# Synthesis and Characterization of Extended Tetrathiafulvalenes with Di-, Tri-, and Tetraethynylethene Cores

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A selection of new acetylenic building blocks has been prepared and employed for construction of extended tetrathiafulvalenes (TTFs) and novel donor–acceptor molecules based on either diethynylethene (DEE), triethynylethene (TriEE), or tetraethynylethene (TEE) cores. The novel chromophores were studied for their redox, chromophoric, and structural properties, which have provided fundamental structure–property relationships.


## Introduction

Tetrathiafulvalene (TTF) is a good electron donor that has been widely exploited in supramolecular and materials chemistry.[1] The extension of π-electron conjugation in tetrathiafulvalene by a spacer unit as well as functionalization by electron acceptors has attracted considerable attention in the quest for electrically conducting or non-linear optical (NLO) materials (Figure 1).[2] We have recently shown that acetylenic scaffolding is a powerful tool for constructing alkyne-extended TTFs by suitable modules, such as the acetylenic dithiafulvene **1** that is readily desilylated to provide the terminal acetylene **2**.[3]

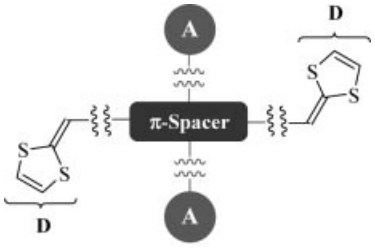
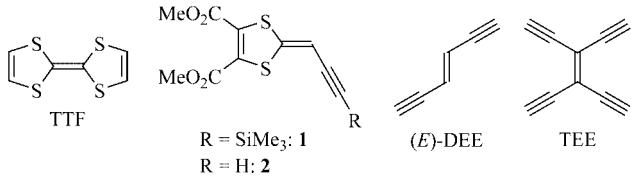



Figure 1. Schematic representation of extended TTF and donor–acceptor (D–A) dyads based hereupon.

Silylated derivatives of (*E*)-diethynylethene [(*E*)-DEE] and tetraethynylethene (TEE) provide examples of other very useful modules that have been successfully employed by Diederich and co-workers for the construction of a large variety of conjugated molecules, such as poly(triacetylene) oligomers and expanded radialenes.[4] The optical properties of these scaffolds were strongly enhanced upon functionalization with aryl groups, such as electron-donating anilino groups and electron-accepting nitrophenyl groups.[5] Thus, donor–acceptor functionalized TEE scaffolds were found to exhibit exceptionally high third-order NLO susceptibilities.[6] For these reasons, we became interested in functionalizing di-, tri-, and tetraethynylethenes with dithiafulvene donor groups. Such target molecules will be termed DEE-, TriEE-, and TEE-extended TTFs. Here we present synthetic protocols together with electrochemical and preliminary photophysical investigations.[7]




## Results and Discussion

**Synthesis:** The synthesis of DEE-extended TTFs proceeds according to Scheme 1. The dialdehyde **3**[8] and the phosphonium salt **4**[9] were prepared according to literature procedures. They were reacted together in a Wittig reaction, after deprotonation of **4** with *n*BuLi, which afforded the DEE-TTF **5** in good yield. This same strategy has found wide application for preparing polyenic analogues of TTF.[10] However, treating **3** with the ylide of **6**[11] gave only the mono-coupled product **7**. It was not possible to force

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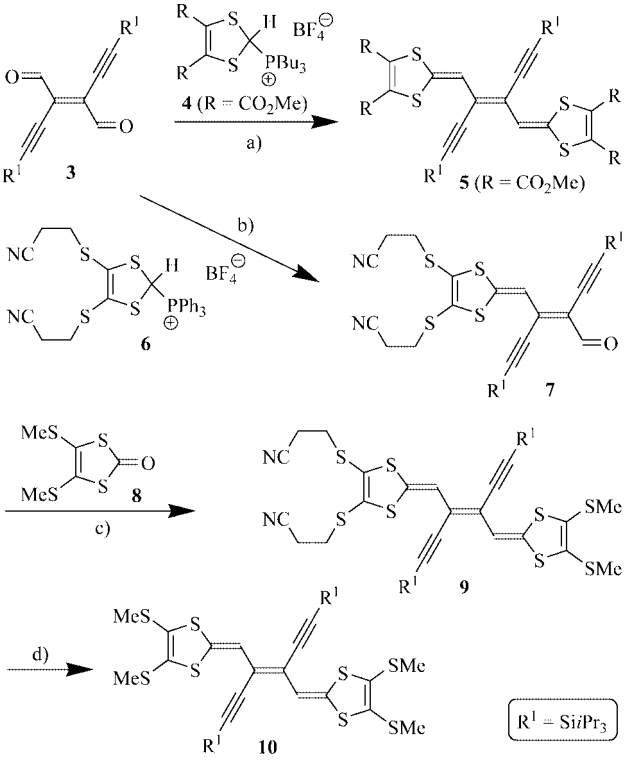
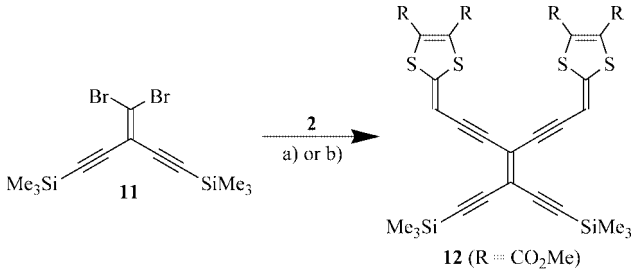
olefination at both aldehyde positions by treating **3** with more than two equivalents of **6**. However, a phosphite-mediated cross-coupling with the 1,3-dithiole-2-one **8** gave the cross-coupled compound **9** in good yield. Accordingly, this latter procedure presents a convenient route to unsymmetrical, alkene-extended TTFs, in this case with one end containing cyanoethyl-protected thiolate groups. Cyanoethylthio-substituted TTFs have proven as versatile building blocks for oligomers and macrocycles via stepwise deprotection-realkylation protocols as shown by Becher and coworkers.[12] The cyanoethyl groups of **9** were removed according to the standard procedure by CsOH, leaving the $Si(iPr)_3$ groups uncleaved. Alkylation with MeI in situ finally afforded the symmetrical TTF **10**.



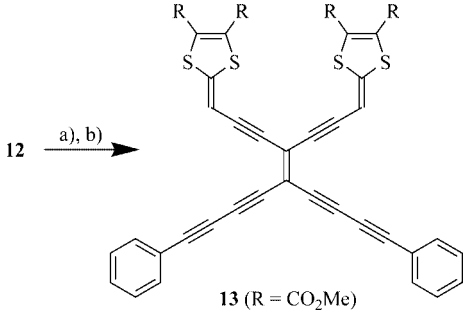

Scheme 1. Synthesis of DEE-extended TTFs. a) *n*BuLi, THF; 60%; b) $NEt_3$, THF; 69%; c) $P(OEt)_3$; 79%; d) $CsOH·H_2O$, MeI, THF, MeOH; 82%.

Geminally functionalized TEEs were previously constructed from Sonogashira cross-couplings[13] between vinylic dibromides and arylacetylenes containing either electron-donating (e.g. $NMe_2$) or withdrawing (e.g. $NO_2$) substituents.[14] The couplings usually proceeded smoothly in the presence of the $[Pd(PPh_3)_2Cl_2]$/CuI catalyst system. Surprisingly, we find that treatment of **11** (Scheme 2) with **2** under these conditions completely failed to provide the TEE-extended TTF **12**.[15] Many cross-couplings are enhanced by using bulky, electron-rich phosphanes.[16] Recently, Hundertmark et al.[17] developed a versatile catalyst system, $[Pd(PhCN)_2Cl_2]$/$P(tBu)_3$/CuI, that allowed room temperature Sonogashira coupling of aryl bromides with a wide variety of terminal acetylenes. We turned to this system and at the same time subjected the reaction mixture to microwave heating at 60 °C for 6 min.[18] Hereby TEE-TTF **12** was obtained in a yield of 38%. The yield was improved further by substituting the microwave heating with ultrasonification at 30 °C for 4 hours.[19] The TEE core was under these conditions constructed in yields as high as 85%.




Scheme 2. Synthesis of TEE-extended TTF. a) $[Pd(PhCN)_2Cl_2]$, $P(tBu)_3$, CuI, $HN(iPr)_2$, THF, toluene, microwave heating, 60 °C, 6 min; 38%; b) $[Pd(PhCN)_2Cl_2]$, $P(tBu)_3$, CuI, $HN(iPr)_2$, THF, toluene, ultrasonification, 30 °C; 85%.

TEE-TTF **12** containing two silyl-protected acetylene groups possesses the possibility for further acetylenic scaffolding. The trimethylsilyl protecting groups were removed by $K_2CO_3$ in THF/MeOH, and the desilylated compound was hereafter subjected to an oxidative Hay coupling[20] with an excess of phenylacetylene (Scheme 3). This cross-coupling reaction provided the large conjugated chromophore **13** in 18%. The rather low yield was partly due to significant decomposition of the desilylated intermediate. We experienced similar stability problems in the desilylation of the DEE-extended TTFs. Attempts of cross-coupling desilylated **12** with *p*-iodonitrobenzene were unsuccessful, since decomposition took over in this slow reaction (as compared to the Hay coupling).

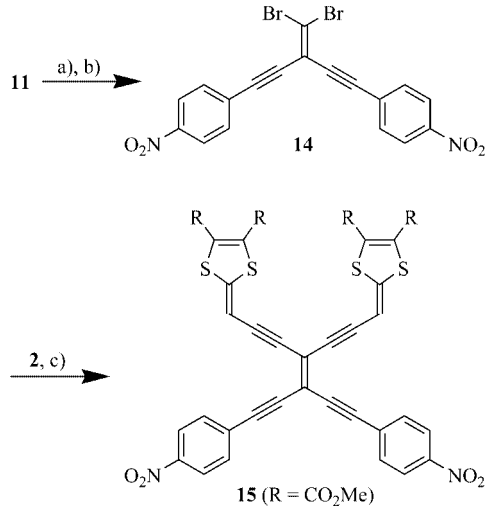



Scheme 3. Synthesis of extended TEE-TTF chromophore. a) $K_2CO_3$, THF, MeOH; b) phenylacetylene, CuCl, TMEDA, $CH_2Cl_2$, air; 18%. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

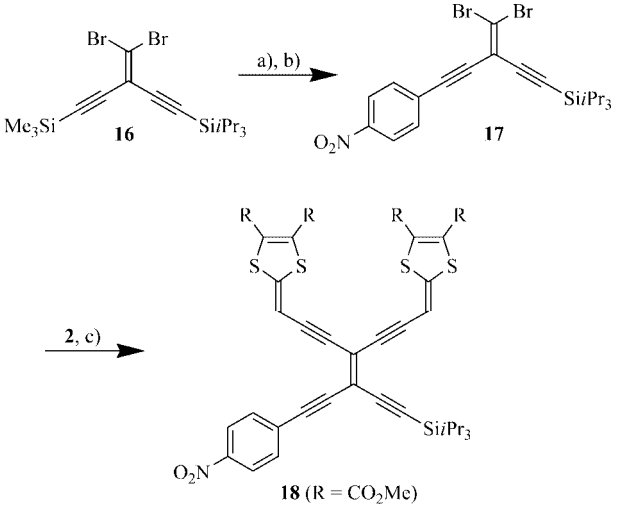
In order to construct a TEE core with dithiafulvene donors and *p*-nitrophenyl acceptors, we decided to incorporate the *p*-nitrophenyl groups first. The synthesis proceeds according to Scheme 4. Compound **11** was desilylated and then subjected to a Pd-catalyzed coupling with an excess of *p*-iodonitrobenzene to provide the new molecular module **14**. An ultrasound-promoted cross-coupling reaction between **14** and two equivalents of **2** ultimately afforded the donor–acceptor TEE **15** in almost quantitative yield. We exploited this same procedure for preparing a donor–ac-

ceptor TEE containing one remaining silyl protecting group (Scheme 5). Thus, selective mono-desilylation of **16** followed by a cross-coupling reaction with *p*-iodonitrobenzene gave compound **17** that was subsequently coupled with two equivalents of **2**, which provided TEE **18**.

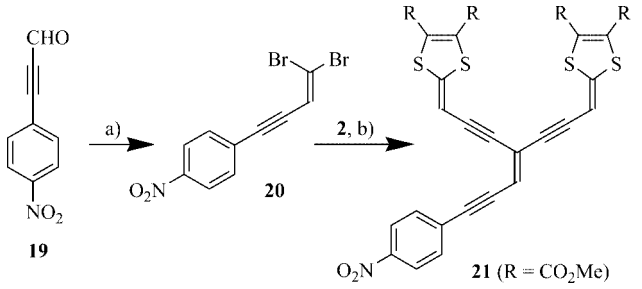



Scheme 4. Synthesis of donor–acceptor TEE. a) $K_2CO_3$, THF, MeOH; b) *p*-iodonitrobenzene, $[PdCl_2(PPh_3)_2]$, CuI, $Et_3N$, THF; 54%; c) $[Pd(PhCN)_2Cl_2]$, P(*t*Bu)$_3$, CuI, HN(*i*Pr)$_2$, THF, toluene, ultrasonification, 30 °C; 97%.



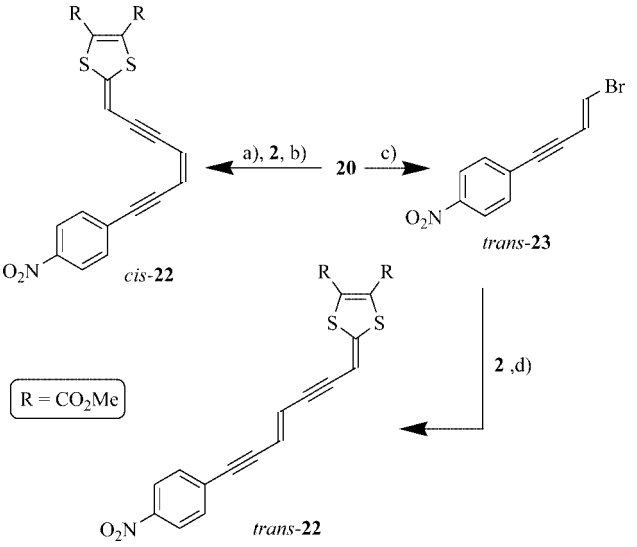

Scheme 5. Synthesis of unsymmetrical donor–acceptor TEE. a) $K_2CO_3$, THF, MeOH; b) *p*-iodonitrobenzene, $[PdCl_2(PPh_3)_2]$, CuI, $Et_3N$, THF; 44%; c) $[Pd(PhCN)_2Cl_2]$, P(*t*Bu)$_3$, CuI, HN(*i*Pr)$_2$, THF, toluene, ultrasonification, 30 °C; 48%.

A new donor–acceptor molecule based on the triethynylethene (TriEE) core was prepared according to the protocol depicted in Scheme 6. First the aldehyde **19**[21] was subjected to a Corey–Fuchs dibromoolefination,[22] which gave the new building block **20**, a vinylic dibromide containing a *p*-nitrophenylacetylene substituent. A cross-coupling reaction between **2** and **20** afforded TriEE **21** in a yield of 30%.[23] For comparison, **21** was only obtained in a yield of 10% with the $[Pd(PPh_3)_2Cl_2]$/CuI catalyst.




Scheme 6. Synthesis of donor–acceptor TriEE. a) $CBr_4$, $PPh_3$, Zn, $CH_2Cl_2$, room temp.; 72%; b) $[Pd(PhCN)_2Cl_2]$, P(*t*Bu)$_3$, CuI, HN(*i*Pr)$_2$, THF, toluene, ultrasonification, 30 °C; 30%.

Finally, synthetic protocols were developed for obtaining DEE-spaced donor–acceptor molecules.[24] The new dibromide **20** conveniently serves as a useful starting material for such target molecules (Scheme 7). Subjecting **20** to the $Pd^0$-catalyzed stereoselective hydrogenolysis procedure developed by Uenishi et al.,[25] followed by in situ cross-coupling with **2** gave *cis*-**22** in good yield. Diethyl phosphite reduction[26] of **20** at 50 °C for 6 h gave *trans*-**23** that was isolated and subsequently cross-coupled with **2** to afford *trans*-**22**. When the reduction of **20** was run instead at 0 °C for 2 h, a mixture of *trans*/*cis*-**22** (53:47) was obtained in an overall yield of 87%. The low stereoselectivity as compared to that reported by Hirao et al.[26] from reduction of β,β-dibromostyrene (*trans*/*cis*, 94:6) is probably due to the presence of the triple bond between the aromatic ring and the dibromo-substituted double bond. A lower stereoselectivity for compounds not having the double bond directly attached to the aromatic ring has been reported by others.[27] We found that *cis*-**22** conveniently decomposed in preference to *trans*-**22** upon prolonged heating at a temperature of 50 °C or higher. Thus, only trace amounts of the *cis*-isomer remained after 6 h at 50 °C.




Scheme 7. Synthesis of donor–acceptor DEEs. a) $[Pd(PPh_3)_4]$, $Bu_3SnH$, toluene; b) CuI, HN(*i*Pr)$_2$, THF; 39%; c) HPO(OEt)$_2$, $Et_3N$, 50 °C; 42%; d) $[Pd(PPh_3)_4]$, CuI, HN(*i*Pr)$_2$, toluene, THF; 67%.

**X-ray Crystallographic Analysis:** Crystals of *cis*-**22** suitable for X-ray crystallographic analyses were grown by slow evaporation of a $CH_2Cl_2$ solution at ca. 8 °C. Crystals of *trans*-**22** were obtained by recrystallization from MeCN. The structures of *cis*-**22** and *trans*-**22** (Figure 2 and Figure 3) confirm the postulated isomer designations. Moreover, the structures reveal that the conjugated section, except for one of the methoxycarbonyl groups, is almost in the same plane for both molecules, with root-mean-square deviations of 0.206 Å and 0.133 Å, respectively. The bond length alternation in the *p*-nitrophenyl ring can be expressed by the quinoid character ($\delta r$) of the ring defined by[28]

$$\delta r = [(a - b) + (c - b)]/2 \approx [(a' - b') + (c' - b')]/2,$$

where *a*, *b* and *c* are defined according to Figure 4. Very small values of $\delta r$ = 0.010 Å (*cis*-**22**) and 0.011 Å (*trans*-**22**) are obtained, which signal a little permanent dipole moment in the ground state. The same quinoid character was determined for the *p*-$NO_2$Ph ring of *p*-$NO_2C_6H_4$–C≡C–$C_6H_4NH_2$ ($\delta r$ = 0.011 Å).[28]

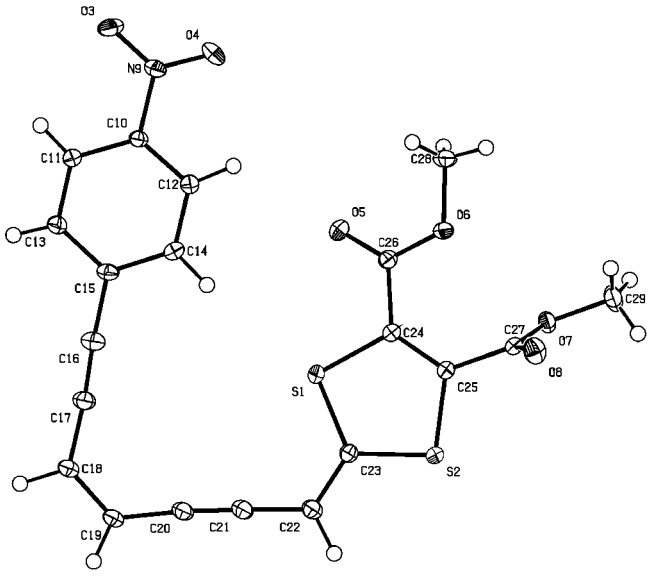



Figure 2. X-ray crystal structure of *cis*-**22**. All atoms, except methyl hydrogen atoms on C28 together with O7, O8 and the C29 methyl group, are approximately planar (rmsd = 0.206 Å for 33 atoms). They make an angle of 78° with the plane formed by O7, O8, C25, C27 and C29 (rmsd = 0.006 Å). Drawing made by ORTEP-II.[34]

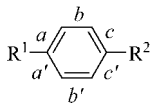



Figure 4. Definition of bond lengths for calculation of quinoid character ($\delta r$).

**Electronic Absorption Spectroscopy:** The UV/Vis spectroscopic data in $CHCl_3$ of the compounds are listed in Table 1, and some selected spectra are displayed in Figure 5 and Figure 6 in comparison to the butadiyne-extended

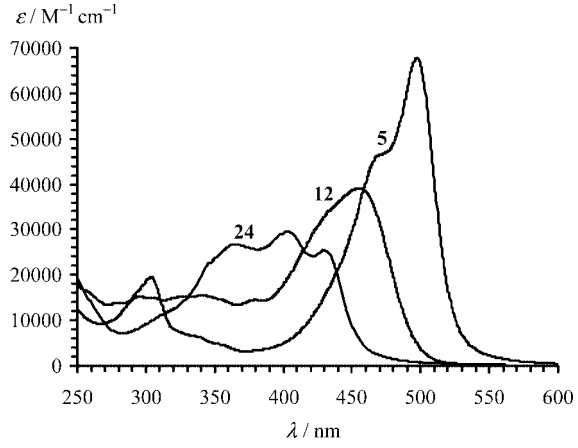



Figure 5. UV/Vis absorption spectra in $CHCl_3$ of extended TTFs.

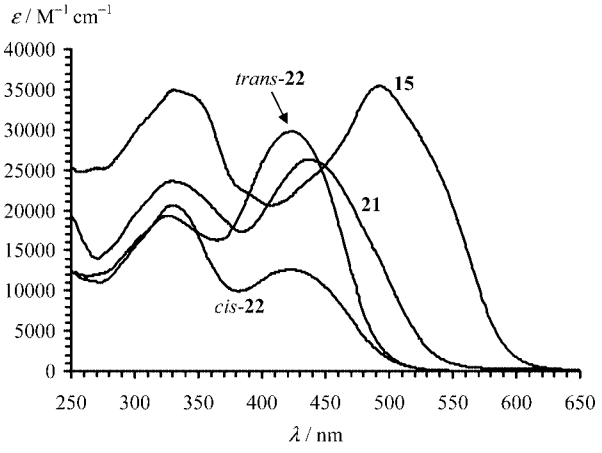



Figure 6. UV/Vis absorption spectra in $CHCl_3$ of donor–acceptor molecules.

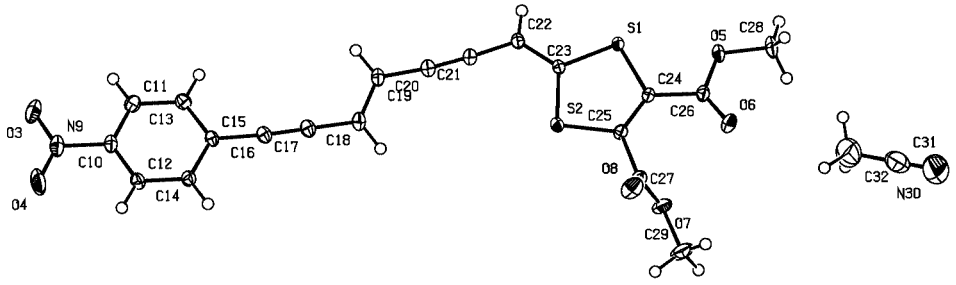



Figure 3. X-ray crystal structure of *trans*-**22**. All atoms of *trans*-**22**, except methyl hydrogens on C28 together with O7, O8 and the C29 methyl group, are almost planar (rmsd = 0.133 Å for 33 atoms). They make an angle of 65° with the plane formed by O7, O8, C25, C27 and C29 (rmsd = 0.009 Å). Drawing made by ORTEP-II.[34]

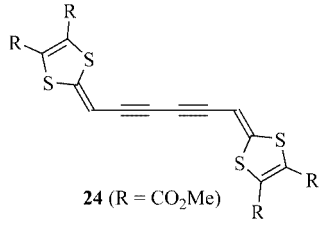
  

Table 1. Absorption band maxima and molar molar absorptivities in the UV/Vis spectra of compounds in $CHCl_3$.[a]

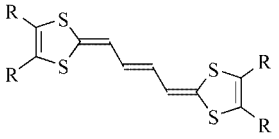
| Compound | $\lambda_{max}$ [nm] ($\varepsilon$ [$M^{-1}$ $cm^{-1}$]) | | | | | | |
|---|---|---|---|---|---|---|---|
| **5** | 294 (sh, 16400) | 303 (19400) | 335 (6550) | 353 (4790) | 468 (46000) | 496 (67500) | |
| **7** | 268 (13200) | 287 (sh, 10500) | 299 (sh, 8110) | 349 (8560) | 365 (sh, 7330) | 483 (35300) | |
| **9** | 273 (19600) | 309 (18300) | 339 (sh, 10200) | 359 (sh, 7670) | 493 (sh, 48100) | 519 (67000) | |
| **10** | 280 (17100) | 312 (14900) | 340 (sh, 8840) | 358 (sh, 6640) | 496 (sh, 40900) | 524 (62500) | |
| **12** | 279 (13800) | 293 (15100) | 303 (15000) | 339 (15400) | 378 (14500) | 453 (38900) | |
| **13** | 263 (42400) | 295 (24600) | 339 (33600) | 389 (17200) | 462 (sh, 27500) | 490 (38500) | 522 (sh, 31100) |
| **15** | 301 (29900) | 327 (34600) | 343 (sh, 33400) | 381 (23000) | 491 (35400) | 525 (sh, 29000) | |
| **18** | 300 (sh, 22900) | 312 (25400) | 330 (25400) | 375 (18800) | 471 (33300) | 516 (sh, 21700) | |
| **21** | 303 (sh, 20000) | 329 (23600) | 437 (26200) | | | | |
| *cis*-**22** | 305 (sh, 16800) | 330 (20600) | 423 (12600) | | | | |
| *trans*-**22** | 305 (sh, 16400) | 325 (19300) | 424 (29800) | | | | |

[a] sh = shoulder.

TTF **24**.[3b] The longest-wavelength absorption maximum is significantly red-shifted along the progression **24** ($\lambda_{max}$ = 429 nm; 2.9 eV) – **12** ($\lambda_{max}$ = 453 nm; 2.7 eV) – **5** ($\lambda_{max}$ = 496 nm, 2.5 eV). Nguyen et al.[10a] found a longest-wavelength absorption at $\lambda_{max}$ = 420 nm (3.0 eV) for **25**, an analogue of **5** devoid of the lateral acetylene appendages. These absorption properties allow us to deduce the following structure-property relationships: i) The HOMO–LUMO gap decreases upon extending the two-dimensional conjugation within the spacer (**5** vs. **25**, **12** vs. **24**); ii) a linear conjugation pathway between the two dithiafulvenes provides a smaller HOMO–LUMO gap than a cross-conjugated pathway (**5** vs. **12**). Moreover, it is worth noting that not only does DEE-TTF **5** exhibit the most red-shifted absorption maximum but also by far the strongest absorption ($\varepsilon$, 67500 $M^{-1}$ $cm^{-1}$). Substituting the $CO_2Me$ by SMe groups (**10**) leads to a further red shift ($\lambda_{max}$ = 524 nm, 2.4 eV).




**24** (R = $CO_2Me$)




**25** (R = $CO_2Me$)

Figure 6 displays the spectra of donor–acceptor dyads *cis*-**22**, *trans*-**22**, **21**, and **15**, based on DEE, TriEE, and TEE spacers, respectively. These compounds exhibit strong charge transfer (CT) transitions, in particular TEE **15**. Interestingly, the CT absorption band of *trans*-**22** exhibits almost twice the molar absorptivity as that of *cis*-**22**. This isomeric difference is similar to that exhibited by *trans*/*cis*-1-(4-dimethylaminophenyl)-6-(4-nitrophenyl)hex-3-ene-1,5-diyne, as reported by Arai and co-workers.[24e] No decomposition or thermal isomerization was observed according to $^1H$ NMR spectroscopy upon heating any of the isomers at 125 °C in [$D_6$]DMSO. Further, isomerization between *cis*-**22** and *trans*-**22** is slow (several days) in artificial daylight (60-W light bulb). However, upon irradiating either *cis*- or *trans*-**22** in $CHCl_3$ at 436 nm, the absorption spectrum changes as a result of isomerization in less than an hour. The photostationary state is characterized by a *cis*/*trans* ratio of 8:2. Similarly as to what was found by Arai,[24e] the ratio of quantum yields $\varphi_{trans\rightarrow cis}/\varphi_{cis\rightarrow trans}$ can be estimated to 6:4 as judged from the ratio of $\varepsilon_{trans}/\varepsilon_{cis} \approx 7:3$.

**$^1H$ NMR Spectroscopy:** The position of the fulvene proton resonances is strongly influenced by the nature of the spacer. Thus, a significant downfield shift is observed when proceeding from **24** ($\delta_H$ = 5.53 ppm)[3b] and TEE-TTF **12** ($\delta_H$ = 5.65 ppm) to DEE-TTF **5** ($\delta_H$ = 6.76 ppm). The fulvene proton resonates at $\delta_H$ = 5.41 (d, $J$ = 2.4 Hz) and 5.43 ppm[3b] for **1** and **2**, respectively. The presence of the electron-withdrawing *p*-nitrophenyl group in *cis*-**22** ($\delta_H$ = 5.69 ppm, d, $J$ = 2.6 Hz) and *trans*-**22** ($\delta_H$ = 5.59 ppm, d, $J$ = 2.6 Hz) results in small downfield shifts.

**Computational Study:** DFT calculations[29] at the B3LYP/6-31+G(d) level on PM3 geometry optimized structures reveal that *trans*-**22** is slightly more stable than *cis*-**22**, namely by 0.3 kcal $mol^{-1}$. At the B3LYP/6-311++G(2d,p) level, a difference of 0.2 kcal $mol^{-1}$ was obtained.

HOMO–LUMO plots of **12**, **13**, **15**, **21**, and *cis*/*trans*-**22** are depicted in Figure 7. The silyl groups were substituted by hydrogen atoms in **12** for calculational convenience. The HOMO of this compound has large coefficients at both the dithiafulvene rings and the central TEE core. The LUMO extends from the TEE to the two dithiafulvene rings with no lobes, however, at the outer C=C sites. The LUMO+1 (and LUMO+2) is located instead at the two outer ethylene biscarbonyl groups. The HOMO and LUMO are further extended in **13** to the two phenyl groups. The HOMO has major coefficients at the dithiafulvene ring(s) and at the spacer system for each of the donor–acceptor molecules **15**, **21**, and *cis*/*trans*-**22**, whereas the LUMO and LUMO+1 mainly involve the *p*-nitrophenyl group(s) as well as the spacer system. The small lobes at the *p*-nitrophenyl group in the HOMO of *cis*/*trans*-**22** sustains the small quinoid character as found by X-ray crystallography. Isomerization between *cis*- and *trans*-**22** is facilitated by light as all MOs participating in the excited state involve the central double bond. Thus, in order to avoid the π* antibonding character across this bond, the excited state results in elongation of the central bond and a decreased rotational barrier.

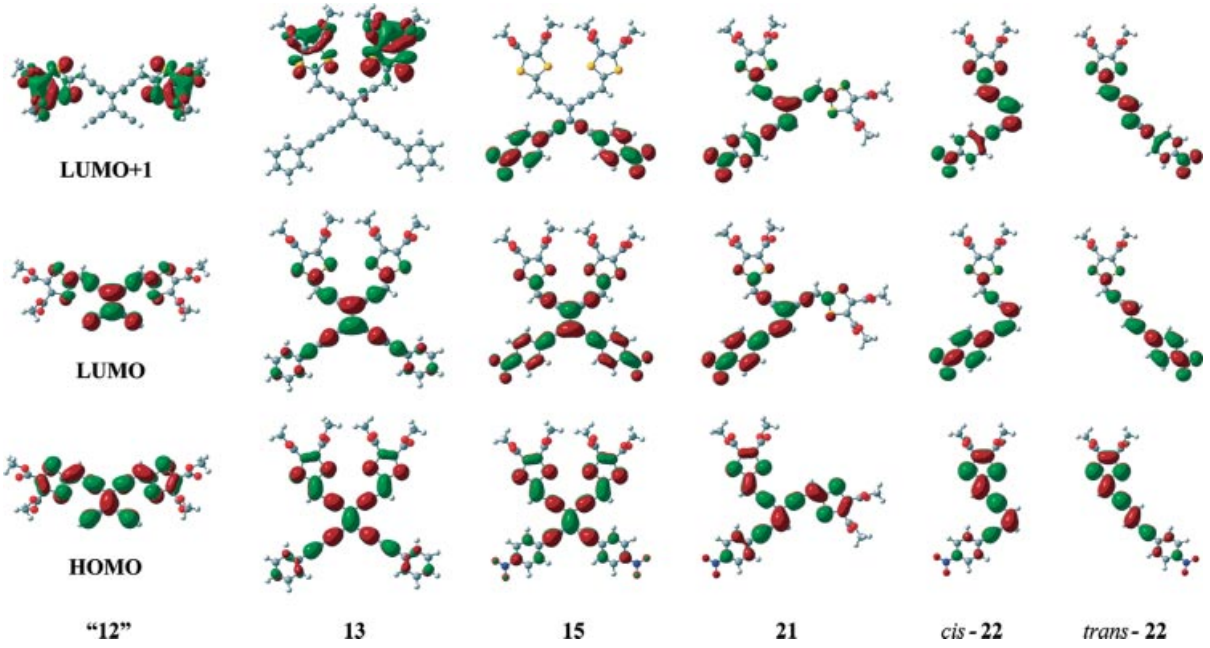



Figure 7. HOMO, LUMO, and LUMO+1 of **12** ($Me_3Si$ groups replaced by hydrogen atoms), **13**, **15**, **21**, *cis*-**22**, and *trans*-**22** calculated at the B3LYP/6-31+G(d) level.

**Electrochemistry:** The electrochemical properties were investigated by cyclic (CV) and rotating disk (RDV) voltammetry. Electrochemical data are collected in Table 2. Comparison of redox potentials of the extended TTFs **5**, **12**, and **24** reveals a strong dependence on the nature of the spacer. We have previously shown by both experimental and theoretical studies that the donor strength is significantly diminished upon replacing double bonds with triple bonds.[3] In agreement with this finding, **5** is a significantly stronger donor than **24**. From the data in Table 2, a significant difference between linear and cross-conjugated extended TTFs appears. Thus, cross-conjugated TTF **12** experiences a remarkable reluctance towards oxidation as compared to both **2** and **24**. In contrast, these three TTFs are reduced at very similar potentials. The mono-nitrophenyl derivatives **21** and **18** undergo an additional reversible one electron reduction occurring on the nitrophenyl moieties at –1.40 V for **21** and –1.35 V (vs. $Fc^+/Fc$) for **18**, whereas the dinitrophenyl derivative **15** undergoes two reversible one-electron steps at –1.34 and –1.39 V occurring on the both nitrophenyls (Figure 8). It is noteworthy that the oxidation potential of compounds **15**, **18**, and **21** are quite similar to those of **12** and **13**, which means that the nitrophenyl substituents have almost no influence on the oxidation potentials of the dithiafulvene moieties. This observation agrees well with the very similar HOMO orbitals obtained in the computational study (Figure 7).

For donor–acceptor molecules **15**, **18**, **21**, *trans*-**22**, and *cis*-**22**, we find a relatively good linear correlation between the optical HOMO–LUMO gap ($E_{max}$, calculated from $\lambda_{max}$) and the electrochemical HOMO–LUMO gap (calculated as the difference between first oxidation potential and first reduction potential) (Figure 9), even though the oxidation occurs irreversibly for all of these compounds. The optical gaps are significantly smaller than those calculated from electrochemistry. Moreover, the best line fitting the data is very steep. Interestingly, *cis*-**22** experiences a much larger electrochemical gap than *trans*-**22**, whereas the optical gaps of these two isomers are very similar.

## Conclusions

Acetylenic scaffolding is a powerful tool for construction of large conjugated TTFs and related donor–acceptor molecules that may find interesting materials applications. It is possible to alter significantly the redox and chromophoric properties by only minor alterations in the acetylenic scaffold. Thus, notable differences are observed between one- and two-dimensional π-spacers and between linear and cross-conjugated π-spacers. Synthetic protocols have been devised for obtaining a wide range of new acetylenic building blocks containing the *p*-nitrophenyl acceptor (**14**, **17**, **20**, *trans*-**23**).

## Experimental Section

**General Methods:** Chemicals were purchased from Aldrich, Fluka, and GFS chemicals and were used as received. THF was distilled from Na/benzophenone. All reactions were carried out under Ar or $N_2$ (except for the Hay coupling reaction forming **13**) by applying a positive pressure of the protecting gas. Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554). The plates were inspected under UV light and, if required, developed in $I_2$ vapour. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). Desilylation of **1** to provide **2** was carried out according to a previously published procedure.[3b] Compound **2** was used directly for the coupling reactions after $Et_2O/H_2O$ extraction (but no further

Table 2. Electrochemical data observed in $CH_2Cl_2$ + 0.1 M $Bu_4NPF_6$. Potentials vs. $Fc^+/Fc$. Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl. Scan rate: 0.1 V $s^{-1}$.

| Compound | Cyclic voltammetry | | | Rotating disk voltammetry | |
|---|---|---|---|---|---|
| | $E°$ (V)[a] | $\Delta E_p$ (mV) | $E_p$ (V)[b] | $E_{1/2}$ (V) | Slope (mV) |
| **5** | +0.18 (1 $e^-$) | | | | |
| | +0.39 (1 $e^-$) | | | | |
| | | | –1.83 (2 $e^-$) | | |
| **9** | +0.09 (1 $e^-$) | 70 | | +0.11 | 65 |
| | –0.09 (1 $e^-$) | 70 | | –0.10 | 70 |
| | –2.08 (1 $e^-$) | 80 | | –2.12 | 80 |
| | | | –2.47 (1 $e^-$) | –2.48 | 80 |
| **10** | +0.15 (1 $e^-$) | 60 | | +0.18 | 65 |
| | +0.00 (1 $e^-$) | 60 | | +0.00 | 70 |
| | –2.04 (1 $e^-$) | 65 | | –2.10 | 100 |
| | | | –2.36 (1 $e^-$) | –2.45 | 100 |
| **12** | | | +0.71 (2 $e^-$)[c] | +0.68 | 75 |
| | | | –1.80 (2 $e^-$) | [d] | |
| **13** | | | +0.65 (2 $e^-$) | +0.69 | 60 |
| | | | –1.44 (1 $e^-$) | –1.42 | 70 |
| | | | –1.92 | –1.92 | 90 |
| **15** | | | +0.66 (2 $e^-$) | [d] | |
| | –1.34 (1 $e^-$) | 60 | | –1.36[e] | 100 |
| | –1.39 (1 $e^-$) | 60 | | | |
| | –1.53 (1 $e^-$) | 60 | | –1.56 | 60 |
| | | | –1.88[f] | –1.93 | 130 |
| **18** | | | +0.67 (2 $e^-$) | +0.66 | 45 |
| | –1.35 (1 $e^-$) | 60 | | –1.40 | 60 |
| | –1.53 (1 $e^-$) | 60 | | –1.57 | 60 |
| | | | –1.95[f] | –1.92 | 100 |
| **21** | | | +0.70 (2 $e^-$) | – | |
| | –1.40 (1 $e^-$) | 75 | | –1.52[e] | 160 |
| | –1.67 (1 $e^-$) | 85 | | | |
| | | | –1.99 | | |
| *trans*-**22** | | | +0.69 (1 $e^-$) | +0.75 | 80 |
| | –1.41 (1 $e^-$) | 70 | | –1.48 | 100 |
| | | | –1.90 | –1.94 | 100 |
| | | | –2.00 | | |
| *cis*-**22** | | | +0.73 (1 $e^-$) | +0.69 | 80 |
| | –1.43 (1 $e^-$) | 100 | | –1.45 | 100 |
| | | | –1.89 | –1.92 | [d] |
| | | | –2.02 | | |
| **24**[g] | | | +0.58 (2 $e^-$) | +0.55 | 60 |
| | | | –1.81 (2 $e^-$) | –1.87 | 175 |

[a] $E° = (E_{pc} + E_{pa})/2$, where $E_{pc}$ and $E_{pa}$ = cathodic and anodic peak potentials. Criteria for reversibility are: i. linear peak current evolution with the square root of the scan rate, ii. anodic to cathodic peak current ratio equal to unity at any scan rate, iii. constant peak potential with scan rate. [b] $E_p$ = irreversible peak potential. [c] Reversible at scan rates > 5 V $s^{-1}$. [d] Spread-out unresolved wave. [e] Overlapping two one-electron transfers. [f] Multielectron transfer. [g] Ref.[3b]

work-up). A Personal Chemistry, Smith Creator oven was employed for microwave-assisted reactions. A Bransonic ultrasonic cleaner, Branson 1510 water bath, was used for ultrasonification. Melting points were determined with a Büchi melting point apparatus and are uncorrected. $^1H$ NMR (300 MHz) and $^{13}C$ NMR (75 MHz) spectra were recorded with Gemini or Varian instruments, using the residual solvent as the internal standard. All chemical shifts are quoted on a $\delta$ scale, and all coupling constants are expressed in Hertz (Hz). Samples were prepared using $CDCl_3$ purchased from Cambridge Isotope Labs. Electron impact ionisation mass spectrometry (EI–MS) was performed with a Varian MAT 311A instrument. Matrix-assisted laser-desorption/ionization time-of-flight mass spectrometry (MALDI–TOF–MS) was performed with Kratos Kompact 2 MALDI–TOF and Bruker Autoflex instruments with 2,5-dihydroxybenzoic acid (DHB) as matrix. High resolution (HR) MALDI mass spectrometry was performed with an IonSpec Fourier Transform mass spectrometer with DHB as matrix. Fast atom bombardment (FAB) spectra were obtained with a Jeol JMS-HX 110 Tandem Mass Spectrometer in the positive ion mode using 3-nitrobenzyl alcohol (NBA) as matrix. Gas chromatography–mass spectrometry (GC-MS) was performed with a HP5890 Series II plus gas chromatograph coupled with a HP5972 Series Mass analysator. Microanalyses were performed at the Microanalytical Laboratory at the Department of Chemistry, University of Copenhagen and at the Atlantic Microlab, Inc., Atlanta, Georgia.

**Absorption Spectroscopy:** UV/Vis spectra were recorded with Cary 50 (Varian Inc.) or Shimadzu UV 1601PC instruments using $CHCl_3$ (LabScan, HPLC-grade) as the solvent. The absorption of $CHCl_3$ in the same cuvette (1 cm path length) was used for baseline correction. The photolysis of *cis*- and *trans*-**22** was performed using the 436-nm line (FWHM 5 nm) from a 200 W high-pressure mercury arc lamp equipped with a Bausch & Lomb monochromator (2700 grooves/mm). The output of this line was 10 mW/$cm^2$ at the cuvette position, with the beam broadened to 5 $cm^2$ to ensure irra-

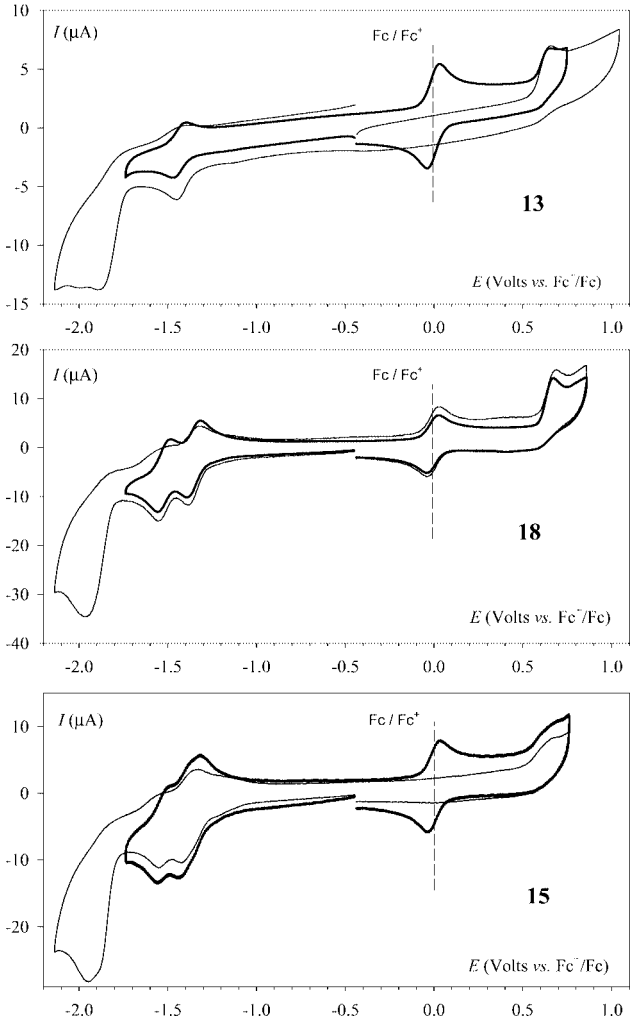



Figure 8. Cyclic voltammetry on a glassy carbon working electrode of compounds **13**, **15**, and **18** in $CH_2Cl_2$ + 0.1 M $Bu_4NPF_6$. Scan rate: 0.1 V $s^{-1}$.

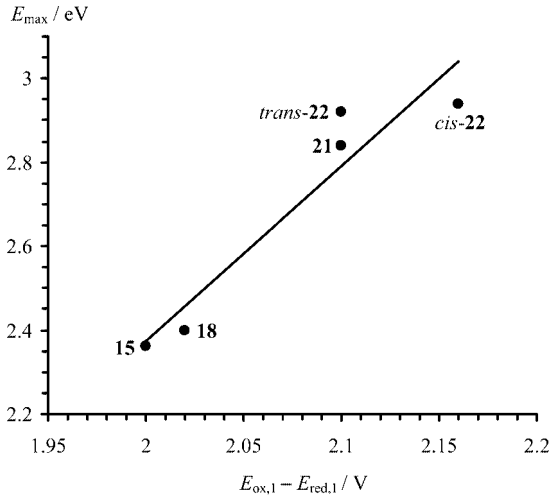



Figure 9. Correlation between optical and electrochemical HOMO–LUMO gaps for donor–acceptor molecules. $E_{max}$ is the longest-wavelength absorption energy, $E_{ox,1}$ is the first oxidation potential, and $E_{red,1}$ is the first reduction potential.

diation of the full sample area (≈ 2 $cm^2$). The irradiance was measured prior to all photolysis experiments using an AvaSpec-2048 diode array spectrometer (Avantes) and a 600 μm optic fiber equipped with a circular diffuser (diameter 3900 μm). As reference for the irradiance an Avantes halogen light source, HL-2000, was used. The photostationary state was obtained from a 40–50 μm solution of pure isomer which was irradiated for 20 min, and the resulting absorption spectrum analyzed to a mixture of pure *cis*-**22** and *trans*-**22** spectra.

**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 RDV. 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 ferrocenium/ferrocene ($Fc^+$/Fc) couple used as an internal standard. The accessible range of potentials on the glassy carbon electrode was +1.4 to –2.4 V vs. $Fc^+$/Fc in $CH_2Cl_2$. All measured potentials are uncorrected for ohmic drop. 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.

**X-ray Structure Determination of Complexes *cis*-22 and *trans*-22:** Intensity data for *cis*-**22** and *trans*-**22** were collected at 122 K with a Bruker–Nonius KappaCCD diffractometer equipped with an Oxford Cryostream unit. Data were reduced with EvalCCD,[30] the structures solved by direct methods using SIR97[31] and refined by least-squares against $F^2$ with SHELXL97[32] as incorporated in the maXus program.[33] Both *cis*-**22** and *trans*-**22** crystallize in space group $P\bar{1}$ with one molecule per asymmetric unit. *trans*-**22** co-crystallizes with one molecule of MeCN per asymmetric unit. For both structures all non-hydrogen atoms were anisotropically refined. All hydrogen atoms were found in subsequent difference Fourier maps and refined using a riding model. Experimental parameters and statistics are summarized in Table 3.

CCDC-266874 and -266875 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Computations:** The compounds were subjected to a computational study employing the Gaussian program package.[29] Structures were optimized at the semiempirical PM3 level. Frequencies were calculated to verify that the calculated structures are local minima on the potential energy surface and to correct for zero-point kinetic energies. Single-point energy and HOMO–LUMO calculations were carried out at the B3LYP/6-31+G(d) level.

**(*E*)-1,4-Bis[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-2,3-bis-[triisopropylsilylethynyl]but-2-ene (5):** To a solution of phosphonium salt **4** (437 mg, 0.86 mmol) in dry THF (20 mL) at –78 °C was slowly added *n*BuLi (0.55 mL, 0.88 mmol, 1.6 M in hexane), resulting in a red solution. Then the dialdehyde **3** (182 mg, 0.41 mmol) in dry THF (10 mL) was slowly added. The solution was stirred at –78 °C for 2 h, whereupon satd. aq. $NH_4Cl$ (200 mL) was added. Then $Et_2O$ (200 mL) was added, the organic phase separated and washed with $H_2O$ (200 mL), dried ($MgSO_4$), and concentrated in vacuo. Column chromatography ($SiO_2$, $CH_2Cl_2$) afforded **5** (207 mg, 60%) as an orange solid. M.p. 129–130 °C. $^1H$

Table 3. X-ray diffraction parameters and statistics of compounds *cis*-**22** and *trans*-**22**.

| | *cis*-**22** | *trans*-**22** |
|---|---|---|
| Empirical formula | $C_{20}H_{13}NO_6S_2$ | $C_{20}H_{13}NO_6S_2/C_2H_3N$ |
| $M_r$ | 427.45 | 427.45/41.05 |
| $T$ [K] | 122(2) | 122(2) |
| $\lambda$ [Å] | 0.71073 | 0.71073 |
| Crystal system | triclinic | triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ [Å]; $\alpha$ [°] | 7.6620(4); 111.425(6) | 7.3880(4); 106.482(5) |
| $b$ [Å]; $\beta$ [°] | 11.3840(9); 91.106(5) | 11.0070(6); 97.778(6) |
| $c$ [Å]; $\gamma$ [°] | 11.7710(9); 94.587(7) | 14.1940(12); 90.717(7) |
| $V$ [Å$^3$] | 951.40(12) | 1095.06(13) |
| $Z$ | 2 | 2 |
| $\rho_{calcd.}$ [g ×cm$^{-3}$] | 1.492 | 1.421 |
| $\mu_{Mo\text{-}K\alpha}$ [mm$^{-1}$] | 0.319 | 0.285 |
| $F(000)$ | 440 | 484 |
| Crystal size [mm$^3$] | 0.46 × 0.34 × 0.14 | 0.51 × 0.28 × 0.10 |
| $\theta$ range [°] | 1.86–35.05 | 1.51–35.01 |
| Reflections collected | 44333 | 44097 |
| Unique data | 8375 [$R_{int}$ = 0.066] | 9611 [$R_{int}$ = 0.058] |
| Obsd. data [$I > 2\sigma(I)$] | 6466 | 7400 |
| GOF on $F^2$ | 1.097 | 1.039 |
| $R$ indices (all data) | $R_1$ = 0.064, $wR_2$ = 0.098 | $R_1$ = 0.064, $wR_2$ = 0.108 |
| Larg.diff.peak/hole [e ×Å$^{-3}$] | 0.50/–0.35 | 0.53/–0.37 |

NMR (300 MHz, $CDCl_3$): $\delta$ = 1.13/1.14 (2×s, 42 H), 3.79 (s, 6 H), 3.84 (s, 6 H), 6.76 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 11.3, 18.7, 53.0, 53.4, 102.5, 112.1, 113.0, 122.1, 131.1, 131.3, 135.1, 159.5, 160.3 ppm. MS (MALDI-TOF): $m/z$ = 848.5 [M$^+$]. $C_{40}H_{56}O_8S_4Si$ (849.29): calcd. C 56.57, H 6.65, S 15.10; found C 56.42, H 6.62, S 15.06.

**(*E*)-[4,5-Bis(2′-cyanoethylthio)-1,3-dithiol-2-ylidene]-2,3-bis[triisopropylsilylethynyl]but-2-enal (7):** The phosphonium salt **6** (384 mg, 0.62 mmol) and the dialdehyde **3** (214 mg, 0.48 mmol) were dissolved in a mixture of dry THF (30 mL) and dry MeCN (10 mL). Then $Et_3N$ (0.2 mL) was added during 5 min at room temp. After stirring for 25 min, $Et_2O$ (300 mL) was added, and mixture was extracted with $H_2O$ (2×250 mL), dried ($MgSO_4$), and concentrated in vacuo. Column chromatography ($SiO_2$, $CH_2Cl_2$) afforded **7** (233 mg, 69%) as a red oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.11–1.16 (m, 42 H), 2.71–2.79 (m, 4 H), 3.05–3.15 (m, 4 H), 7.11 (s, 1 H), 10.12 (s, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 11.2, 11.3, 18.7, 31.3 (× 2), 99.9, 100.0, 109.6, 113.6, 115.8, 117.1, 124.0, 129.3, 137.7, 148.8, 189.3 ppm (two signals overlapping). MS (MALDI-TOF): $m/z$ = 701 [M$^+$]. HR-MS (FT-MALDI): $m/z$ = 723.24260 [M + Na]$^+$ (calcd. for $C_{35}H_{52}N_2NaOS_4Si_2$: 723.23932). $C_{35}H_{52}N_2OS_4Si_2$ (701.22): calcd. C 59.95, H 7.47, N 3.99, S 18.29; found C 59.49, H 7.44, N 4.13, S 18.47.

**(*E*)-1-[4,5-Bis(2′-cyanoethylthio)-1,3-dithiol-2-ylidene]-4-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-2,3-bis[triisopropylsilylethynyl]but-2-ene (9):** Compounds **7** (79 mg, 0.11 mmol) and **8** (94 mg, 0.45 mmol) were dissolved in $P(OEt)_3$ (1.6 mL). The mixture was heated at 120 °C for 15 min. Then $CHCl_3$ (300 mL) was added, and the mixture was extracted with $H_2O$ (2×250 mL), dried ($MgSO_4$), and concentrated in vacuo. Column chromatography ($SiO_2$, $CH_2Cl_2$) gave **9** (78 mg, 79%) as a red oily solid. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.15/1.16 (2×s, 42 H), 2.37 (s, 3 H), 2.40 (s, 3 H), 2.67–2.76 (m, H), 3.00–3.08 (m, 4 H), 6.81 (s, 1 H), 6.83 (s, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 11.4 (× 2), 18.8, 18.9, 30.9, 31.1, 102.8, 103.0, 110.9, 111.2, 112.7, 114.8, 117.3, 120.5, 123.0, 126.4, 126.8, 128.0, 128.2, 132.9, 138.2 ppm; (one signal overlapping). MS (MALDI-TOF): $m/z$ = 878 [M$^+$]. $C_{40}H_{58}N_2S_8Si_2$ (879.56): calcd. C 54.62, H 6.65, N 3.18, S 29.16; found C 54.84, H 6.69, N 3.30, S 29.28.

**(*E*)-1,4-Bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-2,3-bis[triisopropylsilylethynyl]but-2-ene (10):** Compound **9** (78 mg, 0.089 mmol) was dissolved in THF (10 mL), and the solution was degassed with argon. Then MeI (1 mL) was added and hereafter $CsOH·H_2O$ (55 mg, 0.33 mmol) dissolved in argon-degassed MeOH (3 mL). The mixture was stirred for 40 min and then concentrated in vacuo. The residue was subjected to column chromatography ($SiO_2$, $CH_2Cl_2$), affording **10** (58 mg, 82%) as an orange solid. M.p. 186–187 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.15/1.16 (2×s, 42 H), 2.37 (s, 6 H), 2.39 (s, 6 H), 6.81 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 11.5, 18.8, 19.0, 103.2, 110.6, 113.1, 121.5, 126.1, 128.1, 136.4 ppm. MS (MALDI-TOF): $m/z$ = 800 [M$^+$]. $C_{36}H_{56}S_8Si_2$ (801.49): calcd. C 53.95, H 7.04, S 32.00; found C 54.22, H 7.27, S 31.87.

**7-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-4-{[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]propynyl}-1-trimethylsilyl-3-[trimethylsilylethynyl]hept-3-en-1,5-diyne (12): i) Microwave Heating:** To a mixture of CuI (3.5 mg, 0.018 mmol), $[Pd(PhCN)_2Cl_2]$ (20 mg, 0.052 mmol) was added argon-degassed THF (0.5 mL), toluene (0.5 mL), and $HN(iPr)_2$ (0.17 mL). Then $P(tBu)_3$ (0.125 mL, 10% in hexane) was added and hereafter the dibromide **11** (156 mg, 0.413 mmol), which resulted in a dark brown mixture. This mixture was transferred to a capped vial containing solid **2** (1.27 mmol). The mixture was subjected to microwave heating (60 °C, 6 min). Then it was filtered through a short plug of silica ($SiO_2$, $CH_2Cl_2$). Column chromatography ($SiO_2$, $CH_2Cl_2$ → $CH_2Cl_2$/EtOAc, 10:1) afforded **12** (113 mg, 38%) as a red-brown solid. **ii) Ultrasonification:** To a mixture of CuI (3.5 mg, 0.018 mmol) and $[Pd(PhCN)_2Cl_2]$ (20 mg, 0.052 mmol) was added argon-degassed THF (0.5 mL), toluene (0.5 mL), and $HN(iPr)_2$ (0.17 mL). Then $P(tBu)_3$ (0.125 mL, 10% in hexane) was added and hereafter the dibromide **11** (161 mg, 0.426 mmol), which resulted in a dark brown mixture. This mixture was transferred to a flask containing solid **2** (1.35 mmol). The mixture was subjected to ultrasonification at 30 °C for 4 h, whereupon it was filtered through a plug of silica

($SiO_2$, $CH_2Cl_2$). Column chromatography ($SiO_2$, $CH_2Cl_2$ → $CH_2Cl_2$/EtOAc, 10:1) afforded **12** (262 mg, 85%) as a red-brown solid. M.p. 143–146 °C (decomp.). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.23 (s, 18 H), 3.83 (s, 6 H), 3.84 (s, 6 H), 5.65 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 0.2, 53.4 (two signals overlapping), 92.7, 96.1, 97.4, 101.8, 105.2, 112.5, 118.6, 130.6, 132.2, 148.0, 159.3, 159.7 ppm. MS (MALDI-TOF): *m*/*z* = 728 [M$^+$]. HR-MS (FAB): *m*/*z* = 728.0524 [M$^+$] (calcd. for $C_{32}H_{32}O_8S_4Si_2$: 728.0519). $C_{32}H_{32}O_8S_4Si_2$ (729.03): calcd. C 52.72, H 4.42; found C 52.96, H 4.82.

**9-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-6-{[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]propynyl}-1-phenyl-5-[phenylbuta-1,3-diynyl]non-4-en-1,3,7-triyne (13):** To a solution of TEE-TTF **12** (204 mg, 0.280 mmol) in THF (7 mL) and MeOH (20 mL) was added $K_2CO_3$ (84 mg, 0.63 mmol). The deprotection was complete after stirring for ca. 30 min. A difference in $R_f$ values between **12** and its desilylated derivative was difficult to ascertain on TLC, but the desilylated compound appeared darker. Then $Et_2O$ (200 mL) was added, and the organic phase was washed with aq. NaCl (150 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo to almost dryness. The residue was dissolved in dry $CH_2Cl_2$ (50 mL), whereupon phenylacetylene (0.7 mL, 6 mmol) was added. Then Hay catalyst (1 mL) was added. [Hay catalyst: TMEDA (53 mg, 0.46 mmol), CuCl (43 mg, 0.43 mmol), $CH_2Cl_2$ (1.5 mL)]. The mixture was stirred under air for ca. 15 min. Then $CH_2Cl_2$ (200 mL) was added, and the organic phase was washed with $H_2O$ (200 mL). Column chromatography ($SiO_2$, $CH_2Cl_2$ → $CH_2Cl_2$/EtOAc, 20:1) afforded 13 (40 mg, 18%) as a dark red solid. M.p. > 250 °C (decomp. at ca. 180 °C, turning dark). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.50 (s, 6 H), 3.83 (s, 6 H), 5.73 (s, 2 H), 7.33–7.37 (m, 6 H), 7.50–7.53 (m, 4 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 53.4, 53.6, 74.6, 79.1, 83.9, 87.9, 92.5, 98.1, 98.9, 109.8, 121.3, 121.7, 128.6, 129.7, 130.8, 132.7, 133.0, 150.4, 159.4, 159.7 ppm. HR-MS (FAB): *m*/*z* = 784.0359 [M$^+$] (calcd. for $C_{42}H_{24}O_8S_4$: 784.0354).

**3-[Dibromomethylidene]-1,5-bis[4-nitrophenyl]penta-1,4-diyne (14):** To a solution of **11** (584 mg, 1.54 mmol) in THF (14 mL) and MeOH (40 mL) was added $K_2CO_3$ (214 mg, 1.55 mmol). Complete desilylation was accomplished according to TLC after stirring for 15 min. Then $Et_2O$ (250 mL) was added, and the mixture was washed with aqueous NaCl (250 mL), dried ($MgSO_4$), and concentrated in vacuo to a yellowish oil. This oily residue of 3-(dibromomethylidene)penta-1,4-diyne was dissolved in THF (15 mL) and $Et_3N$. Then *p*-iodonitrobenzene (2.0 g, 8.0 mmol), [$PdCl_2(PPh_3)_2$] (50 mg, 0.13 mmol), and CuI (15 mg, 0.079 mmol) were added. After stirring overnight, the mixture was filtered through a short column ($SiO_2$, $CH_2Cl_2$). Column chromatography ($SiO_2$, hexane/$CH_2Cl_2$, 1:1) gave **14** (400 g, 54%) as an off-white solid. M.p. ca. 140 °C (decomp.). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.71 (d, 9.1 Hz, 4 H), 8.24 (d, 9.1 Hz, 4 H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 89.9, 93.9, 112.4, 113.2, 123.9, 128.7, 132.6, 147.9 ppm. MS (FAB): *m*/*z* = 475 [M + H]$^+$.

**7-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-4-{[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]propynyl}-1-[4-nitrophenyl]-3-[4-nitrophenylethynyl]hept-3-en-1,5-diyne (15):** To a mixture of CuI (5.0 mg, 0.026 mmol) and [$Pd(PhCN)_2Cl_2$] (30 mg, 0.078 mmol) was added the dibromide **14** (78.2 mg, 0.164 mmol), and then THF (3.00 mL), toluene (3.00 mL), HN(*i*Pr)$_2$ (0.30 mL), and P(*t*Bu)$_3$ (0.20 mL, 10% in hexane). After vigorous stirring, this mixture was transferred to a flask containing compound **2** (979 mg, 3.82 mmol) and dibromide **14** (173 mg, 0.363 mmol). The mixture was subjected to ultrasonification at 30 °C for 4 h. The product precipitated as a dark red solid. The solid was dissolved in $CH_2Cl_2$ (3 L was required) and washed with $H_2O$. After concentration in vacuo, the residue was dissolved in a minimum amount of $CH_2Cl_2$ and precipitated as a red solid upon addition of hexane. Column chromatography ($SiO_2$, $CH_2Cl_2$ → $CH_2Cl_2$/EtOAc, 10:1) afforded **15** (882 mg, 97%) as a dark red solid. M.p. > 250 °C (decomp. at ca. 170 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.71 (s, 6 H), 3.85 (s, 6 H), 5.77 (s, 2 H), 7.68 (d, 8.8 Hz, 4 H), 8.23 (d, 8.8 Hz, 4 H) ppm. MS (FAB): *m*/*z* = 826 [M$^+$]. $C_{32}H_{22}N_2O_{12}S_4$ (826.85): calcd. C 55.20, H 2.68, N 3.39; found C 54.84, H 2.45, N 3.29.

**3-[Dibromomethylidene]-1-triisopropylsilyl-5-[4-nitrophenyl]penta-1,4-diyne (17):** To solution of **16** (340 mg, 0.872 mmol) in THF (14 mL) and MeOH (30 mL) was added $K_2CO_3$ (121 mg, 0.872 mmol). Complete desilylation was accomplished according to TLC after stirring for 15 min. Then $Et_2O$ (250 mL) was added and the mixture was washed with aqueous NaCl (250 mL), dried ($MgSO_4$), and concentrated in vacuo to a yellowish oil. The majority (83%, 0.724 mmol) of this oily residue of 3-(dibromomethylidene)-1-triisopropylsilylpenta-1,4-diyne was dissolved in THF (15 mL) and $Et_3N$ (3 mL). Then *p*-iodonitrobenzene (1.0 g, 4.0 mmol), [$PdCl_2(PPh_3)_2$] (30 mg, 0.078 mmol), and CuI (10 mg, 0.053 mmol) were added. The mixture was stirred overnight, whereupon it was filtered through a short column ($SiO_2$, $CH_2Cl_2$). Column chromatography ($SiO_2$, hexane/$CH_2Cl_2$, 1:1) afforded **17** (164 mg, 44%) as a crystalline off-white solid. M.p. ca. 140 °C (decomp.). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.1 (s, 21 H), 7.65 (d, 8.8 Hz, 4 H), 8.21 (d, 8.8 Hz, 4 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 11.3, 18.8, 90.9, 93.1, 101.0, 101.5, 111.0, 114.1, 123.8, 129.1, 132.6, 147.7 ppm. HR-MS (FAB): *m*/*z* = 510.0105 [M + H]$^+$ (calcd. for $C_{21}H_{26}Br_2NO_2Si$: 510.0100).

**1-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-4-{[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]propynyl}-1-triisopropylsilyl-3-[4-nitrophenyl]hept-3-en-1,5-diyne (18):** To a mixture of CuI (5.0 mg, 0.026 mmol) and [$Pd(PhCN)_2Cl_2$] (30 mg, 0.078 mmol) was added dibromide **17** (65.0 mg, 0.127 mmol) and then THF (3.00 mL), toluene (3.00 mL), HN(*i*Pr)$_2$ (0.30 mL), P(*t*Bu)$_3$ (0.20 mL, 10% in hexane). This mixture was transferred to a flask containing compound **2** (1.046 g, 4.08 mmol) and dibromide **17** (193 mg, 0.377 mmol). The mixture was subjected to ultrasonification at 30 °C for 4 h, whereupon it was filtered through a short column of silica ($SiO_2$, $CH_2Cl_2$). Column chromatography ($SiO_2$, $CH_2Cl_2$ → $CH_2Cl_2$/EtOAc, 10:1) afforded **18** (210 g, 48%) as a dark red solid. M.p. > 250 °C (decomp. at ca. 180 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.1 (s, 21 H), 3.70 (s, 3 H), 3.84 (s, 3 H), 3.85 (s, 3 H), 3.85 (s, 3 H), 5.60 (s, 1 H), 5.75 (s, 1 H), 7.62 (d, 8.8 Hz, 2 H), 8.20 (d, 8.8 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 11.4, 18.8, 53.6, 53.7, 92.7, 92.8, 93.3, 96.1, 97.1, 97.3, 98.0 (two signals overlapping), 103.4, 103.4, 111.8, 118.9, 123.7, 129.8, 130.9, 131.1, 132.3, 132.5, 133.0, 147.2, 149.0, 149.2, 159.4, 159.5, 159.7, 159.9 ppm. HR-MS (FAB): *m*/*z* = 861.1241 [M$^+$] (calcd. for $C_{41}H_{39}NO_{10}S_4Si$: 861.1226). $C_{41}H_{39}NO_{10}S_4Si$ (862.10): calcd. C 57.12, H 4.56, N 1.62; found C 56.79, H 4.25, N 1.69.

**1,1-Dibromo-4-(4-nitrophenyl)but-1-en-3-yne (20):** The aldehyde **19** (595 mg, 3.40 mmol) and $CBr_4$ (2.25 g, 6.85 mmol) were dissolved in dry $CH_2Cl_2$ (50 mL), whereupon fine Zn powder (< 63 μm) (0.654 g, 10.0 mmol) was added. Then $PPh_3$ (1.81 g, 6.90 mmol) was added, resulting in a dark red solution. After stirring for 45 min, the mixture was filtered through a short plug of silica ($SiO_2$, $CH_2Cl_2$). The filtrate was concentrated in vacuo to a light yellow powder. The product **20** (802 mg, 72%) was obtained pure after washing with cold hexane (to remove any remains of $CBr_4$). Further purification can be performed by column chromatography

($SiO_2$, $CH_2Cl_2$) or recrystallization from hexane. M.p. 101–102 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.81 (s, 1 H), 7.63 (d, 8.8 Hz, 2 H), 8.20 (d, 8.8 Hz, 2 H ppm). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 90.9, 94.7, 104.7, 119.0, 123.9, 129.4, 132.4, 147.6 ppm. MS (FAB): *m*/*z* = 329 [M$^+$]. MS (GC): *m*/*z* = 329 [M$^+$]. $C_{10}H_5Br_2NO_2$ (330.96): calcd. C 36.29, H 1.52, N 4.23; found C 36.57, H 1.42, N 4.18.

**7-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-4-{[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]propynyl}-1-[4-nitrophenyl]hept-3-en-1,5-diyne (21):** To a mixture of CuI (5 mg, 0.03 mmol) and [Pd(PhCN)$_2$Cl$_2$] (30 mg, 0.078 mmol) was added THF (1.0 mL), toluene (1.0 mL), HN(*i*Pr)$_2$ (0.3 mL), and P(*t*Bu)$_3$ (0.2 mL, 10% in hexane) under argon. This mixture was transferred via a syringe to a flask containing the dibromide **20** (162 mg, 0.489 mmol) and **2** (342 mg, 1.33 mmol) under argon. The reaction mixture was subjected to ultrasonification for 2½ h at ca. 25–30 °C. Then it was filtered through a short plug of silica ($SiO_2$, $CH_2Cl_2$). Column chromatography afforded the product **21** (91 mg, 30%) as a red powder. M.p. > 300 °C (decomp.). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.71 (s, 3 H), 3.85 (2×s, 6 H), 3.87 (s, 3 H), 5.59 (s, 1 H), 5.71 (s, 1 H), 6.24 (s, 1 H), 7.62 (d, 9.0 Hz, 2 H), 8.20 (d, 9.0 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 53.7, 91.1, 92.5, 92.8, 93.6, 93.9, 96.8, 97.9, 99.5, 116.6, 118.4, 123.8, 130.1, 131.1, 131.4, 131.9, 132.2, 133.1, 147.2, 148.4, 148.8, 159.5, 159.6, 159.8 (× 2) ppm. MS (FAB): *m*/*z* = 681 [M$^+$]. $C_{30}H_{19}NO_{10}S_4$ (681.74): calcd. C 52.85, H 2.81, N 2.05; found C 52.76, H 2.72, N 1.97.

***cis*-7-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1-[4-nitrophenyl]hept-3-en-1,5-diyne (*cis*-22):** To a solution of the dibromide **20** (331 mg, 1.00 mmol) in toluene (3 mL) was added [Pd(PPh$_3$)$_4$] (46.2 mg, 0.040 mmol) followed by $Bu_3SnH$ (0.30 mL, 1.1 mmol), and the mixture was stirred at room temp. for 1 h. Then **1** (1.25 mmol) in THF (1 mL) was added, followed by HN(*i*Pr)$_2$ (0.85 mL). The mixture was degassed with argon, whereupon CuI (57 mg, 0.30 mmol) was added. The mixture was stirred overnight and filtered through a short plug of silica ($SiO_2$, $CH_2Cl_2$). Column chromatography ($SiO_2$, $CH_2Cl_2$) afforded *cis*-**22** (166 mg, 39%) as a red solid. M.p. 151–153 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.72 (s, 3 H), 3.84 (s, 3 H), 5.69 (d, 2.6 Hz, 1 H), 6.04 (d, 10.8 Hz, 1 H), 6.19 (dd, 10.8/2.6 Hz, 1 H), 7.63 (d, 8.8 Hz, 2 H), 8.20 (d, 8.8 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 53.4, 53.5, 92.6, 93.1, 95.2, 96.0, 98.0, 116.3, 121.0, 123.6, 130.0, 130.9, 131.9, 132.9, 147.0, 147.6, 159.3, 159.7 ppm. MS (FAB): *m*/*z* = 427 [M$^+$]. HR-MS (FAB): *m*/*z* = 427.0192 [M$^+$] (calcd. for $C_{20}H_{13}NO_6S_2$: 427.0184). $C_{20}H_{13}NO_6S_2$ (427.45): calcd. C 56.20, H 3.07, N 3.28; found C 55.80, H 3.01, N 3.02.

***trans*-7-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1-[4-nitrophenyl]hept-3-en-1,5-diyne (*trans*-22):** To a solution of the bromide *trans*-**23** (252 mg, 1.00 mmol) in toluene (3 mL) was added [Pd(PPh$_3$)$_4$] (46.2 mg, 0.04 mmol), and the mixture was stirred at room temp. for 1 h. Then **2** (1.25 mmol) in THF (1 mL) was added, followed by HN(*i*Pr)$_2$ (606 mg, 6 mmol). The mixture was degassed with argon, whereupon CuI (57 mg, 0.30 mmol) was added. After stirring for 3 h at room temp., the mixture was filtered through a short plug of silica ($SiO_2$, $CH_2Cl_2$). Column chromatography ($SiO_2$, $CH_2Cl_2$) afforded *trans*-**22** (287 mg, 67%) as a red solid. Recrystallization from MeCN gave the product as red crystals. M.p. 115–117 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.85 (s, 3 H), 3.87 (s, 3 H), 5.59 (d, 2.6 Hz, 1 H), 6.16 (d, 15.8 Hz, 1 H), 6.35 (dd, 15.8/2.6 Hz, 1 H), 7.57 (d, 8.8 Hz, 2 H), 8.19 (d, 8.8 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 53.5 (two signals overlapping), 92.7 (× 2), 93.5, 93.8, 98.6, 118.0, 122.5, 123.7, 129.8, 131.3, 131.5, 132.2, 147.1, 147.3, 159.4, 159.6 ppm. MS (FAB) *m*/*z* = 427 [M$^+$]. $C_{20}H_{13}NO_6S_2$ (427.45): calcd. C 56.20, H 3.07, N 3.28; found C 55.96, H 2.72, N 3.13.

***trans*-1-Bromo-4-(4-nitrophenyl)but-1-en-3-yne (*trans*-23):** To a solution of the dibromide **20** (1.01 g, 3.05 mmol) in diethyl phosphite (2.0 mL, 15.5 mmol) was added triethylamine (2.0 mL, 14.4 mmol), and the dark brown mixture was stirred at 50 °C for 6 h. Diethyl ether (50 mL) was added, and the $Et_3N$·HBr was removed by filtration. The filtrate was concentrated in vacuo and the residue subjected to column chromatography ($SiO_2$, cyclohexane/$CH_2Cl_2$, 3:2), which afforded *trans*-**23** (320 mg, 42%) as an off-white solid. Removal of trace amounts of the *cis*-isomer can be done by recrystallization from hexane. M.p. 133–135 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.45 (d, 14.1 Hz, 1 H), 6.92 (d, 14.1 Hz, 1 H), 7.57 (d, 9.1 Hz, 2 H), 8.19 (d, 9.1 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 89.6, 90.9, 117.0, 121.3, 123.9, 129.7, 132.4, 147.5 ppm.

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