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Tetrathiafulvalene–acetylene scaffolding: new π-electron systems for advanced materials

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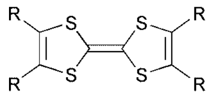
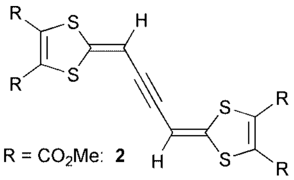
Novel extended tetrathiafulvalenes (TTFs) with hexa-2,4-diyne-1,6-diylidene spacers between the two 1,3-dithiole rings and laterally appended alkynyl moieties for one- and two-dimensional scaffolding were synthesised and investigated for their electronic properties.

Tetrathiafulvalene (TTF) is a reversible, two-electron donor which has found wide applications in both materials and supramolecular chemistry.[1] The on-going quest for TFF-based organic conductors has stimulated much structural variation, in particular the insertion of π-conjugated spacers between the two 1,3-dithiole units.[2] Indeed, a considerable number of olefinic and aromatic spacers have been introduced with the aim to tune the redox properties of the π-electron system.[3] In contrast, only two examples of acetylenic spacers have been reported.[4,5] Thus, Gorgues and co-workers[4] reported the synthesis of substituted 1,4-bis(1,3-dithiol-2-ylidene)but-2-ynes, such as **2**. We decided to expand the family of acetylenic TTFs[6] by members containing a hexa-2,4-diyne-1,6-diylidene spacer between the two dithiole rings while at the same time featuring laterally appended alkynyl moieties for introduction into larger one- and two-dimensional scaffolds.



R = H: TTF
R = CO_2Me: **1**



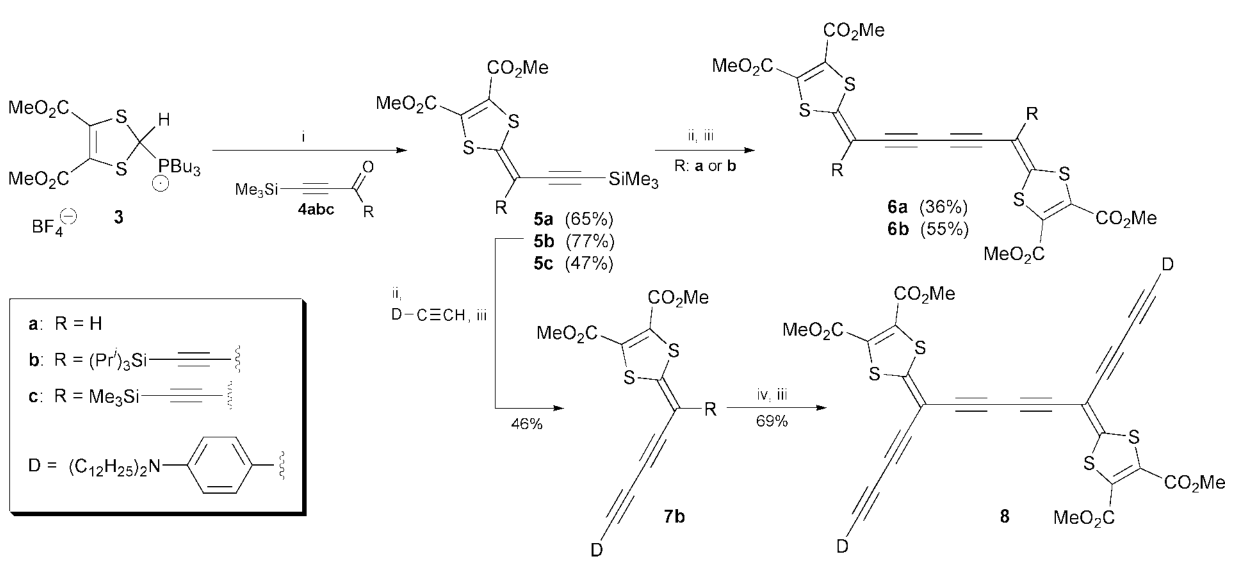
R = CO_2Me: **2**

The first target compound **6a**† was obtained by deprotection of the silylated alkyne **5a** using K_2CO_3 in MeOH–THF (Scheme 1), followed by oxidative coupling under Hay conditions[7] (CuCl, TMEDA, O_2). Precursor **5a** was prepared by a Wittig reaction between phosphonium salt **3**[8] and aldehyde **4a**.[9]

Wittig reaction of **3** with ketones **4bc**[9] gave the dialkynylated dithiafulvenes **5bc**. After selective removal of the $SiMe_3$ group in **5b**, Hay coupling provided the extended TTF **6b**† as an orange solid, whereas cross-coupling with 4-(*N*,*N*-didodecylamino)phenylacetylene (4.5 equiv.) afforded compound **7b**. Alkyne deprotection followed by oxidative coupling provided the extended TTF **8** with two laterally appended electron-donating anilino groups.

The X-ray crystal structure of **6a** (Fig. 1)‡ reveals that the two fulvene double bonds adopt the *s-trans* conformation with respect to the connecting buta-1,3-diynediyl moiety. The two dithiafulvene units are rotated about the central diacetylene core with a torsional angle C1–C14–C19–C20 of −138.6°.

Proceeding from the dithiafulvene monomers **5abc** and **7b** to the extended TTFs **6ab** and **8** results in significant bathochromic shifts of the longest wavelength absorption maxima (Table 1). The origin of this transition was elucidated by a computational study employing the GAUSSIAN 98 program package[10] at the HF/3-21G level of theory. It transpires that the HOMO of **6a** is distributed over the four sulfur atoms and the connecting spacer unit (Fig. 2), whereas the LUMO is located at the two peripheral ethylene biscarbonyl units; both HOMO and



Scheme 1 *Reagents and conditions*: i, *n*-BuLi, THF, −78 °C; ii, K_2CO_3, THF, MeOH, 20 °C; iii, CuCl, TMEDA, CH_2Cl_2, O_2, 20 °C. iv, Bu_4NF, THF, H_2O, 20 °C.

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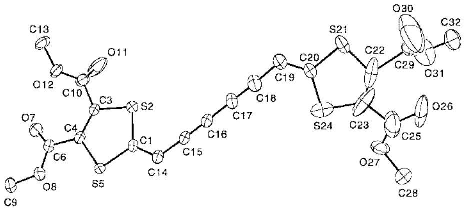

Fig. 1 ORTEP plot of **6a**. Atomic displacement parameters obtained at 248 K are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): C1–S2 1.739(6), C1–S5 1.755(6), S2–C3 1.739(6), C3–C4 1.346(8), C4–S5 1.739(6), C1–C14 1.367(9), C14–C15 1.408(9), C15–C16 1.197(9), C16–C17 1.357(10); C1–C14-C15 122.6(6), C14–C15–C16 175.8(7), C15–C16–C17 175.0(8).

Table 1 Longest wavelength absorption maxima λ_{max}/nm and molar extinction coefficients (ε/M^{-1} cm^{-1}) in $CHCl_3$

	λ_{max}/nm (ε/M^{-1} cm^{-1})		λ_{max}/nm (ε/M^{-1} cm^{-1})		λ_{max}/nm (ε/M^{-1} cm^{-1})
5a[a]	348[b] (6100)	**5b**[a]	372 (15000)	**7b**	422 (25300)
6a	429 (25400)	**6b**	441[b] (18600)	**8**	460[b] (33300)

[a] Compounds **5a** and **5b** experience 'tail' absorptions at λ_{max} 405 nm (ε 1600) and 410 nm (ε 1440), respectively. [b] Shoulder.

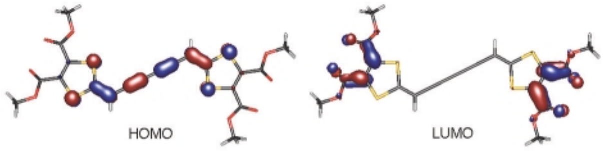

Fig. 2 HF/3-21G-calculated HOMO and LUMO of **6a**.

LUMO are of pure π-nature. A similar intramolecular charge-transfer transition was observed for parent, CO_2Me-substituted TTFs,[11] but with a much smaller extinction coefficient: $\varepsilon_{CT}(\mathbf{1})$ = 1930 M^{-1} cm^{-1} at λ_{max} 445 nm.[12]

The electrochemical data for the new extended TTFs are collected in Table 2. TTF **6b** was oxidised in two reversible one-electron steps in CH_2Cl_2, with a separation of only 120 mV, indicating a lower coulombic repulsion between the two charges in the dication as compared to that of **1** ($E_2^{ox} - E_1^{ox}$ = 320 mV in MeCN)[13] and **2** ($E_2^{ox} - E_1^{ox}$ = 380 mV in MeCN).[4] TTF **6a** was oxidised in an irreversible two-electron step in CH_2Cl_2. Also, **8** experienced irreversible oxidation steps, with the first oxidation occurring at the anilino donors. Thus, structural changes in the acetylenic spacer unit as well as solvent polarity are influencing the oxidation behavior, as was likewise recognised for a series of TTF vinylogues.[14] Interestingly, it was also possible to reduce the acetylenic TTFs.

Table 2 Cyclic voltammetry data in CH_2Cl_2 (+0.1 M n-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}

	$E°$/V[a]	E_p/V[b]		$E°$/V[a]	E_p/V[b]
6a		0.58 (2e)	**7b**	0.42 (1e)	
		−1.81 (2e)		0.67 (1e)	
6b[c]		0.70 (2e)			−1.70 (1e)
		−1.75 (2e)			−1.81 (1e)
6b	0.64 (1e)		**8**		0.43 (2e)
	0.76 (1e)				0.87 (1e)
		−1.86 (2e)			1.12 (1e)
					−1.70 (2e)

[a] $E° = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} = cathodic and anodic peak potentials. [b] E_p = irreversible peak potential. [c] Solvent: MeCN.

In summary, we have developed a new family of dithiafulvene–acetylene hybrid chromophores. We are currently investigating the possibility of employing these versatile building blocks for the construction of expanded radialene-type[15] acetylenic macrocycles containing peripheral dithiole groups.

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Notes and references

† All new compounds were characterised by IR, UV-Vis, ^1H and ^{13}C-NMR, elemental analysis or HR-MS. *Selected data*: for **6a**: δ_H (200 MHz, $CDCl_3$) 3.84 (6 H, s), 3.85 (6 H, s), 5.53 (2 H, s); δ_C (50 MHz, $CDCl_3$) 53.4, 82.9, 84.0, 91.9, 131.1, 131.6, 149.5, 159.3, 159.5; *m*/*z* (HR-MALDI-MS 2,5-dihydroxybenzoic acid (DHB)) 509.9559 (M^+, calcd. 509.9572).

‡ *X-Ray crystal structure of* **6a**: preliminary measurements indicated that crystals of **6a** exhibit a phase transition below *ca*. 230 K. Because of bad crystal quality (large mosaic spread up to 2.8°), the low-temperature phase was not investigated any further. For the present structure, a crystal with linear dimensions of *ca*. 0.28 × 0.22 × 0.10 mm was measured at 248 K. Crystal data for $C_{20}H_{14}O_8S_4$ [M_r = 510.55]: monoclinic, space group $P2_1/c$ (no. 14), D_c = 1.572 g cm^{-3}, Z = 4, a = 25.782(8), b = 4.107(1), c = 21.947(5) Å, β = 111.87(2)°, V = 2156.6(10) $Å^3$. *Nonius-CAD4* diffractometer, CuK_α radiation, λ = 1.5418 Å. The structure was solved by direct methods and refined by full-matrix least-squares analysis (*SHELXL-97*). Static disorder occurs within the sub-unit C20–S21 until C32, and thus the corresponding geometry is somewhat unreliable. Preliminary refinements show that the disorder can be resolved, in principle for C22 and C23, while the corresponding refinements of the ethoxy groups (including restraints) are not satisfactory. All heavy atoms were refined anisotropically (H-atoms of the ordered sub-unit isotropically, whereby H-positions are based on stereochemical considerations). Final $R(F)$ = 0.093, $wR(F^2)$ = 0.255 for 295 parameters and 2512 reflections with $I > 2\sigma(I)$ and $3.69 < \theta < 60.0°$ (the corresponding R-values based on all 3163 reflections are 0.110 and 0.280, respectively). CCDC 164802. See http://www.rsc.org/suppdata/cc/b1/b105749a for crystallographic files in .cif or other electronic format.

1 Recent reviews: M. B. Nielsen, C. Lomholt and J. Becher, *Chem. Soc., Rev*., 2000, **29**, 153; M. R. Bryce, *J. Mater. Chem*., 2000, **10**, 589; J. L. Segura and N. Martín, *Angew. Chem., Int. Ed*., 2001, **40**, 1372.
2 For a review on linearly π-extended TTFs, see: J. Roncali, *J. Mater. Chem*., 1997, **7**, 2307.
3 Some recent examples: S.-G. Liu, I. Pérez, N. Martín and L. Echegoyen, *J. Org. Chem*., 2000, **65**, 9092; M. R. Bryce, M. A. Coffin, P. J. Skabara, A. J. Moore, A. S. Batsanov and J. A. K. Howard, *Chem. Eur. J*., 2000, **6**, 1955.
4 A. Khanous, A. Gorgues and F. Texier, *Tetrahedron Lett*., 1990, **31**, 7307; A. Khanous, A. Gorgues and M. Jubault, *Tetrahedron Lett*., 1990, **31**, 7311.
5 H. Awaji, T. Sugimoto and Z. Yoshida, *J. Phys. Org. Chem*., 1988, **1**, 47.
6 TTFs with alkynyl substituents at the peripheral 2,3,6,7-positions represent another class: D. Solooki, T. C. Parker, S. I. Khan and Y. Rubin, *Tetrahedron Lett*., 1998, **39**, 1327.
7 A. S. Hay, *J. Org. Chem*., 1962, **27**, 3320.
8 M. Sato, N. C. Gonnella and M. P. Cava, *J. Org. Chem*., 1979, **44**, 930.
9 J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler and F. Diederich, *Helv. Chim. Acta*., 1995, **78**, 13.
10 M. J. Frisch *et al*., SGI-G98, Rev. A.5, Gaussian, Inc., Pittsburg, PA, 1998.
11 A. S. Batsanov, M. R. Bryce, J. N. Heaton, A. J. Moore, P. J. Skabara, J. A. K. Howard, E. Ortí, P. M. Viruela and R. Viruela, *J. Mater. Chem*., 1995, **5**, 1689.
12 H. D. Hartzler, *J. Am. Chem. Soc*., 1973, **95**, 4379.
13 S.-G. Liu, M. Cariou and A. Gorgues, *Tetrahedron Lett*., 1998, **39**, 8663.
14 N. Bellec, K. Boubekeur, R. Carlier, P. Hapiot, D. Lorcy and A. Tallec, *J. Phys. Chem. A*, 2000, **104**, 9750.
15 M. B. Nielsen, M. Schreiber, Y. G. Baek, P. Seiler, S. Lecomte, C. Boudon, R. R. Tykwinski, J.-P. Gisselbrecht, V. Gramlich, P. J. Skinner, C. Bosshard, P. Günter, M. Gross and F. Diederich, *Chem. Eur. J*., 2001, **7**, 3263.