bond increases from 1.357 Å (C16–C17 in **8a**) to 1.430 Å (C4–C4′ in **22**). The single bond C14–C15 (1.408 Å) in **8a** increases slightly in length to 1.428 Å in **22** (C3–C17), whereas the fulvene bond lengths are almost unaltered. Complexation also goes along with a disruption of the linearity of the bridge; thus, the angles C3-C4-C4′ and C4-C3-C17 in **22** are 142.2° and 136.3°, respectively. In contrast to **8a**, complex **22** has an inversion center in the crystal.

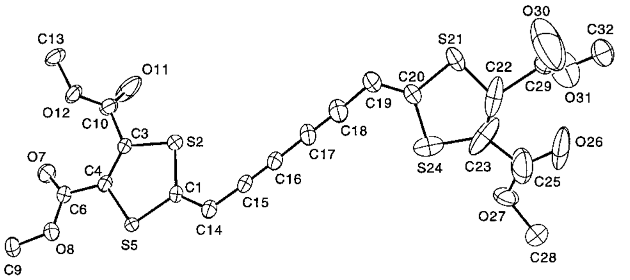


Figure 2. Structure of **8a** (ORTEP plot; atomic displacement parameters obtained at 248 K are drawn at the 30 % probability level. Hydrogen atoms have been omitted for clarity).

Electronic absorption spectroscopy: The UV/Vis spectral data in CHCl$_3$ of the dithiafulvene monomers and extended TTFs are displayed in Table 2, together with those of the parent, MeO$_2$C-substituted TTF **1**.[25] Some selected spectra are displayed in Figure 4. Evidently, all the new compounds are very strong chromophores. Proceeding from monomeric **5a** to TTF **8a** results in a significant bathochromic shift of the longest wavelength absorption from $\lambda_{max} = 405$ to 429 nm, corresponding to a decrease in the HOMO–LUMO gap from 3.06 to 2.89 eV. Furthermore, the molar extinction coefficient of the highest wavelength absorption is very high for **8a** ($\varepsilon = 25400\,\text{M}^{-1}\text{cm}^{-1}$). This value should be compared to the very small absorption displayed by **1** at 445 nm ($\varepsilon = 1930\,\text{M}^{-1}\text{cm}^{-1}$).[25] As revealed by calculational studies (vide infra), this HOMO–LUMO transition can be assigned to an intramolecular charge-transfer transition. A similar bathochromic shift is observed when going from dithiafulvene **5b** ($\lambda_{max} = 410$ nm (tail), $\varepsilon = 1440\,\text{M}^{-1}\text{cm}^{-1}$) to TTF **8b** ($\lambda_{max} = 441$ nm (shoulder) (2.81 eV), $\varepsilon = 18600\,\text{M}^{-1}\text{cm}^{-1}$). The end-absorption is not significantly different from that of **8a**, signalling that electron delocalization through cross-conjugation to the lateral alkynyl groups in **8b** is not very effective. In contrast, extension of the linear π-electron conjugation in the spacer unit has a very large effect, revealed by the strong absorption of **16** at $\lambda_{max} = 484$ nm ($\varepsilon = 30700$ nm), corresponding to a reduced HOMO–LUMO gap of 2.56 eV. The dimeric DEE-spaced TTF **17** shows about the same end-absorption (at ≈550 nm) as **16**. Both this absorption onset as well as the longest wavelength absorption maximum of **17** at $\lambda_{max} = 453$ nm are, however, significantly bathochromically shifted relative to those of a trimethylsilyl-endcapped DEE dimer ($\lambda_{max} = 376$ nm, $\varepsilon = 24700\,\text{M}^{-1}\text{cm}^{-1}$, end-absorption at ≈410 nm).[15a] Increasing the donor strength by insertion of thiophene into the spacer only slightly increases the longest wavelength absorption shoulders from $\lambda_{max} = 441$ nm (**8b**) to 452 nm (**21**).

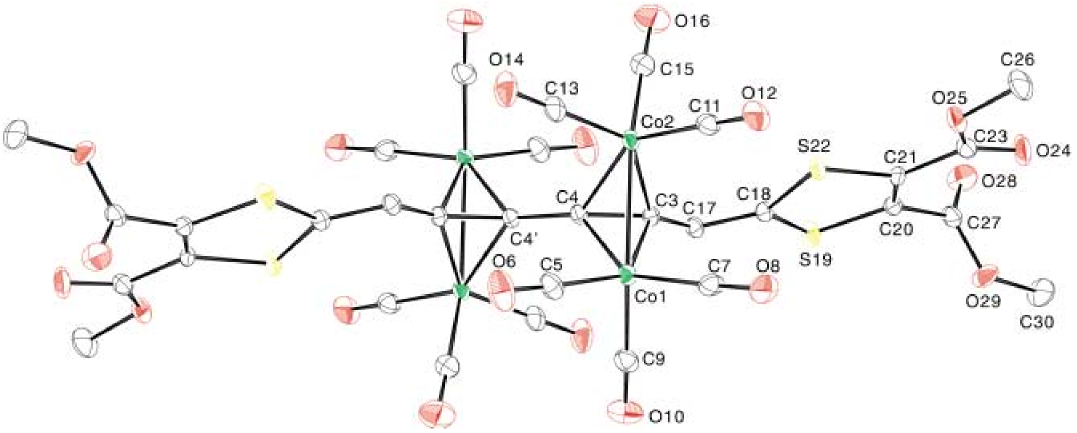


Figure 3. Structure of **22** (ORTEP plot; atomic displacement parameters obtained at 193 K are drawn at the 30 % probability level. Hydrogen atoms have been omitted for clarity).

Table 2. Absorption band maxima and molar extinction coefficients in the UV/Vis spectra of compounds in $CHCl_3$.[a]

Compound	λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])				
1[b]	245 (15500)	284 (14300)	315 (13100)	445 (1930)	
5a	318 (17900)	348 (sh, 6140)	405 (1610)		
5b	346 (17900)	358 (17600)	372 (15000)	410 (t, 1440)	
5c	347 (17300)	359 (17500)	372 (15100)	412 (t, 1420)	
8a	314 (sh, 11500)	347 (sh, 22800)	363 (26700)	402 (29500)	429 (25400)
8b	274 (sh, 14600)	360 (21900)	381 (25500)	408 (25600)	441 (sh, 18600)
9	269 (12600)	337 (29400)	353 (28100)	393 (28700)	422 (25300)
10	296 (30600)	354 (76200)	425 (sh, 50200)	460 (sh, 33300)	
11	281 (25200)	298 (27300)	317 (33100)	338 (33200)	424 (br, 31700)
13	353 (sh, 17900)	363 (19800)	375 (18700)	411 (t, 2990)	
14	274 (sh, 16800)	361 (24200)	383 (29200)	409 (30200)	444 (sh, 22100)
15	261 (15900)	276 (12300)	351 (sh, 12900)	369 (19600)	380 (20900)
	395 (18900)	441 (t, 2150)			
16	257 (75300)	268 (84800)	282 (74600)	323 (17300)	335 (sh, 19200)
	346 (22200)	383 (sh, 25200)	412 (42900)	442 (47200)	484 (30700)
17	314 (sh, 31900)	328 (36400)	358 (sh, 38900)	378 (47700)	400 (49300)
	453 (61400)				
18	259 (27600)	284 (19600)	305 (sh, 25100)	313 (27700)	386 (sh, 23300)
	396 (26300)	428 (23900)			
21	305 (sh, 21900)	315 (27700)	363 (sh, 26100)	378 (29600)	423 (34300)
	452 (sh, 21900)				
22	318 (32100)	366 (26000)	449 (br sh, 7340)	610 (br, 2730)	

[a] sh = shoulder, t = tail, br = broad. [b] Solvent: EtOH; values taken from ref. [25].

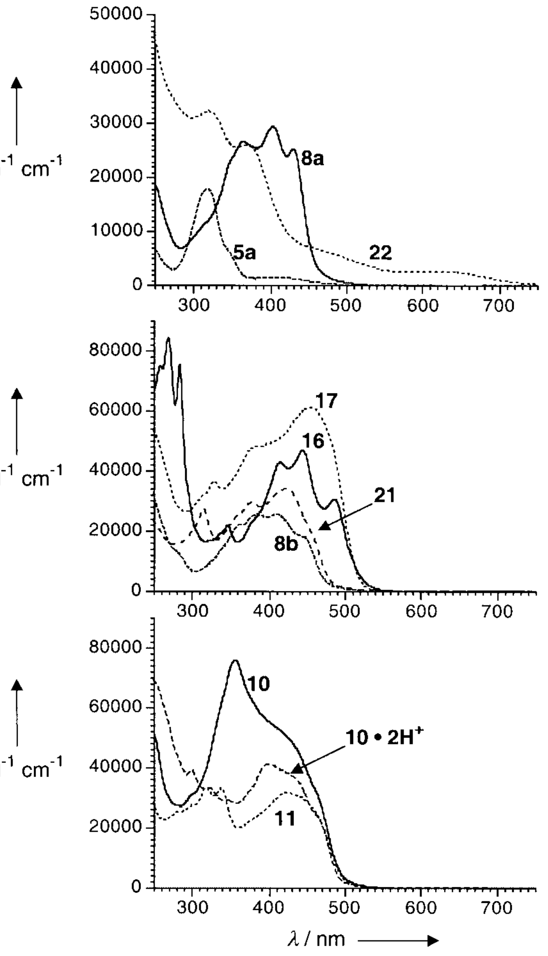


Figure 4. UV/Vis spectra in $CHCl_3$.

Protonation of the laterally appended anilino groups in TTF **10** by treatment of the $CHCl_3$ solution with a drop of concentrated HCl resulted in a substantial decrease of the absorption band at λ_{max} = 354 nm (more than halved, Figure 4), whereas the end-absorption was unaltered. Treatment of the protonated compound with aqueous KOH regenerated the neutral form with an absorption spectrum virtually identical to that before the treatment with acid. From this experiment, the transition at 354 nm is assigned substantial charge-transfer character originating from the electron-donating anilino substituents. The donor–acceptor compound **11**, containing electron-withdrawing 4-nitrophenylacetylene groups, displays a very strong end-absorption as compared to dithiafulvene monomer **5c**.

Computational study: To shed further light upon the longest wavelength (HOMO → LUMO) transitions, we subjected TTFs **8a** and **8b** to a computational study employing the Gaussian 98 program package[26] at the HF/3-21G level of theory. However, for decreasing calculational time, the triisopropylsilyl groups were substituted by H atoms in **8b**, which should have little effect on the electronic properties. The HOMOs and LUMOs resulting from this study are depicted in Figure 5. It transpires that the HOMO of **8a** is distributed over the four S atoms and the connecting spacer unit, whereas the LUMO (as well as the nearly equally energetic LUMO + 1) is located at the two peripheral ethylene biscarbonyl units. Both HOMO and LUMO are of pure π nature. Thus, the highest wavelength transition in **8a** is an intramolecular charge-transfer transition, as was likewise realized for parent, MeO_2C-substituted TTFs.[27] A large energetic separation (ca. 0.6 eV (B3LYP/3-21G//HF/3-21G), Figure 5) between the LUMO + 2, with high coefficients on the buta-1,3-diynediyl spacer, and the LUMO/LUMO + 1 strongly suggests that this higher energy orbital is not involved in the longest wavelength electronic transition. The HOMO of **8b** is almost identical to that of **8a**, with only small coefficients on the laterally appended alkyne residues, which is in good agreement with the similar end-absorptions found experimentally for the two compounds. For comparison, HOMO–LUMO gaps were obtained by single point calculations at the B3LYP/3-21G level on the HF-optimized geometries. Indeed, about the same value (3.2 eV) was obtained for **8a** and **8b**, this value being, however, somewhat larger than those determined experimentally in solution.

Electrochemistry: The redox properties of the extended TTFs were examined by cyclic (CV) and steady-state (SSV) voltammetry. The redox potentials (versus Fc/Fc$^+$ (ferrocene/ferricinium couple)) are listed in Table 3. Whereas TTF **8a** was oxidized in an irreversible two-electron step in CH_2Cl_2, TTF **8b** experienced two reversible one-electron

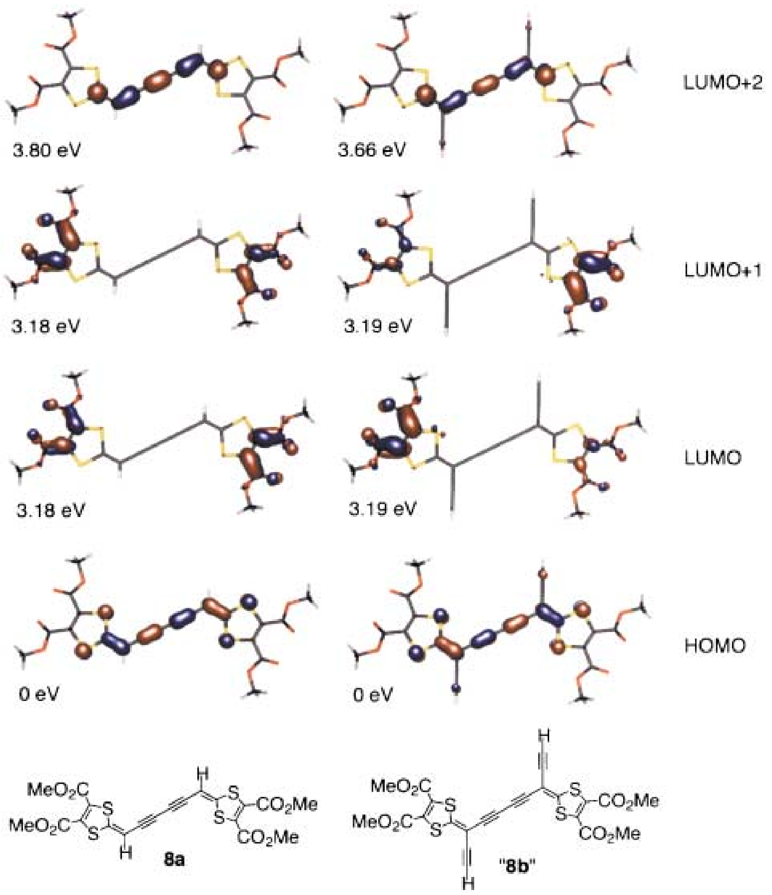


Figure 5. HOMO, LUMO, LUMO + 1, and LUMO + 2 of **8a** and **8b** (iPr$_3$Si groups replaced by hydrogen atoms) calculated at the HF/3–21G level of theory. Relative orbital energies were obtained from B3LYP/3–21G single-point calculations on the HF-optimized conformations.

steps in CH_2Cl_2, anodically shifted relative to **8a** and with a separation of 120 mV. However, in MeCN, **8b** was oxidized in an irreversible two-electron step. In contrast, TTFs **1** and **2c** ($R = CO_2Me$) were oxidized in MeCN in two steps with separations of 320 mV[28] and 380 mV,[8] respectively. These results indicate a lower Coulombic repulsion between the two charges in the dications of **8a** and **8b** relative to those of **1** and **2c**. The anilino-substituted TTF **10** was oxidized in three steps, the first two-electron oxidation step (+0.42 V) centered at the two anilino units which act as independent redox centers, and the two subsequent one-electron steps (+0.87 V, +1.12 V) at the two dithiole rings. Thus, the close proximity of two positive charges at the lateral anilino groups induces a substantial anodic shift (compared with **8b**) of the oxidations centered at the two 1,3-dithiole rings. Interestingly, it was also possible to reduce the compounds at negative potentials in either one or two steps. All these reductions were irreversible.

When increasing the length of the linker from buta-1,3-diynediyl (**8b**) to octa-1,3,5,7-tetraynediyl (**16**), the 1,3-dithiole-centered two-electron oxidations occur at a significantly anodically shifted potential of +0.81 V. Also the dimeric DEE-spaced TTF **17** experiences an anodically shifted two-electron oxidation (+0.78 V). Consequently, the two dithioles in **16** and **17** not only are so far apart that they behave as independent redox centers; they are also oxidized at higher potential owing to the strong electron-withdrawing effect of the acetylenic spacer unit.[29] It may therefore be more meaningful to classify **17** as a dithiafulvene end-capped DEE dimer rather than an extended TTF. Insertion of a thiophene ring between two acetylene units in the spacer, as in TTF **21**, also results in a one-step, dithiole-centered two-electron oxidation. This oxidation occurs at +0.63 V, which is quite similar to the stepwise oxidations of **8b**. Interestingly, the first (irreversible) reduction potential of **21** is less negative by 80 mV, despite the electron-rich character of the heteroaromatic spacer. For comparison, previous studies on shorter TTFs containing only a thiophene unit between the two dithiafulvenes revealed two separate one-electron oxidations.[6a–c] Regarding the reversibility, it is not clear why the radical cations or dications of some of the studied TTFs are stable at the timescale of the experiments, whereas others are not.

The cobalt-complexed TTF **22** deserves some special attention. Whereas SSV gave well-defined oxidation and reduction waves, cyclic voltammetry gave non-reproducible CVs on account of electrode inhibition and passivation, and possibly decomposition. The first reduction step gave an irreversible reduction peak at −1.43 V. Thus, the first reduction of **22** occurs at much less negative potential than for the uncomplexed TTFs (in the range of −1.7 to −1.8 V). According to the LUMO calculations (vide supra), the reductions of the uncomplexed TTFs are likely to occur at the ethylene bis(carbonyl) groups. Instead, the first reduction of **22** is probably occurring at the cobalt cluster-containing bridge, in agreement with reported data in the literature on cobalt carbonyl derivatives.[30] Yet, no data are, to our knowledge, available for a cobalt cluster array similar to that present in **22**. The first oxidation of **22** at +0.53 V in the SSV was not observed in the CV, and this oxidation is perhaps an absorption pre-wave in the SSV. Indeed, it is more reasonable to anticipate the first oxidation of **22** to occur at a value of +0.62 V, as measured by CV, since this value is anodically shifted relative to the first oxidation at +0.58 V of its uncomplexed precursor **8a**. It should be pointed out, however, that the oxidation peak amplitude in the CV was quite large compared to the first reduction, which also in this case may be attributed to accumulation of the compound at the electrode surface by adsorption. Moreover, the peak shape and amplitude were changing significantly during iterative cycling.

Table 3. Electrochemical data measured in CH_2Cl_2 (if not otherwise stated) + 0.1 M $n\mathrm{Bu_4NPF_6}$. All potentials versus Fc/Fc^+. Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl or Pt as pseudo reference.

Compound	Cyclic voltammetry[a] E°[b] [V]	ΔE_p[c] [mV]	E_p[d] [V]	Steady state voltammetry $E_{1/2}$[e] [V]	slope[f] [mV]
8a			+0.58 (2 e^-)	+0.55	60
			−1.81 (2 e^-)	−1.87	175
8b	+0.64 (1 e^-)	60		+0.64	60
	+0.76 (1 e^-)	60		+0.76	60
			−1.86 (2 e^-)	−1.80	100
8b[g]			+0.70[h] (2 e^-)		
			−1.75 (2 e^-)		
9	+0.42 (1 e^-)	80		+0.42	70
	+0.67 (1 e^-)	60		+0.71	60
			−1.70 (1 e^-)	−1.71	70
			−1.81 (1 e^-)		
10			+0.43 (2 e^-)		
			+0.87 (1 e^-)		
			+1.12 (1 e^-)		
			−1.70 (2 e^-)		
16			+0.82 (2 e^-)[i]	+0.81	75
			−1.73 (2 e^-)	−1.60	100
17	+78 (2 e^-)	90		+0.81	60
			+1.13	+1.21	[j]
			−1.73 (2 e^-)		
			−2.07		
21	+0.63 (2 e^-)	100		+0.65	75
			−1.78 (2 e^-)		
			−2.08		
22				+0.53	50
			+0.62[k]	+0.67	100
			+0.77[k]		
			−1.43[k]	−1.43	125
			−1.68[k]		
			−1.98[k]		

[a] Scan rate 0.1 $V s^{-1}$. [b] $E^{\circ} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c] $\Delta E_p = E_{ox} - E_{red}$, where subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [d] Peak potential E_p for irreversible electron transfer. [e] Half-wave potential $E_{1/2}$. [f] Slope of the linearized plot of E versus log $[I/(I_{lim} - I)]$. [g] Solvent: MeCN. [h] Irreversible at scan rates < 1 $V s^{-1}$, reversible at scan rates > 1 $V s^{-1}$. [i] The irreversible oxidation became reversible for sweep rates higher than 5 $V s^{-1}$. [j] Electrode inhibition avoided wave analysis. [k] Observed values for the first scan on a polished electrode.

The electrochemical investigations clearly show that structural changes in the acetylenic spacer and lateral functionalization, as well as solvent polarity, strongly influence the electrochemical behavior of acetylene-extended TTFs, in particular the position and separation of the first and second dithiole oxidation potentials and the degree of reversibility.[31]

Nonlinear optical properties: The nonlinear optical properties were investigated by third-harmonic generation (THG) measurements[32] for four representative dithiafulvene compounds (**5b**, **8b**, **10**, and **11**), and the second-order hyperpolarizabilities γ were determined (Table 4). All measurements were calibrated against fused silica (fs) as the reference, using $\chi^{(3)}_{fs} = 1.6 \times 10^{-22}\ m^2V^{-2}$ (1.16×10^{-14} esu).[33] Second-order hyperpolarizabilities were also calculated (Table 4) for the four compounds investigated, employing the semiempirical finite field method within the MOPAC software[34] and the PM3 parametrization. Owing to the several approximations of the SCF methods,[35] the reliability of absolute γ values is usually poor. However, for a series of analogous compounds, a qualitative trend is often evident,[36] and theoretical calculations have managed to validate the most active compound in a series when employing the same computational settings.[37] For the studied dithiafulvene compounds, the calculated values appeared systematically higher than the experimental ones. Indeed, the calculated γ values are about a factor of 2 higher. This very same difference was found for molecules with similar electronic resemblance to those studied in this report.[38] It is therefore reasonable to introduce an empirical correction factor (multiplication by 0.49; standard deviation 0.06), affording a set of corrected values, which are in very good agreement with the experimental ones, within the limits of the experimental error.

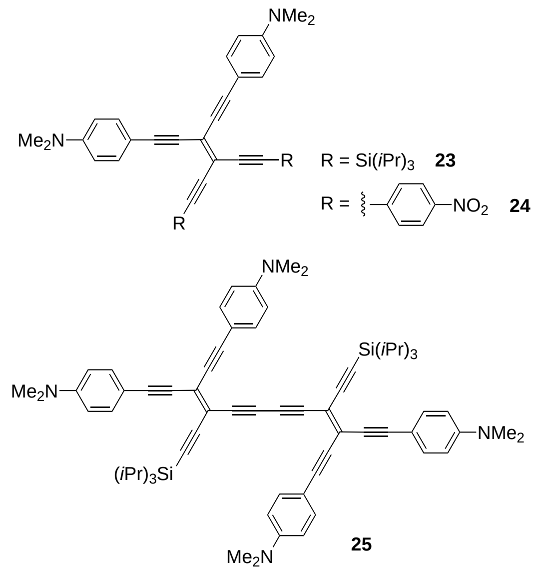
Looking at the structural differences accounting for the different NLO responses, one finds that the extension of the linear π-electron conjugation upon changing from dithiafulvene **5b** to its linear dimer, extended TTF **8b**, results in a doubling of the second-order hyperpolarizability. The introduction of additional electron-donating anilino groups at the lateral positions (**10**) leads to a further significant increase in γ. The γ value can also be in-

Table 4. Results of the third harmonic generation (THG) experiments at fundamental and third harmonic wavelengths of 1.907 μm and 636 nm, respectively.[a]

Compound	ε[b] [$M^{-1}\ cm^{-1}$]	γ [10^{-36} esu]	γ [$10^{-48}\ m^5V^{-2}$]	$\gamma_{calculated}$[c] [10^{-36} esu]	$\gamma_{corrected}$[d] [10^{-36} esu]
5b[e]	0	38	0.53	67	33
8b	0	87	1.21	197	96
10	0	220	3.07	569	278
11	0	310	4.35	450	220
23[e]	0	130	1.8		
24[e]	430	1300	18		
25[f]	230	2036	28		

[a] The values are calibrated relative to the third-order nonlinear susceptibility of fused silica, for which a value of $\chi^{(3)}_{fs} = 1.6 \times 10^{-22}\ m^2V^{-2}$ (1.16×10^{-14} esu) was used. Experimental error: 15%. [b] Molar extinction coefficient at the third harmonic wavelength. [c] Obtained with the PM3 semiempirical method. [d] Calculated values corrected by a factor of 0.49. [e] Adjusted values from ref. [39] where a value of $\chi^{(3)}fs = 3.9 \times 10^{-22}\ m^2V^{-2}$ was used (conversion factor: multiplication with 1.6/3.9 = 0.41). [f] Ref. [40].

creased by adding electron-withdrawing 4-nitrophenylacetylene groups to the dithiafulvene monomer, as revealed by the value obtained for the asymmetric, donor-acceptor compound **11**. It is moreover interesting to compare the NLO properties of these acetylenic compounds with those of the arylated tetraethynylethenes (TEEs) **23** and **24**,[39] and TEE dimer **25**[40] (Scheme 11). Formal substitution of the two geminally situated 4-(*N,N*-dimethylamino)phenylacetylene units in **23** and **24** with the dithiole unit in **5b** and **11**, respectively, leads to a decrease of one order of magnitude in the γ values. Also the extended TTFs **8b** and **10** exhibit significantly smaller γ values than the TEE-dimer **25**. Nevertheless, the values exhibited by the dithiafulvenes are still promising for future NLO applications. Although arylated TEEs exhibit some of the highest known third-order nonlinear optical susceptibilities, they are of limited stability for real applications and new, more stable scaffolds are accordingly desired.



Scheme 11. Arylated tetraethynylethene monomers and dimers.[39, 40]

Conclusion

An efficient protocol for synthesizing a selection of mono- and diacetylenic dithiafulvenes has been developed. These modules are readily dimerized to extended TTFs, employing homo- and hetero-coupling reactions. Moreover, functional groups, such as *N,N*-didodecylaniline, are readily attached to the lateral positions of the extended TTFs, offering a way to control the physico-chemical properties. The electrochemical response to increasing the length of the spacer present in **8b** is a decrease in the Coulombic interaction between the two oxidized dithioles which, as a result, are oxidized in a single two-electron step in TTFs **16** and **17**. This oxidation occurs, however, at an anodically shifted potential relative to comparison compound **8b** on account of the electron-withdrawing effect of the acetylene-rich bridge. Yet, the presence of an electron-rich thiophene ring in **21** modified much more the reduction than the oxidation potential. The acetylenic spacer units offer sites for complexation of cobalt carbonyl clusters, with concomitant changes in both spectroscopic and electrochemical properties.

The extended TTFs are strong chromophores with bathochromically shifted end-absorptions relative to the parent TTF with the same outer substitution. Increasing the number of acetylene units in the spacer from two (**8b**) to four units (**16**) results in a significant reduction of the HOMO-LUMO gap from 2.81 eV to 2.56 eV, whereas extending the linear conjugation further has little effect, as revealed by the similar end-absorptions of **16** and the dimeric DEE-spaced TTF **17**.

The compounds display good third-order nonlinear optical properties, enforced by donor-acceptor substitution. The study shows that the semiempirical PM3 computational method provides good NLO predictions, after introduction of an empirical correction factor, for materials based on alkynylated dithiafulvene modules.

The new chromophores reported here are promising building blocks for further scaffolding in either one or two dimensions. Indeed, future work will focus on constructing long oligomers from the very well soluble dithiafulvene modules **12a–c** and **14**. One long-term prospect of such efforts is to combine the polaron/bipolaron conduction mechanism of an extended, linearly π-conjugated spacer that becomes conducting upon doping[41] with the mixed valence migration operational in stacks of TTF/TTF$^{\bullet+}$.[3]

Experimental Section

Materials and general methods: Chemicals were purchased from Aldrich and Fluka and used as received. Compound **6** was prepared according to ref. [16] and **7a–d** according to ref. [17]. All reactions, except from the Hay couplings, were carried out under an inert atmosphere of Ar or N_2 by applying a positive pressure of the protecting gas. For the Hay couplings, the following mixture was used as "Hay catalyst": CuCl (0.13 g, 1.3 mmol) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 0.16 g, 1.4 mmol) in CH_2Cl_2 (4.5 mL). Column chromatographic (CC) purification refers to flash chromatography using solvent mixture in the given ratio on SiO_2 60 (230–400 mesh). Melting points (m.p.) were measured on a Büchi 510 melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200 or 300 MHz spectrometers or on a Bruker 500 MHz spectrometer. Chemical shift values are reported in ppm relative to residual solvent peaks. IR spectra (cm^{-1}) were obtained with a Nicolet 600 FT-IR spectrometer; signal designations: s = strong, m = medium, w = weak. UV/Vis measurements (λ_{max} [nm] (ε [$M^{-1}\,cm^{-1}$])) were performed on CARY 5 and CARY 500 UV/Vis/NIR spectrophotometers. High-resolution (HR) MALDI mass spectra were measured on an IonSpec Fourier Transform (FT) Instrument, using a two-layer technique (tl), with 2,5-dihydroxybenzoic acid (DHB) or 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix, and the compound typically dissolved in CH_2Cl_2. MALDI-TOF mass spectra were recorded on a Bruker Reflex instrument, with the compound dissolved in CH_2Cl_2 and using as matrix DCTB. Elementary analyses were done by Mikrolabor des Laboratorium für Organische Chemie at ETH Zürich.

Electrochemistry: CH_2Cl_2 was purchased spectroscopic grade from Merck, dried over molecular sieves (4 Å), and stored under argon prior to use. Bu_4NPF_6 was purchased electrochemical grade from Fluka and used as received. The electrochemical experiments were carried out at 20 ± 2 °C in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 in a classical three-electrode cell. The working electrode was a glassy carbon disk electrode (3 mm in diameter) used either motionless for CV (0.1 to 10 V s^{-1}) or as rotating-disk electrode for SSV. The counter electrode was platinum wire and the reference electrode either an aqueous Ag/AgCl electrode or a platinum wire used as pseudo reference. All potentials are referenced to the ferrocene/ferrici-

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nium (Fc/Fc$^+$) couple used as an internal standard. The accessible range of potentials on the glassy carbon electrode was $+1.4$ to -2.4 V versus Fc/Fc$^+$ in CH_2Cl_2. The electrochemical cell was connected to a computerized multipurpose electrochemical device AUTOLAB (Eco Chemie BV, Utrecht, The Netherlands) controlled by the GPSE software running on a personal computer.

Third-harmonic generation: The second-order hyperpolarizabilities γ were measured by third-harmonic generation (THG) with a H_2-Raman shifted Nd:YAG laser (5 ns pulses, 10 Hz repetition rate). The fundamental and the harmonic wavelengths of 1.907 µm and 635.7 nm are in the transparency region of the absorption spectra. Therefore, the hyperpolarizabilities are assumed not to be resonance enhanced. The samples were dissolved in chloroform and measured at various concentrations to elucidate the second-order hyperpolarizability. THG measurements were performed by rotating the 1 mm or 0.2 mm thick fused silica cuvette with the solution parallel to the polarization to generate well known Maker-fringe interference patterns. The analysis of the Maker-fringe patterns was done as described in the literature.[42] The THG setup was calibrated with a fused silica plate[33] ($\chi^{(3)}_{fs} = 1.6 \times 10^{-22}$ m^{2}V^{-2} (1.16×10^{-14} esu) at $\lambda =$ 1.907 µm). For each compound, measurements of $\chi^{(3)}$ for pure solvent and for five solutions of the molecules in different concentration were done, and the second hyperpolarizability γ was obtained. The measurement procedure has been repeated several times to obtain a reasonable error. The relative error for these measurements is approximately 15%.

X-ray crystallography: *X-ray crystal structure of* **22**: Crystals of **22** were grown by slow diffusion of hexane into a CH_2Cl_2 solution. Crystal size: $0.15 \times 0.15 \times 0.10$ mm. Crystal data at 193 K for $C_{32}H_{14}O_{20}S_4Co_4 \cdot CH_2Cl_2$ ($M_r = 1167.32$): monoclinic space group $C2/c$, $\rho_{calcd} = 1.768$ g cm^{-3}, $Z = 4$, $a = 18.642(3)$, $b = 8.8570(10)$, $c = 26.722(3)$ Å, $\beta = 96.180(10)^\circ$, $V =$ 4386.5(10) Å^3. Nonius CAD4 diffractometer, $Cu_{K\alpha}$ radiation, $\lambda =$ 1.5418 Å. The structure was solved by direct methods[43] and refined by full-matrix least-squares analysis[44] including an isotropic extinction correction, and $w = 1/[\sigma^2(F_o^2) + (0.0029P)^2 + 14.380P]$, where $P = (F_o^2 + 2F_c^2)/3$. All heavy atoms were refined anisotropically (hydrogen atoms isotropic, whereby hydrogen positions are based on stereochemical considerations). Final $R(F) = 0.0327$, $wR(F^2) = 0.0749$ for 297 parameters and 3022 reflections with $I > 2\sigma(I)$ and $\theta < 69.87^\circ$ (corresponding R values based on all 4155 reflections are 0.0658 and 0.0943, respectively).

X-ray crystal structure of **8a**: See ref. [13].

CCDC-164802 (**8a**), CCDC-178156 (**22**) contain the supplementary crystallographic data (excluding structure factors) for the structures reported in this paper. These data can be can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

3-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1-(trimethylsilyl)propyne (5a): A solution of **6** (615 mg, 1.21 mmol) in THF (20 mL) was cooled to $-78\,^\circ$C, whereupon *n*BuLi (1.6 M in hexane, 0.80 mL, 1.3 mmol) was added, causing the color to turn red. A solution of **7a** (211 mg, 1.67 mmol) in THF (10 mL) was added, and the solution turned orange. After stirring for 1.5 h at $-78\,^\circ$C, the solution was warmed gradually to 0 °C. It was poured into H_2O (150 mL) and extracted with Et_2O (2×200 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Column chromatography (SiO_2; CH_2Cl_2/hexanes 1:1 $\rightarrow$ 2:1) afforded **5a** (260 mg, 65%) as an orange oil. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.19$ (s, 9H), 3.81 (s, 3H), 3.84 (s, 3H), 5.42 ppm (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -0.2$, 53.3 (two overlapping), 93.5, 101.6, 105.4, 130.5, 131.7, 146.6, 159.6, 160.0 ppm; IR (CCl_4): $\tilde{\nu} = 2954$ (m), 2927 (w), 2120 (m), 1736 (s), 1672 (w), 1582 (m), 1456 (w), 1435 (m), 1252 (s), 1095 (m), 1029 (m), 998 (w), 849 (s) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 328.0251 ([*M*]$^+$, calcd $C_{13}H_{16}O_4S_2Si$: 328.0259). $C_{13}H_{16}O_4S_2Si$ (328.47): calcd: C 47.54, H 4.91, S 19.52; found: C 47.56, H 5.11, S 19.62.

Compounds **5b,c,d** were prepared in a similar way from **6** and ketones **7b,c,d**, respectively.

3-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1-(triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyne (5b): Orange oil. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.22$ (s, 9H), 1.10 (s, 21H), 3.86 ppm ($2 \times$ s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta =$ -0.2, 11.1, 18.5, 53.4 (two overlapping), 89.5, 99.9, 100.6, 101.3, 103.9, 132.4, 132.7, 154.2, 159.8 ppm (two overlapping); IR (CCl_4): $\tilde{\nu} = 2956$ (m), 2923 (w), 2892 (w), 2865 (m), 2141 (m), 2126 (m), 1736 (s), 1580 (m), 1488 (w), 1463 (w), 1435 (m), 1252 (s), 1096 (w), 1029 (w), 998 (w), 962 (m), 883 (w), 847 (s) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 508.1593 ([*M*]$^+$, calcd $C_{24}H_{36}O_4S_2Si_2$: 508.1594), 531.1490 ([*M* + Na]$^+$, calcd $C_{24}H_{36}NaO_4S_2Si_2$: 531.1491).

3-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1,5-bis(trimethylsilyl)-penta-1,4-diyne (5c): Red solid. M.p. 86–88 °C. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.22$ (s, 18H), 3.86 ppm (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -0.2$, 53.5, 89.0, 99.5, 104.2, 132.6, 154.9, 159.8 ppm; IR (CCl_4): $\tilde{\nu} = 2956$ (m), 2900 (w), 2142 (m), 2127 (m), 1736 (s), 1579 (m), 1489 (w), 1435 (m), 1251 (s), 1096 (m), 1030 (m), 998 (w), 964 (m), 847 (s) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 424.0651 ([*M*]$^+$, calcd $C_{18}H_{24}O_4S_2Si_2$: 424.0655), 447.0553 ([*M* + Na]$^+$, calcd $C_{18}H_{24}NaO_4S_2Si_2$: 447.0552).

3-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1,5-bis(triisopropylsilyl)penta-1,4-diyne (5d): Orange oil. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.09$ (s, 42H), 3.86 ppm (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.1$, 18.5, 53.4, 90.0, 100.2, 101.8, 132.5, 152.9, 159.8 ppm; IR (CCl_4): $\tilde{\nu} = 2955$ (s), 2945 (s), 2924 (m), 2891 (m), 2865 (s), 2140 (m), 2125 (m), 1736 (s), 1580 (m), 1496 (w), 1463 (m), 1435 (m), 1383 (w), 1260 (s), 1095 (m), 1073 (w), 1029 (m), 1018 (m), 997 (m), 961 (m), 919 (w), 883 (m) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 592.2527 ([*M*]$^+$, calcd $C_{30}H_{48}O_4S_2Si_2$: 592.2533), 615.2429 ([*M* + Na]$^+$, calcd $C_{30}H_{48}NaO_4S_2Si_2$: 615.2430); $C_{30}H_{48}O_4S_2Si_2$ (593.00): calcd: C 60.76, H 8.16, S 10.81; found: C 60.68, H 8.01, S 10.65.

1,6-Bis[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]hexa-2,4-diyne (8a): A solution of **5a** (305 mg, 0.93 mmol) and K_2CO_3 (144 mg, 1.04 mmol) in THF (7 mL) and MeOH (20 mL) was stirred at room temperature for 1.5 h. Et_2O (200 mL) was added, and the organic phase was washed with H_2O (200 mL), dried ($MgSO_4$), and concentrated in vacuo at room temperature The residue was dissolved in CH_2Cl_2 (15 mL), whereupon Hay catalyst (2.0 mL) was added, and the mixture was stirred under air for 15 min. Evaporation in vacuo at room temperature followed by column chromatography (SiO_2; CH_2Cl_2) afforded **8a** (155 mg, 65%) as an orange solid. M.p. 150–151 °C. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 3.84$ (s, 6H), 3.85 (s, 6H), 5.53 ppm (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 53.4$ (two overlapping), 82.9, 84.0, 91.9, 131.1, 131.6, 149.5, 159.3, 159.5 ppm; IR (CCl_4): $\tilde{\nu} = 2954$ (m), 2927 (w), 2177 (w), 2116 (w), 1737 (s), 1657 (w), 1581 (m), 1520 (w), 1435 (m), 1259 (s), 1095 (m), 1028 (m) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 509.9559 ([*M*]$^+$, calcd $C_{20}H_{14}O_8S_4$: 509.9572), 532.9461 ([*M* + Na]$^+$, calcd $C_{20}H_{14}NaO_8S_4$: 532.9469). $C_{20}H_{14}O_8S_4$ (510.57): calcd: C 47.05, H 2.76, S 25.12; found: C 47.12, H 2.97, S 24.96.

3,8-Bis[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1,10-bis(triisopropylsilyl)deca-1,4,6,9-tetrayne (8b): A solution of **5b** (107 mg, 0.21 mmol) and K_2CO_3 (27 mg, 0.20 mmol) in THF (3 mL) and MeOH (14 mL) was stirred at room temperature for 2.5 h. Et_2O (150 mL) was added, and the organic phase was washed with H_2O (150 mL) and saturated aqueous NaCl (150 mL), dried ($MgSO_4$), and concentrated in vacuo at room temperature. The residue was dissolved in CH_2Cl_2 (15 mL), whereupon Hay catalyst (2.5 mL) was added, and the mixture was stirred under air for 30 min. Evaporation in vacuo at room temperature followed by column chromatography (SiO_2; CH_2Cl_2) afforded **8b** (50 mg, 55%) as an orange oil, which slowly solidified. M.p. 60–62 °C. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.10$ (s, 42H), 3.87 (s, 6H), 3.88 ppm (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.1$, 18.6, 53.5 ($\times$ 2), 81.3, 82.5, 88.0, 100.3, 101.6, 132.4, 133.4, 157.3, 159.3, 159.6 ppm; IR (CCl_4): $\tilde{\nu} = 2954$ (m), 2925 (w), 2892 (w), 2866 (m), 2133 (w), 1736 (s), 1579 (m), 1465 (m), 1435 (m), 1254 (s), 1096 (w), 1027 (w), 998 (w), 881 (w) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 870.2235 ([*M*]$^+$, calcd $C_{42}H_{54}O_8S_4Si_2$: 870.2240), 893.2116 ([*M* + Na]$^+$, calcd $C_{42}H_{54}NaO_8S_4Si_2$: 893.2138).

5-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1-[4-(*N,N*-didodecylamino)phenyl]-7-(triisopropylsilyl)hepta-1,3,6-triyne (9): KOH (1.40 g, 14.1 mmol) in H_2O (5 mL) was added to a solution of 4-[(trimethylsilyl)ethynyl]-(*N,N*-didodecylamino)benzene(351 mg, 0.67 mmol) in THF (10 mL) and MeOH (5 mL). The mixture was stirred at room temperature for 2.5 h, then Et_2O (200 mL) was added, and the organic phase was washed with H_2O (200 mL) and saturated aqueous NaCl (200 mL), dried ($MgSO_4$), and concentrated in vacuo at room temperature to give crude deprotected alkyne. Compound **5b** (74 mg, 0.15 mmol) was mono-deprotected according to the above procedure (see **8b**). The two crude products were dissolved in CH_2Cl_2 (15 mL), whereupon Hay catalyst (1.5 mL) was added. The mixture was stirred under air for 30 min. Evaporation in vacuo at room temperature followed by column chromatography (SiO_2; CH_2Cl_2/hexanes

4:1) afforded **9** (60 mg, 46%) as an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (t, 6.4 Hz, 6H), 1.10 (s, 21H), 1.26 (br s, 36H), 1.56 (br s, 4H), 3.26 (t, 7.2 Hz, 4H), 3.86 (s, 3H), 3.87 (s, 3H), 6.52 (d, 9.0 Hz, 2H), 7.33 ppm (d, 9.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.1$, 14.0, 18.6, 22.6, 27.0, 27.1, 29.3, 29.4, 29.5 (four overlapping), 31.8, 50.9, 53.4, 53.5, 71.7, 76.0, 83.8, 88.4, 88.8, 100.8 (×2), 106.5, 111.2, 132.1, 133.3, 134.0, 148.7, 155.2, 159.4, 159.8 ppm; IR (CCl_4): $\tilde{\nu} = 2955$ (m), 2926 (s), 2854 (m), 2195 (w), 2138 (w), 2128 (w), 1736 (s), 1602 (s), 1579 (w), 1520 (m), 1466 (w), 1435 (w), 1402 (w), 1368 (w), 1259 (s), 1189 (w), 1096 (w), 1028 (w), 997 (w), 883 (w) cm^{-1}; HR-MALDI-MS (DCTB): *m/z*: 887.5371 ([*M*]$^+$, calcd $C_{53}H_{81}NO_4S_2Si$: 887.5376).

5,10-Bis[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1,14-bis[4-(*N,N*-didodecylamino)phenyl]tetradeca-1,3,6,8,11,13-hexayne (10): Bu_4NF (1 M in THF, 0.8 mL, 0.8 mmol) was added to a solution of **9** (51 mg, 0.057 mmol) in THF (8 mL) and H_2O (0.3 mL). The mixture was stirred for 10 min (further reaction time causes decomposition), whereupon Et_2O (200 mL) was added. The organic phase was washed with H_2O (2 × 200 mL), dried ($MgSO_4$), and concentrated in vacuo at room temperature The residue was dissolved in CH_2Cl_2 (15 mL); then Hay catalyst (0.7 mL) was added. After the mixture had been stirred for 20 min, the solvent was removed in vacuo. Column chromatography (SiO_2; CH_2Cl_2/hexanes 4:1 → 1:0) afforded **10** (29 mg, 69%) as an orange semicrystalline oil. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (t, 6.4 Hz, 12H), 1.26 (br s, 72H), 1.54 (br s, 8H), 3.26 (t, 7.2 Hz, 8H), 3.87 (s, 6H), 3.88 (s, 6H), 6.52 (d, 9.1 Hz, 4H), 7.33 ppm (d, 9.1 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.1$, 22.7, 27.1, 27.2, 29.3, 29.5, 29.6 (×4), 31.9, 51.0, 53.6 (×2), 71.6, 74.8, 80.9, 82.7, 84.7, 86.9, 88.9, 106.2, 111.1, 133.0 (×2), 134.0, 148.7, 158.1, 159.1, 159.2 ppm; IR (CCl_4): $\tilde{\nu} = 2959$ (m), 2927 (s), 2855 (m), 2198 (w), 2129 (w), 1737 (s), 1603 (s), 1579 (w), 1520 (m), 1467 (w), 1435 (w), 1404 (w), 1370 (w), 1261 (s), 1189 (w), 1097 (s), 1016 (s), 865 (w) cm^{-1}; MALDI-TOF-MS (DCTB): *m/z*: 1461 ([*M* + H]$^+$). $C_{88}H_{120}N_2O_8S_4$ (1462.16): calcd: C 72.29, H 8.27, N 1.92; found: C 72.45, H 8.54, N 2.05.

5-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1,9-bis(4-nitrophenyl)-nona-1,3,6,8-tetrayne (11): Bu_4NF (1 M in THF, 1.4 mL, 1.4 mmol) was added to a solution of **5c** (50 mg, 0.12 mmol) in THF (15 mL) and H_2O (0.7 mL). The mixture was stirred for 30 min, whereupon Et_2O (150 mL) was added. The organic phase was extracted with H_2O (3 × 150 mL), dried ($MgSO_4$), and concentrated in vacuo at room temperature. The residue was dissolved in CH_2Cl_2 (15 mL), (4-nitrophenyl)acetylene (100 mg, 0.68 mmol) and subsequently Hay catalyst (1.5 mL) were added, affording a dark red solution. After the mixture had been stirred for 30 min, the solvent was removed in vacuo. Column chromatography (SiO_2; CH_2Cl_2/hexanes 4:1 → 1:0) afforded **11** (27 mg, 40%) as an orange solid. M.p. ca. 150 °C (decomp/subl.). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 3.90$ (s, 6H), 7.65 (d, 9.0 Hz, 4H), 8.22 ppm (d, 9.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 53.8$, 78.1, 78.3, 83.2, 84.3, 85.1, 123.8, 128.4, 133.0, 133.4, 147.6, 158.8, 162.7 ppm; IR (CCl_4): $\tilde{\nu} = 2953$ (w), 2930 (w), 2854 (w), 2209 (m), 2191 (m), 1739 (s), 1594 (s), 1580 (m), 1525 (s), 1494 (m), 1467 (m), 1435 (m), 1342 (s), 1283 (m), 1268 (m), 1250 (s), 979 (w), 854 (s) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 570.0192 ([*M*]$^+$, calcd $C_{28}H_{14}N_2O_8S_2$: 570.0192).

3-[4,5-Bis(propoxycarbonyl)-1,3-dithiol-2-ylidene]-1,5-bis(triisopropylsilyl)penta-1,4-diyne (12a): A mixture of **5d** (169 mg, 0.28 mmol), 1-propanol (10 mL), and K_2CO_3 (570 mg, 4.12 mmol) in THF (10 mL) was stirred for 1.5 h. The mixture was diluted with Et_2O (200 mL), filtered, and then H_2O (200 mL) was added. The organic phase was separated, dried ($MgSO_4$), and concentrated in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 4:1 → 1:1) afforded **12a** (167 mg, 90%) as an orange solid. M.p. 70–71 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.96$ (t, 7.5 Hz, 6H), 1.10 (s, 42H), 1.62–1.80 (m, 4H), 4.20 ppm (t, 6.7 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 10.2$, 11.1, 18.5, 21.6, 68.3, 89.6, 100.1, 101.9, 132.7, 153.7, 159.3 ppm; IR (CCl_4): $\tilde{\nu} = 2961$ (s), 2943 (s), 2892 (w), 2866 (s), 2140 (w), 2125 (w), 1738 (s), 1579 (m), 1463 (m), 1261 (s), 1240 (s), 1094 (m), 1057 (w), 1016 (m), 997 (m), 960 (m), 883 (m) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 648.3161 ([*M*]$^+$, calcd $C_{34}H_{56}O_4S_2Si_2$: 648.3159), 671.3048 ([*M* + Na]$^+$, calcd $C_{34}H_{56}NaO_4S_2Si_2$: 671.3056). $C_{34}H_{56}O_4S_2Si_2$ (649.11): calcd: C 62.91, H 8.70, S 9.88; found: C 62.80, H 8.54, S 10.06.

3-[4,5-Bis(pentoxycarbonyl)-1,3-dithiol-2-ylidene]-1,5-bis(triisopropylsilyl)penta-1,4-diyne (12b): Compound **12b** was obtained in a similar way, from **5d** and 1-pentanol, as an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 0.91 (t, 6.8 Hz, 6H), 1.09 (s, 42H), 1.33 (m, 8H), 1.68 (t, 6.9 Hz, 4H), 4.23 ppm (t, 6.7 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.1$, 13.8, 18.5, 22.1, 27.8, 27.9, 66.9, 89.6, 100.0, 101.9, 132.7, 153.7, 159.3 ppm; IR (CCl_4): $\tilde{\nu} = 2960$ (s), 2943 (s), 2892 (w), 2865 (s), 2141 (w), 2130 (w), 1732 (s), 1579 (m), 1463 (m), 1383 (w), 1260 (s), 1243 (s), 1097 (m), 1072 (w), 1045 (w), 1018 (m), 997 (m), 961 (m), 919 (w), 882 (m) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 704.3768 ([*M*]$^+$, calcd $C_{38}H_{64}O_4S_2Si_2$: 704.3785), 727.3649 ([*M* + Na]$^+$, calcd $C_{38}H_{64}NaO_4S_2Si_2$: 727.3682).

3-[4,5-Bis(dodecyloxycarbonyl)-1,3-dithiol-2-ylidene]-1,5-bis(triisopropylsilyl)penta-1,4-diyne (12c): Compound **12c** was obtained in a similar way, from **5d** and 1-dodecanol, as an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (t, 6.4 Hz, 6H), 1.10 (s, 42H), 1.26 (s, 36H), 1.60–1.72 (m, 4H), 4.23 ppm (t, 6.6 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.1$, 14.0, 18.5, 22.6, 25.7, 28.2, 29.5 (br), 31.8, 66.9, 89.6, 100.0, 101.8, 132.7, 153.6, 159.2 ppm; HR-MALDI-MS (DHB-tl): *m/z*: 900.5985 ([*M*]$^+$, calcd $C_{52}H_{92}O_4S_2Si_2$: 900.5976), 923.5866 ([*M* + Na]$^+$, calcd $C_{52}H_{92}NaO_4S_2Si_2$: 923.5873). $C_{52}H_{92}O_4S_2Si_2$ (901.59): calcd: C 69.27, H 10.28, S 7.11; found: C 69.46, H 10.21, S 6.97.

3-[4-Hydroxymethyl-5-methoxycarbonyl-1,3-dithiol-2-ylidene]-1,5-bis(triisopropylsilyl)penta-1,4-diyne (13): LiCl (11 mg, 0.26 mmol) and $NaBH_4$ (10 mg, 0.26 mmol) were added at 15 °C to a solution of **5d** (71 mg, 0.12 mmol) in THF (20 mL) and MeOH (5 mL). The mixture was stirred at 15 °C for 1 h and then another 1 h at room temperature. Et_2O (200 mL) was added, then the mixture was washed with H_2O (2 × 200 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was subjected to column chromatography (SiO_2; CH_2Cl_2), affording **13** (31 mg, 46%) as a yellow solid. M.p. 100.5–102 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.10$ (s, 42H), 3.17 (t, 7.1 Hz, 1H), 3.83 (s, 3H), 4.70 ppm (d, 7.1 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.2$, 18.6, 52.9, 59.5, 88.7, 98.9, 99.5, 102.2 (two overlapping), 120.6, 153.9, 154.4, 160.7 ppm; IR (CCl_4): $\tilde{\nu} = 2957$ (s), 2944 (s), 2923 (m), 2892 (w), 2866 (s), 2140 (w), 2124 (w), 1716 (s), 1704 (s), 1569 (m), 1463 (m), 1435 (w), 1261 (s), 1056 (w), 1033 (w), 996 (w), 961 (w), 883 (m) cm^{-1}; MALDI-MS (DHB-tl): *m/z*: 564 ([*M*]$^+$), 587 ([*M* + Na]$^+$). $C_{29}H_{48}O_3S_2Si_2$ (564.99): calcd: C 61.65, H 8.56, S 11.35; found: C 61.81, H 8.34, S 11.55.

3,8-Bis[4,5-bis(propoxycarbonyl)-1,3-dithiol-2-ylidene]-1,10-bis(triisopropylsilyl)deca-1,4,6,9-tetrayne (14): Compound **14** was obtained, from **8b** and 1-propanol, as an orange oil, employing the same procedure as for **12a**. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.97$ (t, 7.3 Hz, 12H), 1.10 (s, 42H), 1.62–1.81 (m, 8H), 4.21 ppm (t, 6.6 Hz, 8H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta =$ 10.2, 11.2 (two overlapping), 18.6, 21.7 (two overlapping), 68.5, 68.6, 81.3, 82.5, 87.7, 100.5, 101.4, 132.9, 133.0, 157.6, 158.9 ppm (two overlapping); IR (CCl_4): $\tilde{\nu} = 2962$ (m), 2944 (m), 2925 (w), 2892 (w), 2865 (m), 2132 (w), 1738 (s), 1578 (m), 1467 (m), 1390 (w), 1311 (w), 1240 (s), 1095 (w), 1056 (w), 1012 (w), 997 (w), 929 (w), 882 (w) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 982.3522 ([*M*]$^+$, calcd $C_{50}H_{70}O_8S_4Si_2$: 982.3492), 1005.3483 ([*M* + Na]$^+$, calcd $C_{50}H_{70}NaO_8S_4Si_2$: 1005.3390). $C_{50}H_{70}O_8S_4Si_2$ (983.51): calcd: C 61.06, H 7.17, S 13.04; found: C 61.08, H 7.07, S 12.93.

5-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-7-(triisopropylsilyl)-1-(trimethylsilyl)hepta-1,3,6-triyne (15): Compound **5b** (90 mg, 0.18 mmol) was mono-deprotected according to above procedure (see **8b**) and dissolved in CH_2Cl_2 (15 mL), whereupon (trimethylsilyl)acetylene (0.5 mL, 3.6 mmol) was added, followed by Hay catalyst (1.0 mL), and the mixture was stirred under air for 15 min. Evaporation in vacuo at room temperature followed by column chromatography (SiO_2; CH_2Cl_2/hexanes 1:1) afforded **15** (52 mg, 55%) as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.22$ (s, 9H), 1.09 (s, 21H), 3.86 (s, 3H), 3.87 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -0.5$, 11.1, 18.6, 53.5, 53.6, 71.9, 83.0, 87.4, 87.5, 95.5, 100.2, 101.6, 132.1, 133.3, 157.5, 159.2, 159.5 ppm; IR (CCl_4): $\tilde{\nu} =$ 2955 (m), 2945 (m), 2892 (w), 2866 (m), 2202 (w), 2134 (w), 2094 (w), 1736 (s), 1580 (m), 1479 (m), 1435 (m), 1252 (s), 1099 (m), 1029 (w), 997 (w), 882 (w), 862 (s), 846 (m) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 532.1604 ([*M*]$^+$, calcd $C_{26}H_{36}O_4S_2Si_2$: 532.1594), 555.1478 ([*M* + Na]$^+$, calcd $C_{26}H_{36}NaO_4S_2Si_2$: 555.1491).

3,12-Bis[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1,14-bis(triisopropylsilyl)tetradeca-1,4,6,8,10,13-hexayne (16): A solution of **15** (79 mg, 0.15 mmol) and K_2CO_3 (22 mg, 0.16 mmol) in THF (4 mL) and MeOH (13 mL) was stirred at room temperature for 1 h. Et_2O (200 mL) was added, and the organic phase was washed with H_2O (200 mL), dried ($MgSO_4$), and concentrated in vacuo at room temperature. The residue was dissolved in CH_2Cl_2 (15 mL), whereupon Hay catalyst (1.0 mL) was added, and the mixture was stirred under air for 15 min. Evaporation in vacuo at room temperature followed by column chromatography (SiO_2; CH_2Cl_2) afforded **16** (35 mg, 51 %) as an orange semicrystalline oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.10$ (s, 42 H), 3.88 (s, 6 H), 3.89 ppm (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.1$, 18.6, 53.6, 53.7, 66.1, 72.6, 74.5, 83.8, 86.8, 99.5, 102.6, 132.3, 133.7, 159.0, 159.3, 160.4 ppm; IR (CCl_4): $\tilde{\nu} = 2954$ (m), 2945 (m), 2892 (w), 2866 (m), 2179 (m), 2134 (w), 1738 (s), 1580 (m), 1469 (m), 1435 (m), 1260 (s), 1096 (m), 1028 (m), 997 (w), 883 (w) cm^{-1}; HR-MALDI-MS (DHB-tl): *m/z*: 918.2252 ([*M*]$^+$, calcd $C_{46}H_{54}O_8S_4Si_2$: 918.2240), 941.2192 ([*M* + Na]$^+$, calcd $C_{46}H_{54}NaO_8S_4Si_2$: 941.2138).

(*E*)-1-Bromo-3,4-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-(trimethylsilyl)hex-3-ene-1,5-diyne (19): *n*BuLi (1.6 M in hexane, 0.32 mL, 0.50 mmol) was slowly added at −78 °C to a solution of **20** (200 mg, 0.46 mmol) in dry THF (30 mL). After the mixture had been stirred for 30 min, Br_2 (0.026 mL, 0.51 mmol) was added, and the mixture was allowed to reach room temperature during 1 h. Saturated aqueous $Na_2S_2O_3$ (20 mL) and saturated aqueous NH_4Cl (20 mL) were added to the mixture, and it was extracted with CH_2Cl_2 (150 mL). The water phase was extracted with CH_2Cl_2 (2 × 40 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was subjected to column chromatography (SiO_2; hexanes/CH_2Cl_2 2:1), affording **19** (120 mg, 51 %) as a light-yellow oil. The compound is unstable and should be stored in solution (CH_2Cl_2) at 4 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.09$ (s, 12 H), 0.19 (s, 9 H), 0.91 (s, 18 H), 4.39 (s, 2 H), 4.44 ppm (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.3$ (two overlapping), −0.1, 18.2, 18.3, 25.8 (two overlapping), 61.0, 63.7, 63.8, 77.3, 101.4, 107.5, 130.4, 131.2 ppm; IR (film): $\tilde{\nu} = 2957$ (s), 2922 (s), 2889 (s), 2144 (w), 1472 (m), 1251 (m), 1183 (w), 1104 (m), 1006 (w), 939 (w), 841 (s), 776 (s) cm^{-1}; EI-MS (DHB-tl): *m/z*: 451 ([$M - C(CH_3)_3$]$^+$).

(*E*)-2,3-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-9-[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-11-(triisopropylsilyl)-1-(trimethylsilyl)undeca-3-ene-1,5,7,10-tetrayne (18): Compound **5b** (77 mg, 0.15 mmol) was mono-deprotected according to above procedure (see **8b**) and dissolved in benzene (4 mL). Then LiI (3.2 mg, 0.023 mmol), 1,2,2,6,6-pentamethylpiperidine (0.0585 mL, 0.324 mmol), and [$Pd_2(dba)_3$] (3.0 mg, 0.004 mmol) were added. The mixture was vigorously degassed with Ar, whereupon CuI (0.65 mg, 0.003 mmol) was added, followed by an Ar-degassed solution of bromide **19** (58 mg, 0.11 mmol) in benzene (4 mL). After stirring overnight, the mixture was filtered through a short plug of SiO_2 (CH_2Cl_2). The orange fraction containing at this stage impure product was concentrated at room temperature. To facilitate chromatographic separation of product from remaining deprotected **5b**, the residue was dissolved in a small amount of CH_2Cl_2 (ca. 5 mL) and subjected to Hay catalyst (0.3 mL). Shaking for 5 min resulted in homo-coupling of deprotected **5b** yielding more polar and more readily separable **8b**. The mixture was concentrated in vacuo at room temperature. Column chromatography (SiO_2; CH_2Cl_2/hexanes 1:1) afforded pure **18** (50 mg, 50 %) as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.11$ (2 × s, 12 H), 0.21 (s, 9 H), 0.92 (s, 18 H), 1.10 (s, 21 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 4.42 (s, 2 H), 4.48 ppm (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.0$ (two overlapping), −0.1, 11.3, 18.5 (two overlapping), 18.8, 26.0 (two overlapping), 53.6, 53.7, 63.8, 64.0, 80.3, 82.8, 83.3, 85.3, 88.0, 100.2, 101.3, 101.5, 109.2, 129.6, 132.0, 132.5, 133.4, 156.8, 159.0, 159.4 ppm; IR (CCl_4): $\tilde{\nu} = 2956$ (m), 2929 (m), 2894 (w), 2865 (m), 2139 (w), 1737 (m), 1580 (w), 1472 (w), 1462 (w), 1435 (w), 1252 (s), 1097 (m), 1028 (w), 845 (s) cm^{-1}; HR-MALDI-MS (DCTB mix): *m/z*: 893.3595 ([*M* + Na]$^+$, calcd $C_{44}H_{70}NaO_6S_2Si_4$: 893.3589).

(*E,E*)-8,9,14,15-Tetrakis{[(*tert*-butyl)dimethylsilyloxy]methyl}-3,20-bis[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1,22-bis(triisopropylsilyl)docosa-8,14-diene-1,4,6,10,12,16,18,21-octayne (17): A solution of **18** (43 mg, 0.049 mmol) and K_2CO_3 (7 mg, 0.05 mmol) in THF (1.5 mL) and MeOH (5 mL) was stirred at room temperature for 1 h and 45 min. Et_2O (200 mL) was added, and the organic phase was washed with H_2O (2 × 200 mL), dried ($MgSO_4$), and concentrated in vacuo at room temperature. The residue was dissolved in CH_2Cl_2 (15 mL), whereupon Hay catalyst (0.6 mL) was added, and the mixture was stirred under air for 20 min. Evaporation in vacuo at room temperature followed by column chromatography (SiO_2; CH_2Cl_2/hexanes 4:1 → 1:0) afforded **17** (19 mg, 48 %) as an orange semicrystalline oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.12$ (s, 24 H), 0.93 (s, 36 H), 1.11 (s, 42 H), 3.87 (s, 6 H), 3.88 (s, 6 H), 4.46 ppm (s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.2$ (two overlapping), 11.2, 18.4 (two overlapping), 18.6, 25.9 (two overlapping), 53.5, 53.7, 63.8, 64.0, 81.7, 82.7, 83.3, 83.4, 87.2, 87.6, 87.9, 100.1, 101.6, 131.4, 132.1, 132.7, 133.6, 157.5, 159.1, 159.5 ppm; IR (CCl_4): $\tilde{\nu} = 2954$ (s), 2929 (s), 2892 (m), 2865 (m), 2181 (w), 2135 (w), 1737 (s), 1580 (m), 1471 (m), 1463 (m), 1435 (m), 1259 (s), 1097 (m), 1027 (m), 883 (w), 839 (s) cm^{-1}; MALDI-TOF-MS (DCTB): *m/z*: 1595 ([*M* + H]$^+$), 1618 ([*M* + H + Na]$^+$). $C_{82}H_{122}O_{12}S_4Si_6$ (1594.64): calcd: C 61.69, H 7.70; found: C 61.95, H 7.75.

2,5-Bis{3-[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-5-(triisopropylsilyl)penta-1,4-diynyl}thiophene (21): Compound **5b** (372 mg, 0.74 mmol) was mono-deprotected according to above procedure and dissolved in Ar-degassed THF (12 mL), whereupon 2,5-diiodothiophene and [$Pd(PPh_3)_4$] (8.6 mg, 0.0074 mmol) were added. Ar-degassed diethylamine (1.5 mL) was added, and the mixture was degassed with argon, whereupon CuI (2.3 mg, 0.012 mmol) was added. The mixture was stirred under argon for 15 h, then Et_2O (200 mL) was added, and the organic phase was washed with H_2O (200 mL), NH_4Cl (200 mL), dried ($MgSO_4$), and concentrated in vacuo at room temperature column chromatography (SiO_2; CH_2Cl_2/hexanes 1:1 → 1:0) afforded **21** (97 mg, 68 %) as an orange semicrystalline oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.12$ (s, 42 H), 3.87 (s, 6 H), 3.88 (s, 6 H), 7.09 ppm (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.3$, 18.8, 53.6 (× 2), 88.6, 89.8, 90.6, 100.7, 100.8, 124.3, 131.8, 131.9, 133.1, 153.7, 159.2, 159.5 ppm; IR (CCl_4): $\tilde{\nu} = 2954$ (m), 2944 (m), 2925 (w), 2891 (w), 2866 (m), 2135 (w), 1736 (s), 1580 (m), 1479 (w), 1462 (w), 1435 (m), 1254 (s), 1095 (w), 1029 (w), 997 (w), 921 (w), 883 (w) cm^{-1}; HR-MALDI-MS (DCTB): *m/z*: 952.2119 ([*M*]$^+$, calcd $C_{46}H_{56}O_8S_5Si_2$: 952.2117).

Tetrakis-cobalt complex (22): [$Co_2(CO)_8$] (90–95 %, 356 mg, ca. 1 mmol) was added under argon to a solution of **8a** (89 mg, 0.17 mmol) in dry THF (10 mL). After stirring for 30 min, the solvent was removed in vacuo. The residue was purified by column chromatography (SiO_2; CH_2Cl_2), affording **22** (178 mg, 94 %) as a red-brown solid (dark green in solution). M.p. > 250 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.87$ (s, 6 H), 3.88 (s, 6 H), 6.63 ppm (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 53.6$ (× 2), 88.2, 91.8, 107.7, 131.6, 132.2, 143.4, 159.5, 159.7, 198.6 ppm; IR (CCl_4): $\tilde{\nu} = 2962$ (w), 2097 (w), 2077 (m), 2061 (s), 2030 (m), 2023 (m), 1737 (w), 1719 (w), 1582 (w), 1434 (w), 1261 (m), 1096 (m), 1015 (m) cm^{-1}; MALDI-MS (DCTB): *m/z*: 1054 ([$M - CO$]$^+$), 883 ([$M - Co - 5CO$]$^+$), 880 ([$M - 2Co - 3CO$]$^+$), 737 ([$M - 3Co - 6CO$]$^+$), 567 ([$M - 3Co - 12CO - 2H$]$^+$); $C_{32}H_{14}O_{20}S_4Co_4$ (1082.42): calcd: C 35.51, H 1.30, S 11.85; found: C 35.61, H 1.32, S 11.72.

Decomplexation of 22: Trimethylamine oxide (21 mg, 0.28 mmol) was added to a solution of **22** (29.2 mg, 0.027 mmol) in THF (20 mL). After stirring for 20 min, Et_2O (250 mL) was added, and the organic phase was washed with H_2O (250 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography on a short column (SiO_2; CH_2Cl_2), affording **8a** (4.8 mg, 35 %).

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