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Synthesis and characterization of alkene-extended tetrathiafulvalenes with lateral alkyne appendages

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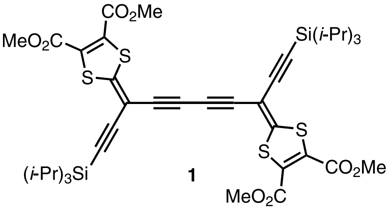
Abstract—Tetrathiafulvalene (TTF) derivatives containing a diethynyl-substituted alkene spacer were synthesized and investigated for their electronic and structural properties. Co-planarity of the central diethynylethene unit and the two dithiole rings were confirmed by X-ray crystallographic analysis.

The extension of π-electron conjugation in tetrathiafulvalene (TTF) by a spacer unit has attracted considerable attention in the quest for electrically conducting or non-linear optical (NLO) materials.[1] We have recently shown that acetylenic scaffolding is a powerful tool for constructing extended TTFs, such as **1**, based on *sp*-carbon atoms.[2] Our synthetic protocols allowed tuning of the electronic properties by incorporation of functionalized alkyne groups at the fulvene carbon attached to each dithiole ring and hence in cross-conjugation to the acetylenic spacer. We next turned our attention to two-dimensional spacer units within which both linear and cross-conjugative π-electron delocalization pathways can be operative. For this purpose, we chose the diethynylethene (DEE) unit which has been employed successfully by Diederich and co-workers[3] for construction of poly(triacetylene) (PTA) oligomers.



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The synthetic protocol is shown in Scheme 1. A double Wittig olefination between dialdehyde **2**[4] and phosphonium salt **3**[5] gave the new TTF derivative **4** in good yield.[6] This strategy has found wide application for preparing polyenic analogues of TTF.[7,8] However, treating **2** with **5**[9] only gave the mono-aldehyde **6**. It was not possible to force olefination at both aldehyde positions by treating **2** with more than two equivalents of **5**. Alternative methods for building the central ethylenic spacer are thermal dimerization–desulfurization of thials[10] or titanium-mediated coupling of aldehydes.[11] We reasoned, however, that the diminished electrophilicity of the carbonyl carbon of **6** might facilitate a phosphite-mediated cross-coupling with the 1,3-dithiole-2-one **7**. As a matter of fact, this method provided **8** in good yield, and presents a convenient route to unsymmetrical, alkene-extended TTFs, in this case with one end containing cyanoethyl-protected thiolate groups. As shown by Becher and co-workers,[12] cyanoethylthio-substituted TTFs are versatile building blocks for oligomers and macrocycles via stepwise deprotection–realkylation protocols. The cyanoethyl groups of **8** were removed according to the standard procedure by CsOH, leaving, gratifyingly, the Si(i-Pr)$_3$ groups uncleaved. Alkylation with MeI in situ finally afforded the symmetrical TTF **9**.

The UV–vis absorption spectra of the new TTFs are shown in Figure 1. The highest wavelength absorption

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Keywords: chromophore; π-conjugation; diethynylethene; NLO; tetrathiafulvalene.

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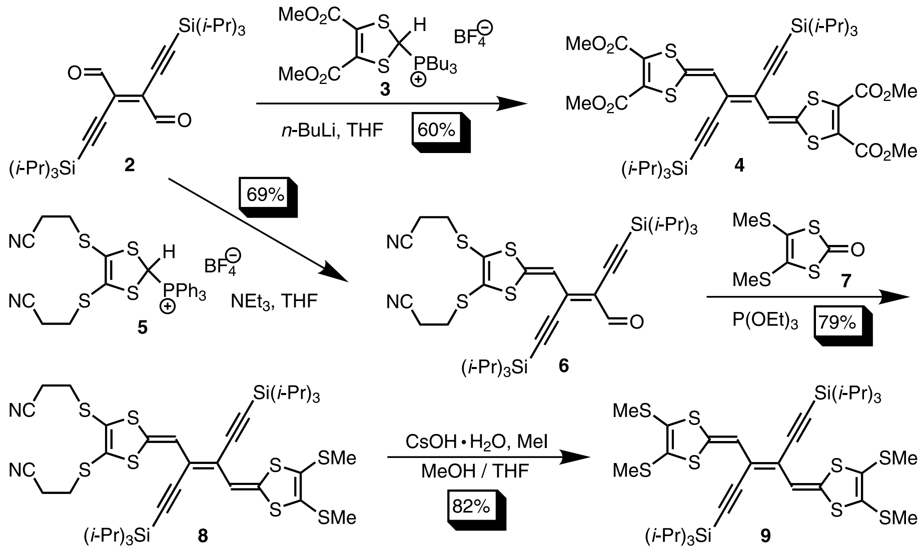

Scheme 1.

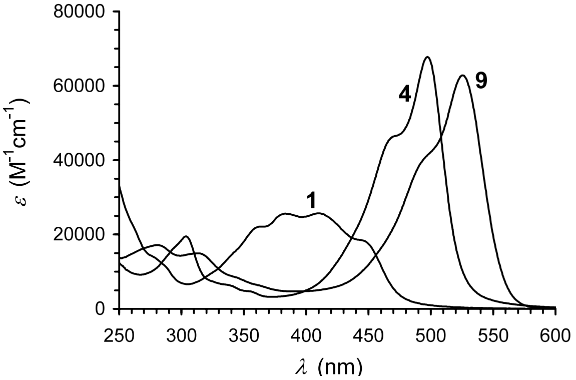

Figure 1. UV–vis absorption spectra in $CHCl_3$.

maximum of **4** at λ_{max} 496 nm is red-shifted by as much as 76 nm relative to a TTF devoid of the lateral acetylene appendages, but with the same substituent groups at the dithiole rings,[7] and by 55 nm relative to **1**.[2] Substitution by SMe groups leads to a further red-shift (+28 nm) of λ_{max}, which corresponds to a decrease in the HOMO-LUMO gap from 2.50 eV (**4**) to 2.37 eV (**9**).

The X-ray crystal structure of **9** is depicted in Figure 2.[13] The structure confirms the *E*-configuration at the central ethylenic linkage. Moreover, it transpires that the central DEE unit and the two dithiole units comprise a plane with a maximum deviation of 0.109(1) Å.

The electrochemical data for the new DEE-spaced TTFs are collected in Table 1. TTFs **4**, **8** and **9** were oxidized in two reversible one-electron steps at very low potential. Indeed, TTF **4** is a much stronger π-donor molecule than the buta-1,3-diynediyl-extended TTF **1** (oxidized at +0.64 V and +0.76 V versus Fc/Fc$^+$),[2] while it experiences a larger difference in the first and second oxidation potentials (210 mV), which indicates a larger electrostatic repulsion between the two positive charges in the dication. Interestingly, all three TTFs, no matter the substituents, were able to take up a total of two electrons upon reduction. The differences in redox potentials originate mainly from the character of the substituents. However, the electrochemical HOMO-LUMO gaps, obtained as the potential difference between the first oxidation and reduction, is the same (2.0 eV) for all three compounds. It transpires that this value is smaller than the energies corresponding to the absorption maxima by 0.4–0.5 eV.

A total of six linear or cross-conjugative π-electron delocalization pathways can be imagined within the planar two-dimensional spacer unit of **4**, and it resembles in this respect tetraethynylethene, a molecule that upon arylation reaches very high third-order optical nonlinearities.[14] We have shown in earlier work that PM3 calculations on acetylenic dithiafulvenes, such as **1**, give second hyperpolarizabilities γ in good agreement with experimental values measured by third-harmonic generation (THG) measurements.[2] From such calculations, we predict a γ value for **4** and **9** of about 219 and 174×10^{-36} esu, respectively, hence a value for **4** more than twice as high as that obtained for **1** (THG (1907 nm): 87×10^{-36} esu, calcd: 96×10^{-36} esu). The Connolly solvent-excluded volumes of **4** and **9** were calculated as 777 and 758 Å^3, respectively. Keeping in mind that the Si(i-Pr)$_3$ groups are very bulky and do not contribute to the expected γ values, the desilylated molecules are attractive candidates for NLO films with high third-order susceptibilities $\chi^{(3)}$. Unfortunately, however, initial attempts at desilylation by fluoride ions were accompanied by considerable decomposition. It is clear that this step requires optimization of the reaction conditions. Moreover, the possibility for carrying out acetylenic coupling reactions at these positions is a fascinating goal, targeting for example new PTA oligomers with lateral dithiafulvene groups.

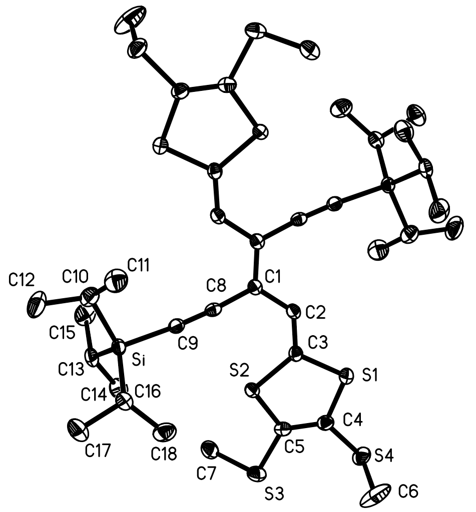

Figure 2. ORTEP plot of **9** at the 50% probability level. Hydrogens were omitted for clarity. Selected bond lengths (Å) and angles (°): C1–C1′ 1.389(4), C1–C2 1.436(3), C2–C3 1.353(3), C3–S1 1.753(2), C3–S2 1.755(2), S1–C4 1.748(2), C4–C5 1.345(3), C5–S2 1.757(2), C8–C9 1.206(3); C1–C8–C9 174.1(2), C2–C1–C8 120.42(18), C2–C3–S1 119.95(16), C3–S1–C4 96.63(10), S1–C4–C5 116.49(16), C4–C5–S2 117.09(16), C3–S2–C5 95.97(10).

Table 1. Cyclic voltammetry data in CH_2Cl_2 (+0.1 M *n*-Bu_4NPF_6); potentials versus Fc/Fc^+. Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl. Scan rate: 0.1 V s^{-1}

	4	8	9
$E°$ (V)[a]	+0.18 ($1e^-$)	+0.00 ($1e^-$)	−0.09 ($1e^-$)
	+0.39 ($1e^-$)	+0.15 ($1e^-$)	+0.09 ($1e^-$)
		−2.04 ($1e^-$)	−2.08 ($1e^-$)
E_p (V)[b]	−1.83 ($2e^-$)	−2.36 ($1e^-$)	−2.47 ($1e^-$)

[a] $E° = (E_{pc}+E_{pa})/2$, where E_{pc} and E_{pa} = cathodic and anodic peak potentials.

[b] E_p = irreversible peak potential.

In conclusion, we have developed efficient synthetic protocols for obtaining large π-extended redox systems based on dithiole and diethynylethene entities.

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13. X-Ray crystal structure of **9** ($C_{36}H_{56}S_8Si_2$): Crystal size: 0.50×0.17×0.13 mm. $T = 120$ K. Crystal data: orthorhombic, space group *Pbca*, $a = 8.4469(11)$, $b = 21.202(3)$, $c = 24.124(3)$ Å, $V = 4320.4(10)$ $Å^3$, $D_c = 1.232$ g cm^{-3}, $Z = 4$, $\mu = 0.493$ mm^{-1}. MoKα radiation, $\lambda = 0.71073$ Å. 43400 reflections measured, 4419 unique ($R_{int} = 0.0866$), which were all used in the refinement. Final $R(F) = 0.0359$ (for $F^2 > 2\sigma(F^2)$), $wR(F^2) = 0.0899$ (for all data). CCDC reference number 209173.
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