Acetylenic tetrathiafulvalene-dicyanovinyl donor-acceptor chromophores†

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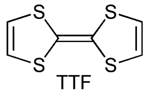
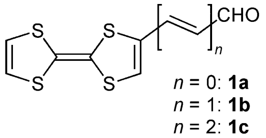
Compounds incorporating the tetrathiafulvalene (TTF) donor unit and one or two cyanoethynylethene (CEE) acceptor units were prepared by Knoevenagel condensations of highly unstable, TTF-linked propargylic aldehyde or ketone derivatives. The resulting TTF-CEEs are very strong chromophores with low-energy end-absorptions beyond 900 nm. The molecules experience reversible oxidations of the TTF unit, and the optical properties of the oxidised species were elucidated by spectroelectrochemistry.

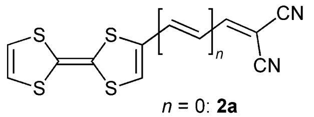
Introduction

Tetrathiafulvalene (TTF) is a strong electron donor that has been explored widely as a building block in both supramolecular and materials chemistry.[1] Much work has focused on employing TTF as a donor unit in intramolecular charge-transfer systems with potential applications as molecular electronics devices, organic metals, chromophores for dyes, nonlinear optics, and excited-state energy transfer processes.[2] Cyanoalkenes, such as dicyanoethylene, tetracyanoethylene (TCNE), and cyanoethynylethenes (CEEs), represent interesting acceptor units to incorporate in such donor-acceptor (D-A) dyads owing to their powerful electron-accepting properties.[3] Martín and co-workers[4] have previously devised efficient synthetic protocols for attaching the dicyanovinyl acceptor to TTF *via* an ethylenic spacer. Thus, Knoevenagel condensations of aldehydes **1a**, **1b**, and **1c** provided the D-A chromophores **2a**, **2b**, and **2c**, respectively.





n = 0: **1a**
n = 1: **1b**
n = 2: **1c**



n = 0: **2a**
n = 1: **2b**
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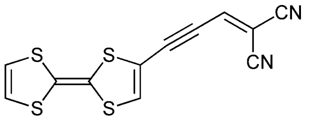

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We became interested in developing a method for instead separating the TTF and dicyanovinyl units by an acetylenic bridge as in compound **3**. Elucidation of its electronic properties should shed further light on the role played by the bridge separating the donor and acceptor entities, that is, the donor-acceptor coupling transmitted by an alkyne bridge in comparison to an alkene bridge. Compound **3** can also be characterised as a TTF-substituted CEE. Here, we describe a synthetic protocol for the first derivatives of **3** and their optical and electrochemical properties. Extreme care was required in handling these compounds to avoid formation of unidentified products, which is not surprising when considering the fact that they should be susceptible to attack by nucleophiles, and, in addition, incorporate a triple bond with a dual reactivity in regard to [2 + 2]cycloadditions. Thus, a C≡C bond adjacent to an electron-accepting $CHC(CN)_2$ unit is activated for [2 + 2]cycloaddition to the central fulvalene double bond of TTF.[5,6] On the other hand, a C≡C bond adjacent to an electron-donating unit is able to undergo [2 + 2]cycloaddition to the central double bond of the strong electron acceptor TCNE,[6,7] as well as to weaker dicyanovinyl acceptors.[8]

Results and discussion

Synthesis

In order to assure solubility, a TTF with two *n*-hexyl chains was employed.[9] First, 4,5-dihexyl-4′-iodo-TTF **4**[10] was subjected to a Sonogashira cross-coupling reaction[11] with commercially available 3,3-diethoxypropyne to furnish compound **5** (Scheme 1). Several conditions for converting acetal **5** into aldehyde **6** were attempted. Using acetic acid or formic acid in dichloromethane gave only starting material after 24 h at rt. Instead, treatment with HCl (1 M) in wet acetone for 5 h at 50 °C resulted in complete conversion of the acetal, according to a TLC analysis, but the aldehyde was only isolated in a yield of 40% as its isolation was accompanied by significant decomposition, in particular upon removing the solvent. No such problems were reported during isolation of the related ethylenic compound **1b**.[4] According to TLC analysis, we found that treatment with *p*-toluenesulfonic acid in wet acetone also resulted in generation of the aldehyde. The smallest degree of decomposition was observed when running the reaction under dilute conditions (*ca.* 5 mM) for a total of 12 days at rt. The need for storing aldehyde **6** under dilute conditions signals that it readily undergoes intermolecular reactions. The reaction mixture containing the dark red-violet product was then extracted into toluene, used as solvent for the following step. After routine washing and drying steps, and avoiding concentration to dryness, the aldehyde was subjected to a Knoevenagel condensation[12]

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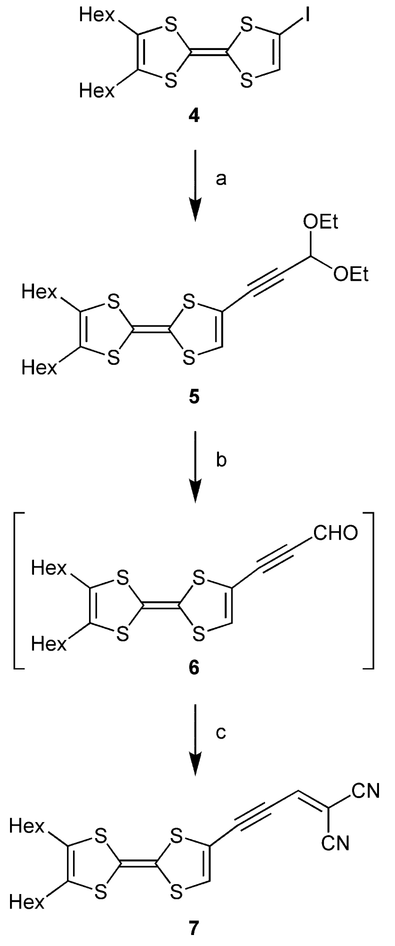
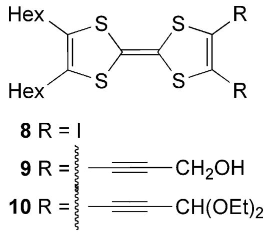


Scheme 1 *Reagents and conditions*: (a) HC≡CCH(OEt)$_2$, [Pd(PPh$_3$)$_2$Cl$_2$], CuI, Et$_3$N, 40 °C, 77%; (b) *p*-TsOH, acetone (wet); (c) CH$_2$(CN)$_2$, NH$_4$OAc, toluene, 62% (2 steps).

upon addition of malononitrile and ammonium acetate to the toluene solution. The resulting deep-blue product **7** was purified by column chromatography using SiO$_2$ as column material. When purifying TTF compounds by column chromatography, it is often advantageous to add a small amount of NEt$_3$ to avoid protonation, but in this case not; it results in immediate color change from blue to dark brown. Alternative column materials, such as Florisil® and Al$_2$O$_3$ (Act. II-III, Merck 90), were also found to cause significant decomposition. Gratifyingly, compound **7** was isolated in a total yield of 62% from the two steps.

Next, a TTF functionalised with two CEE-substituents was targeted. A Sonogashira cross-coupling reaction of diiodo-TTF **8**[9] with an excess of propargyl alcohol gave diol **9** in a yield of 74%. Due to the electron-rich nature of the TTF core, only very few oxidations of TTF alcohols to TTF aldehydes have been reported.[13,14] Andreu *et al.*[13] showed that di(hydroxymethyl)-TTF could be oxidised to diformyl-TTF in 45% using selenium dioxide. However, only decomposition of **9** was observed when oxidation was attempted with either SeO$_2$, act. MnO$_2$, Dess-Martin periodinane, tetrapropylammonium perrhutenate (TPAP), PCC, or BaMnO$_4$.

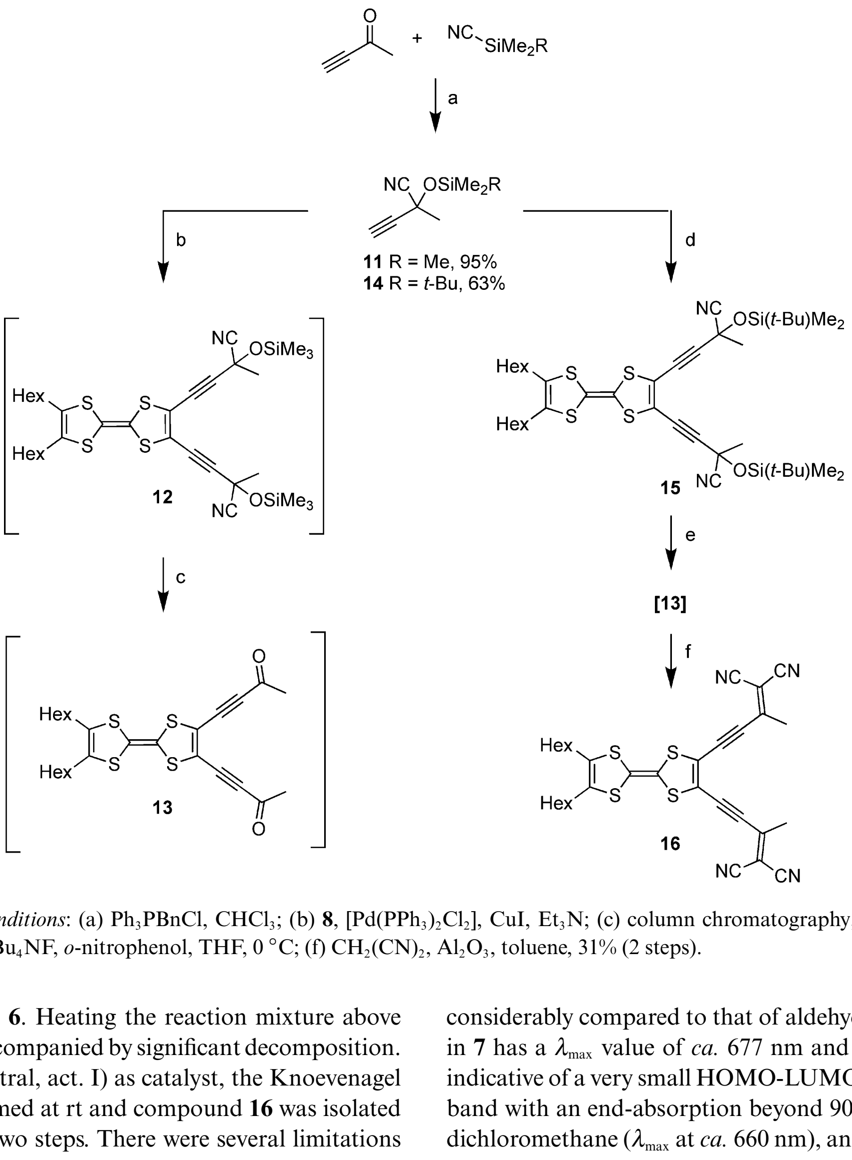


We therefore turned to the acetal route that was successful for the preparation of the TTF with one CEE acceptor group. A Sonogashira reaction of **8** with 3,3-diethoxypropyne gave a 9:1 mixture (judged by ^{1}H NMR) of the diacetal **10** and the homo-coupled 1,1,6,6-tetraethoxyhexa-2,4-diyne. Further separation of these two compounds by column chromatography was not possible on account of very similar polarities. Unfortunately, neither HCl (1 M) nor *p*-TsOH in wet acetone effected deprotection to the dialdehyde. The use of LiBF$_4$ in wet acetone at 40 °C resulted in extensive decomposition, but also in formation of an unknown product with a color similar to that of the aldehyde **6**. However, it was not possible to isolate or characterise this product.

Then we sought a protecting group which ideally would be very easily cleaved, yet withstand the alkaline and nucleophilic conditions required in the Sonogashira reaction. *O*-Trimethylsilyl cyanohydrin seemed to be a promising candidate for this purpose.[15] Combining butynone, trimethylsilyl cyanide and a catalytic amount of benzyltriphenylphosphonium chloride afforded the cyanohydrin **11**[16] in 95% yield (Scheme 2).[17] The Sonogashira reaction between **11** and diiodo-TTF **8** gave the red-colored product **12**, but this *O*-trimethylsilyl cyanohydrin was so labile that deprotection to the purple diketone **13** occurred both on TLC and when purification attempts by column chromatography were made. It was not possible to isolate the ketone, as it decomposed when concentrated *in vacuo*, but mass spectral analysis confirmed its identity (electrospray ionisation, $m/z = 527$ [M + Na]$^+$).

We hoped that the use of a more bulky substituent on silicon would allow us to isolate the cyanohydrin functionalised TTF and thus enable the deprotection step to occur under more controlled conditions. The addition of *tert*-butyldimethylsilyl cyanide to butynone and a catalytic amount of benzyltriphenylphosphonium chloride gave the cyanohydrin **14**, which was reacted with **8** in a Sonogashira reaction to give **15** in a high yield of 78%. The yield of the isolated product probably would have been even higher, if repeated column chromatography had not been necessary in order to separate **15** from the acetylenic homo-coupling byproduct.

It was not possible to deprotect **15** to provide diketone **13** using either HF (aq., 40%) in acetonitrile, HCl (aq, conc.) in 96% ethanol, or *p*-TsOH in wet acetone; instead, the starting material was recovered. In contrast, treatment with tetrabutylammonium fluoride (TBAF) in wet THF at −10 °C resulted in complete decomposition. It has been shown that undesired reactions owing to the basicity of TBAF can be minimised by the presence of acidic additives.[18] Fortunately, addition of TBAF to a solution of **15** and *o*-nitrophenol in THF at 0 °C afforded the desired diketone **13**. Isolation of the unstable diketone was avoided and instead the reaction mixture was filtered on Celite, toluene was added, and routine washing and drying steps were performed. However, addition of malononitrile and ammonium acetate to the solution of **13** in toluene did not effect Knoevenagel condensation as was



Scheme 2 *Reagents and conditions*: (a) Ph_3PBnCl, $CHCl_3$; (b) **8**, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N; (c) column chromatography; (d) **8**, $[Pd(PPh_3)_2Cl_2]$, CuI, *i*-Pr_2NH, dioxane, 78%; (e) Bu_4NF, *o*-nitrophenol, THF, 0 °C; (f) $CH_2(CN)_2$, Al_2O_3, toluene, 31% (2 steps).

the case for the aldehyde **6**. Heating the reaction mixture above room temperature was accompanied by significant decomposition. Using instead Al_2O_3 (neutral, act. I) as catalyst, the Knoevenagel condensation was performed at rt and compound **16** was isolated in 31% yield from **15** in two steps. There were several limitations of the last step: a) It was not possible to drive the reaction to completion even when using malononitrile in large excess or when molecular sieves were added, b) prolonged reaction times or heating were accompanied by extensive decomposition, and c) significant decomposition was also observed when the necessary purification of **16** by column chromatography was performed.

UV-Vis absorption data

The UV-vis absorption data for **5**–**7** and **16** are collected in Table 1, and Fig. 1 shows the UV-vis absorption spectra in chloroform. Compounds **6** and **7** exhibit charge-transfer (CT) absorptions at low energy. As expected, the CT absorption in CEE **7** is red-shifted considerably compared to that of aldehyde **6**. The broad CT band in **7** has a λ_{max} value of *ca.* 677 nm and extends beyond 900 nm, indicative of a very small HOMO-LUMO gap. A similar broad CT band with an end-absorption beyond 900 nm is observed for **7** in dichloromethane (λ_{max} at *ca.* 660 nm), and this absorption is hence significantly red-shifted relative to that of compound **2b** (λ_{max} = 618 nm in CH_2Cl_2),[4a] which has a double bond instead of a triple bond as spacer (and lacks the hexyl chains). The CT absorption is further red-shifted for compound **16** that exhibits a broad band at *ca.* 743 nm and an end-absorption beyond 1000 nm.

Table 1 UV-vis absorption maxima (λ_{max}) and molar absorptivities (ε) given in brackets of **5**–**7** and **16** in $CHCl_3$. (sh = shoulder; br = broad)

Compound	λ_{max} [nm] (ε [M^{-1} cm^{-1}])
5	290 (12700), 330 (13200), 412 (2370)
6	285, 320, 388 (sh), 493 (br)
7	301 (15700), 330 (15800), 377 (15200), 677 (br, 3920)
16	312 (sh, 28000), 335 (40400), 424 (13400), 743 (br, 1700)

The HOMO and LUMO of **3** (lacking the hexyl substituents) were calculated using Gaussian 03[19] at the B3LYP/6-31G(d) level and are shown in Fig. 2. While the HOMO is mainly located on the TTF unit, the LUMO is extending from the cyanoethynylethene unit to a part of the TTF unit.

Electrochemistry

The electrochemical properties of **7** and **16** were investigated by cyclic voltammetry in CH_2Cl_2 (+ 0.1 M Bu_4NPF_6) and are collected in Table 2 together with literature data for compound **17**[10] and **18**.[9] Both TTF-CEEs exhibit two reversible oxidations (Fig. 3) and an irreversible reduction. The anodic shift of the oxidation potentials of **7** and **16** relative to **17** and **18**, respectively, is explained by the presence of the strongly electron-withdrawing 2,2-dicyanovinyl group.

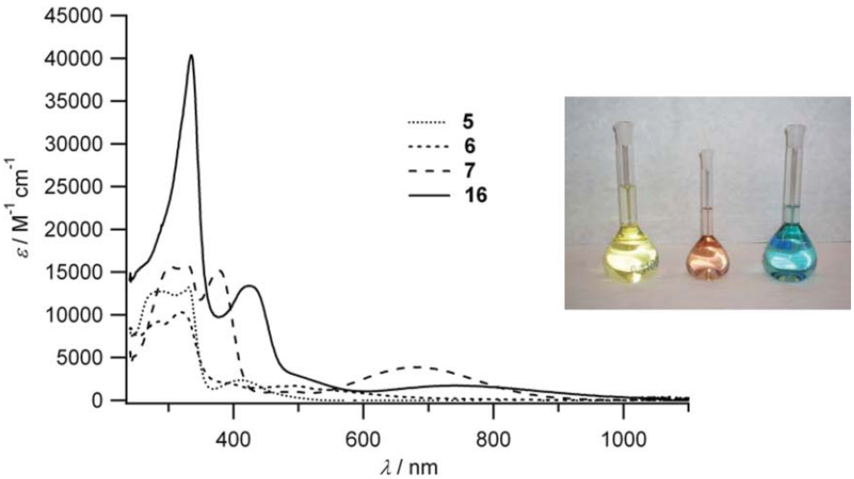


Fig. 1 UV-vis spectra of compounds **5–7** and **16** in chloroform together with a photograph of the coloured solutions (from left to right: **5**, **6**, and **7**). Extinction coefficients for **6** are only approximate.

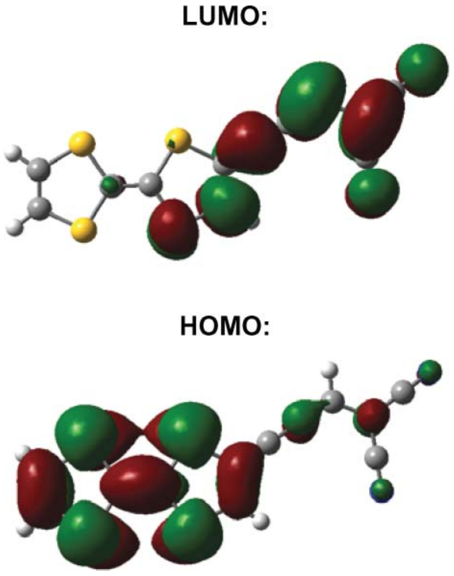
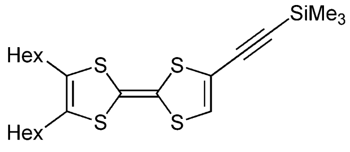


Fig. 2 Frontier orbitals of **3** (B3LYP/6-31G(d)).



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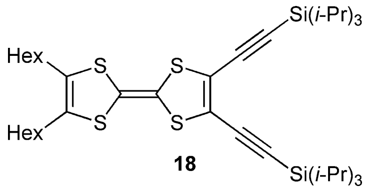

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Spectroelectrochemical studies of **7** and **16** were performed in CH_2Cl_2 and the results are shown in Fig. 4. For the first oxidation step of **7**, nice isosbestic points were observed, and the generated radical cation $\mathbf{7}^{\bullet+}$ is characterised by absorptions at $\lambda_{max} = 260$, 451 and 630 nm. The low-energy absorption at 630 nm is now assigned to an intrinsic absorption of the TTF radical cation, being slightly red-shifted relative to that of the parent TTF that was previously found to absorb at 580 nm.[20] As expected, the CT band situated at 677 nm for the neutral chromophore has disappeared. Upon further oxidation to the dication $\mathbf{7}^{2+}$, the absorptions at $\lambda_{max} =$ 260 and 630 nm decrease, while the absorption at $\lambda_{max} = 451$ remains. Reduction of the generated species led only to recovery of about 80% of the original spectrum of the neutral chromophore, which means that oxidation has resulted in some degradation. The changes in the low-energy absorptions of **16** upon oxidation

Table 2 Cyclic voltammetry data measured in CH_2Cl_2 + 0.1 M Bu_4NPF_6. All potentials *vs* Fc^+/Fc

Compd	E^0_1 [V]^a	E^0_2 [V]^a	E_p [V]^b
7	+0.03	+0.54	–1.28
16	+0.16	+0.62	–1.04
17	–0.07	+0.45	
18	+0.00	+0.52	

[a] $E^0 = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively. Subscript 1 and 2 refers to the first and second reversible oxidation steps, respectively. [b] Peak potential E_p for irreversible electron transfer.

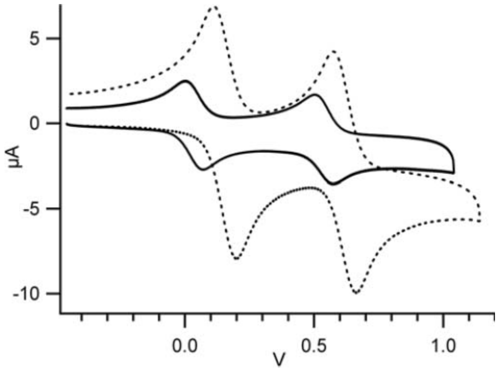

Fig. 3 Cyclic voltammograms showing oxidations of **7** (—) and **16** (···) in CH_2Cl_2 + 0.1 M Bu_4NPF_6 referenced against the Fc^+/Fc redox couple.

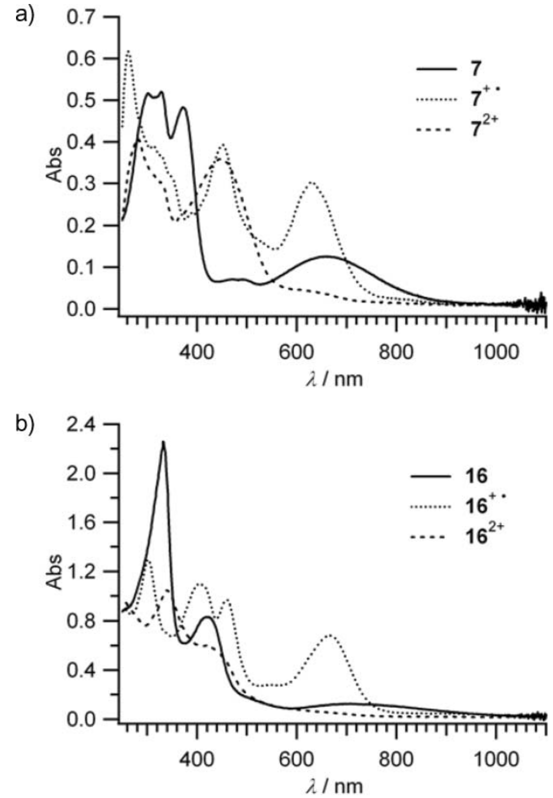

Fig. 4 UV-vis spectroelectrochemistry of **7** in CH_2Cl_2 + 0.2 M Bu_4NPF_6 (a) and **16** in CH_2Cl_2 + 0.1 M Bu_4NPF_6 (b).

resemble those of **7**: the broad CT band disappears and a new absorption maximum at 667 nm emerges for the radical cation.

Conclusions

By *in situ* formation of suitable TTF-linked propargylic carbonyls, we have prepared the first acetylenic scaffolds in which both a TTF donor and a CEE acceptor are present. The carbonyl precursors should be handled under dilute conditions in order to avoid degradation, and they were, accordingly, not isolated but subjected to the final Knoevenagel condensations after only minor work-up. Isolation of the pure TTF-CEEs was, however, possible, but some decomposition could not be avoided during chromatographic purification. These compounds are very strong donor-acceptor chromophores with end-absorptions in the near-IR. The red-shift in the longest-wavelength absorption of **7** relative to that of **2b** is in line with previous findings that donor-acceptor conjugation is more efficient (stronger coupling) through olefinic than through acetylenic spacers.[21] The more efficient mixing of inherent donor and acceptor orbitals transmitted by an alkene spacer will lower the HOMO energy and raise the LUMO energy, resulting in a larger optical gap. The TTF-CEEs are oxidised reversibly, while electrochemical reduction occurs irreversibly. Oxidation is accompanied by disappearance of the low-energy charge-transfer absorption band, while instead the characteristic absorption for the TTF radical cation appears. The donor-acceptor character of the compounds renders them particularly interesting as future candidates for nonlinear optical materials.

Experimental

General methods

Chemicals were purchased from Aldrich, Fluka, and GFS Chemicals and were used as received. Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554). Column chromatography was carried out using silica gel 60 (Merck 9385, 0.040–0.063 mm). ^1H NMR (300 MHz) and ^{13}C NMR (75 or 100 MHz) spectra were recorded on Varian instruments. Fast atom bombardment (FAB) spectra were obtained on a Jeol JMS-HX 110 Tandem Mass Spectrometer in the positive ion mode using 3-nitrobenzyl alcohol (NBA) as matrix. Electrospray ionisation (ESI) spectra were obtained on a Micromass Q-TOF spectrometer. Cyclic voltammetry was measured using a glassy carbon working electrode and a Pt wire counter electrode. All potentials are expressed relative to that of Fc^+/Fc and were measured in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte; scan rate 0.1 V s^{-1}. All measured potentials are uncorrected for ohmic drop. Spectroelectrochemical experiments were performed in a 1 mm absorption cuvette (Quartz), the counter-electrode was separated from the solution by a glass frit, and a Pt grid (mesh 400) was used as working electrode. Setting the potential at *ca.* 0.1 V more oxidative value than the peak potentials found from cyclic voltammetry, the UV-vis spectra of the neutral and cationic species were recorded on a Cary 50 Bio UV-vis spectrophotometer. The same spectrophotometer was used to determine the molar absorptivities of the neutral species (1 cm path length cuvette).

4-(3,3-Diethoxyprop-1-ynyl)-4′,5′-dihexyltetrathiafulvalene (5)

To an Ar-degassed solution of **4** (365 mg, 0.732 mmol) and 3,3-diethoxypropyne (0.15 cm^3, 1.05 mmol) in Et_3N (10 cm^3), $[Pd(PPh_3)_2Cl_2]$ (26 mg, 37 μmol) and CuI (14 mg, 73 μmol) were added and the mixture was stirred for 3 h at 40 °C under Ar. Et_2O (100 cm^3) was added and the organic phase washed with H_2O (2 × 50 cm^3) and brine (50 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, EtOAc/heptane 4:96) afforded **5** as an orange oil (281 mg, 77%). δ_H(300 MHz; $CDCl_3$) 0.88 (t, 6.4 Hz, 6 H), 1.17–1.53 (m, 22 H), 2.33 (t, 7.5 Hz, 4 H), 3.56–3.78 (m, 4 H), 5.39 (s, 1 H), 6.53 (s, 1 H). δ_C(100 MHz; $CDCl_3$) 14.0, 15.1, 22.5, 28.8 (× 2), 29.7, 31.5, 61.1, 76.4, 88.3, 91.6, 106.0, 112.5, 114.6, 126.5, 128.5, 128.9. IR (KBr): $\tilde{\nu}$ = 3082 (w), 2955 (s), 2927 (s), 2856 (s), 2221 (s), 1613 (w), 1526 (w), 1456 (s), 1352 (s), 1326 (s), 1186 (s), 1091 (s), 1054 (s), 1013 (s), 944 (m), 884 (w), 821 (m), 779 (s), 725 (w) cm^{-1}. HR-MS (FAB): m/z = 498.1749 $[M^+]$ (calcd for $C_{25}H_{38}O_2S_4$: 498.1755).

4-(4,4-Dicyanobut-3-en-1-ynyl)-4′,5′-dihexyltetrathiafulvalene (7)

To a solution of acetal **5** (39 mg, 78 μmol) in acetone/water (98:2, 15 cm^3), *p*-toluenesulfonic acid (1.5 mg, 8 μmol) was added and the mixture was protected from light and stirred for 12 days at rt. Toluene (100 cm^3) was added, and the organic phase was washed with H_2O (2 × 50 cm^3) and brine (50 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to a volume of *ca.* 50 cm^3. To this solution of the aldehyde **6**, ammonium acetate (4 mg, 52 μmol) and malononitrile (12 mg, 182 μmol were added and the mixture was protected from light and stirred for 2 days at rt. The organic phase was washed with H_2O (2 × 50 cm^3) and brine (50 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, EtOAc/heptane 1:6) afforded **7** as a blue oil (23 mg, 62%). δ_H(300 MHz; $CDCl_3$) 0.88 (t, 6.3 Hz, 6 H), 1.2–1.4 (m, 12 H), 1.50 (m, 4 H), 2.35 (t, 7.4 Hz, 4 H), 7.02 (s, 1 H), 7.06 (s, 1 H). δ_C(75 MHz; $CDCl_3$) 14.1, 22.5, 28.8 (× 2), 29.7, 31.5, 89.6, 92.9, 103.5, 105.5, 111.3, 112.4, 114.2, 116.3, 128.6, 129.1, 137.1, 139.1. HR-MS (FAB): $m/z = 472.1155$ [M^+] (calcd for $C_{24}H_{28}N_2S_4$: 472.1135).

4,5-Dihexyl-4′,5′-bis(3-hydroxyprop-1-ynyl)tetrathiafulvalene (9)

To an Ar-degassed solution of diiodo-TTF **8** (240 mg, 0.384 mmol) in Et_3N (5 cm^3), [$Pd(PPh_3)_2Cl_2$] (27 mg, 38 μmol) and CuI (22 mg, 0.12 mmol) were added and the mixture was stirred for 15 min under Ar. Propargyl alcohol (0.2 cm^3, 3.4 mmol) in Ar-degassed THF (2 cm^3) was added dropwise over 1 h and the mixture was stirred for another 2 h. CH_2Cl_2 (50 cm^3) was added and the organic phase washed with H_2O (2 × 100 cm^3) and brine (100 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, EtOAc/heptane 3:2) afforded **9** as a red oil (137 mg, 74%). δ_H(300 MHz; $CDCl_3$) 0.89 (t, 6.6 Hz, 6 H), 1.2–1.4 (m, 12 H), 1.49 (m, 4 H), 1.92 (br s, 2 H), 2.33 (t, 7.5 Hz, 4 H), 4.48 (s, 4 H). δ_C(75 MHz; $CDCl_3$) 14.0, 22.5, 28.8 (× 2), 29.7, 31.5, 76.8, 96.7, 102.8, 115.3, 120.8, 128.6. IR (KBr): $\tilde{\nu} = 3300$ (br), 2922 (w), 2854 (w), 2370 (w), 2340 (w), 1352 (m), 1219 (w), 1151 (s), 1025 (vs), 969 (m), 777 (s), 723 (m) cm^{-1}. MS (FAB): $m/z = 480$ [M^+]. HR-MS (FAB): $m/z = 480.1271$ [M^+] (calcd for $C_{24}H_{32}O_2S_4$: 480.1285).

2-Methyl-2-(*tert*-butyldimethylsilyloxy)but-3-ynenitrile (14)

To a solution of 3-butyn-2-one (244 mg, 3.58 mmol) and *tert*-butyldimethylsilyl cyanide (0.56 g, 3.96 mmol) in dry $CHCl_3$ (1.0 cm^3), benzyltriphenylphosphonium chloride (19 mg, 44 μmol) was added and the mixture was allowed to stand overnight without stirring. The mixture was subjected directly to column chromatography (SiO_2, Et_2O/pentane 3:7) to afford **14** as a colourless oil (472 mg, 63%). δ_H(300 MHz; $CDCl_3$) 0.26 (s, 3 H), 0.31 (s, 3 H), 0.90 (s, 9 H), 1.86 (s, 3 H), 2.70 (s, 1 H). δ_C(75 MHz; $CDCl_3$) −4.3, −3.7, 17.9, 25.3, 32.3, 60.2, 74.5, 80.9, 119.1. GC-MS: $m/z = 209$ [M^+]. HR-MS (ESI): $m/z = 210.1318$ [$(M + H)^+$] (calcd for $C_{11}H_{20}NOSi$: 210.1314).

4,5-Dihexyl-4′,5′-bis[3-cyano-3-(*tert*-butyldimethylsilyloxy)but-1-ynyl]tetrathiafulvalene (15)

To an Ar-degassed solution of diiodo-TTF **8** (194 mg, 0.311 mmol) in dioxane/diisopropylamine (5 cm^3, 4:1), [$Pd(PPh_3)_4$] (38 mg, 0.033 mmol), CuI (21 mg, 0.11 mmol) and **14** (210 mg, 1.00 mmol) were added. The mixture was stirred for 2 h under Ar, which resulted in a colour change from orange to dark red. Then it was filtered on a silica plug (EtOAc/heptane 1:9) and concentrated *in vacuo*. Repeated column chromatography (SiO_2, EtOAc/heptane 1:19) afforded **15** as a red oil (192 mg, 78%). δ_H(300 MHz; $CDCl_3$) 0.26 (s, 6 H), 0.32 (s, 6 H), 0.85–0.95 (m, 24 H), 1.2–1.4 (m, 12 H), 1.50 (m, 4 H), 1.92 (s, 6 H), 2.35 (t, 7.3 Hz, 4 H), 4.48 (s, 4 H). δ_C(75 MHz; $CDCl_3$) −4.1, −3.4, 14.0, 17.9, 22.5, 25.3, 28.7 (× 2), 29.7, 31.5, 32.2, 60.9, 76.5, 95.3, 100.8, 117.9, 118.6, 121.4, 128.8. IR (KBr): $\tilde{\nu} = 2940$ (s), 2928 (s), 2859 (m), 1630 (m), 1464 (m), 1377 (m), 1257 (m), 1146 (m), 993 (m), 839 (s), 784 (m) cm^{-1}. MS (FAB): $m/z = 786$ [M^+]. HR-MS (FAB): $m/z = 786.3210$ [M^+] (calcd for $C_{40}H_{62}N_2O_2S_4Si_2$: 786.3233).

4,5-Bis(4,4-dicyano-3-methylbut-3-en-1-ynyl)-4′,5′-dihexyltetrathiafulvalene (16)

To a solution of **15** (59 mg, 0.075 mmol) in THF (50 mL), *o*-nitrophenol (42 mg, 0.30 mmol) was added and the solution was cooled to 0 °C. Bu_4NF (0.15 cm^3, 1.0 M in wet THF, 0.15 mmol) was added and the solution stirred for 1.5 h. Toluene (200 cm^3) was added and the solution washed with Na_2CO_3 (aq., 5%, 4 × 50 cm^3) to remove *o*-nitrophenol, dried ($MgSO_4$) and filtered on Celite. The blue-purple solution of diketone **13** was concentrated *in vacuo* to a volume of *ca.* 50 cm^3, whereupon malononitrile (364 mg, 5.5 mmol) and Al_2O_3 (46 mg, neutral, act. I) were added and the reaction mixture was protected from light and stirred for 4 h at rt. The mixture was filtered through Celite, washed with H_2O (4 × 100 cm^3) and brine (50 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, toluene/heptane 2:3) afforded **16** as a brown-yellow oil (14 mg, 31%). δ_H(300 MHz; $CDCl_3$) 0.89 (t, 6.7 Hz, 6 H), 1.2–1.4 (m, 12 H), 1.50 (m, 4 H), 2.37 (t, 7.5 Hz, 4 H), 2.43 (s, 6 H). δ_C(75 MHz; $CDCl_3$) 14.0, 22.5, 22.9, 28.7, 28.8, 29.7, 31.5, 92.4, 96.7, 98.3, 98.7, 111.4, 111.9, 121.9, 125.8, 128.9, 153.2. IR (KBr): $\tilde{\nu} = 2940$ (m), 2926 (s), 2856 (m), 2229 (w), 2166 (vs), 1629 (w), 1549 (m), 1458 (w), 1430 (w), 1376 (w), 1305 (w), 1123 (w), 934 (w), 779 (w) cm^{-1}. MS (FAB): $m/z = 600$ [M^+]. HR-MS (FAB): $m/z = 600.1511$ [M^+] (calcd for $C_{32}H_{32}N_4S_4$: 600.1510).

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