Synthesis of New Tetrathiafulvalene Modules for Acetylenic Scaffolding

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Abstract: Benzene-extended derivatives of tetrathiafulvalene (TTF) containing silyl-protected acetylene groups at the *exo*-cyclic fulvene carbons were prepared by a double Wittig olefination of a diacetylenic derivative of terephthalaldehyde. Acetylenic coupling reactions at the lateral acetylene appendages with phenylacetylene and 4-iodonitrobenzene afforded large π -conjugated chromophores.





Figure 1 Structures of TTF and 1.

Tetrathiafulvalene (TTF) is a reversible, two-electron donor that has been widely exploited in both materials and supramolecular chemistry.¹ Many structural variations of the parent TTF system have been carried out during the last 30 years, mainly with the aim of developing low-temperature organic superconductors.² Yet, owing to the three reversible redox states of TTF, the possibility for employing TTF in molecular sensors, switches, and devices has also attracted an enormous focus recently.^{1a,3} Synthetic protocols are today available for stepwise functionalization of the TTF core, which has allowed its ready incorporation into macrocyclic and oligomeric structures.⁴ Efficient procedures for incorporating π -conjugated spacers between the two dithiole rings offer access to so-called extended TTFs that in many cases exhibit enhanced π -donor properties and a stabilization of the dication state.⁵ Very recently, the versatility and high functional group tolerance of acetylenic couplings⁶ stimulated synthesis of acetylenic derivatives of either TTF itself or of the 1,4dithiafulvene half-unit.7 Indeed, some of these compounds were successfully employed as precursors for TTF-polymers and alkyne-extended TTFs. This approach is now continued by the development of a synthetic protocol for obtaining acetylenic derivatives of the benzene-extended TTF 1,⁸ that is, derivatives containing acetylenic appendages at the exo-cyclic fulvene carbons. These new modules for acetylenic scaffolding were subjected to different cross-coupling conditions, which allowed construction of new large π -conjugated chromophores.

Extended TTFs are conveniently prepared by a double Wittig olefination reaction between a dialdehyde and a phosphorus ylide.^{8,9} In order to follow this strategy, the acetylenic functions were first attached to the benzene spacer before forming the TTF skeleton. The synthetic procedure is outlined in Scheme 1. In the first step, tere-

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phthalaldehyde (2) was treated with lithium triisopropylsilylacetylide generated in situ. The resulting diol 3 was subsequently oxidized by PCC to the diketone 4. This compound was then reacted with the ylide of 5^{10} (2.2) equivalents), generated by treating 5 with *n*-butyllithium. The outcome of this double Wittig reaction was the new TTF derivative 6.¹¹ Although this compound experiences good solubility in common organic solvents such as THF and CH2Cl2, it was decided to enhance the solubility further in order for it to be incorporated into larger soluble scaffolds. Transesterification under basic conditions was accomplished by reacting 6 with 1-decanol and potassium carbonate, affording the decyl ester 7. Both TTFs 6 and 7 are very stable compounds that were subjected to normal chromatographic work-up and stored at room temperature. Removal of the silvl protecting groups was carried out by the action of a fluoride source such as tetrabutylammonium fluoride (2 equivalents). This deprotection step was very fast, and the mixture was worked up after 15 min of stirring at room temperature. After chromatographic purification, TTF 8 containing two terminal acetylene units was obtained. This desilylated compound was very unstable and decomposed (turning dark) after prolonged standing at room temperature. Nevertheless, it was completely characterized by mass spectrometry (High-res FT-MALDI-MS) and ¹H- and ¹³C NMR spectroscopies. The terminal acetylene protons were found resonating as a singlet at δ_H 3.76 ppm. The presence of CCH groups was furthermore confirmed by IR spectroscopy that revealed the C-H stretching band at 3307 cm⁻¹. Moreover, the CC stretching band was shifted from 2126 cm^{-1} in **6** to 2085 cm^{-1} in **8**.

The possibility for performing acetylenic coupling reactions with **8** was exploited next. Thus, it was treated with an excess of phenylacetylene under oxidative Hay conditions¹² (Scheme 2), i.e. employing the CuCl, N,N,N',N'-tetramethylethylenediamine (TMEDA) catalyst system in the presence of oxygen (from the air). This reaction afforded in good yield the extended TTF **9** in which each dithiole ring is in linear conjugation to a



Scheme 1 Synthesis of benzene-extended TTF with lateral alkyne appendages.

phenyl ring via a buta-1,3-diynediyl spacer.¹¹ This compound seemed very stable and suffered from no apparent decomposition under chromatographic work-up on normal silica gel. In order to explore further the synthetic versatility of 8, it was subjected to a Pd-catalyzed crosscoupling reaction with 4-iodonitrobenzene under Sonogashira conditions¹³ (Scheme 2). This reaction gave in a modest yield of 29% the desired TTF 10, containing two electron-withdrawing 4-nitrophenyl groups.¹¹ Yet, since two cross-couplings are carried out in this step, the yield corresponds to an efficiency of 54% for each coupling reaction. The separation of 10 from by-products, not yet identified, of similar polarity was very tedious and required repeated chromatographic purification. [2+2]Cycloadditions with subsequent ring-openings have earlier been observed between the central TTF double bond and electron-deficient acetylenes¹⁴ and may possibly account for the by-products. Owing to the large donor-acceptor substituted π -system, compound **10** might be a good candidate for NLO applications.^{7f} It is a very strong chromophore exhibiting a charge-transfer transition at λ_{max} 426 nm (ε 38500 M⁻¹cm⁻¹). This longest wavelength absorption maximum is bathochromically shifted by +32 nm and +29 nm relative to the maxima of 7 and 9, respectively (7: λ_{max} 394 nm, ϵ 32900 $M^{-1}cm^{-1};$ 9: λ_{max} 397 nm, ϵ 43600 M⁻¹cm⁻¹). The CC stretching band of 10 was observed at 2183 cm⁻¹.

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In conclusion, a synthetic protocol has been developed for obtaining benzene-extended TTFs that – via alkyne appendages – act as new modules for acetylenic scaffolding.

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Scheme 2 Functionalization at the lateral positions. TMEDA = N, N, N', N'-tetramethylethylenediamine.

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- (11) All new compounds were fully characterized by ¹H- and ¹³C NMR spectroscopy, elemental analysis and/or HR-MS. Selected experimental procedures: Compound 6: To a solution of the phosphonium salt 5 (1.23 g, 2.42 mmol) in dry THF (40 mL) at -78 °C was slowly added *n*-BuLi (1.6 M in hexane, 1.5 mL, 2.4 mmol), resulting in a red solution. Then 4 (0.543 g, 1.10 mmol) in dry THF (15 mL) was slowly added. The resulting orange solution was stirred at -78 °C for 2 h, whereupon sat aq NH₄Cl (200 mL) was added. Then

Et₂O (300 mL) was added, the organic phase was separated, dried (MgSO₄), and concentrated in vacuo. Column chromatography (SiO₂, CH₂Cl₂) afforded 6 (0.652 g, 66%) as an orange solid. Mp 155–156 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.14 (s, 42 H), 3.84 (s, 6 H), 3.89 (s, 6 H), 7.55 (s, 4 H). ¹³C NMR (75 MHz, CDCl₃): δ = 11.3, 18.7, 53.3, 53.5, 101.6, 104.8, 107.7, 126.5, 129.6, 133.0, 135.4, 141.2, 159.4, 160.2. MALDI-TOF-MS [matrix: 2,5dihydroxybenzoic acid (DHB)]: m/z = 898 (M⁺). Elemental analysis: Calcd for C44H58O8S4Si2 (899.35): C, 58.76; H, 6.50; S, 14.26; Found: C, 58.94; H, 6.38; S, 14.38. Compound 9: To a solution of 8 (126 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) was added phenylacetylene (1 mL) and thereafter Hay catalyst (1 mL) [Hay catalyst: CuCl (0.13 g, 1.3 mmol) and TMEDA (0.16 g, 1.4 mmol) in CH₂Cl₂ (4.5 mL)]. The mixture was stirred for 20 min and then concentrated in vacuo without heating. Column chromatography (SiO₂, CH₂Cl₂/cyclohexane, 1:1) afforded 9 (89 mg, 60%) as an orange oily solid. ¹H NMR (300 MHz, CDCl₃): δ = 0.88 (t, 6.6 Hz, 12 H), 1.27 (br s, 56 H), 1.66-1.74 (m, 8 H), 4.22 (t, 7.0 Hz, 4 H), 4.27 (t, 6.5 Hz, 4 H), 7.34-7.36 (m, 6 H), 7.53 (dd, 2.1/7.2 Hz, 4 H), 7.56 (s, 4 H). ¹³C NMR (75 MHz, CDCl₃): δ = 14.1, 22.7, 25.7, 25.8, 28.3,29.1, 29.2, 29.3, 29.5 (×2), 31.9, 67.0, 67.2, 73.8, 79.9, 83.6, 86.2, 105.4, 121.8, 126.9, 128.4, 129.2, 130.4, 132.3, 132.7, 135.4, 145.5, 158.9, 159.5. MALDI-TOF-MS (DHB): m/z = 1291 (M⁺). HR-FT-MALDI-MS (DHB): Calcd for C₇₈H₉₈O₈S₄ (M⁺): 1290.6145; Found: 1290.6161. Compound 10: 8 (209 mg, 0.19 mmol) and 4-iodonitrobenzene (490 mg, 1.97 mmol) were dissolved in dry THF (10 mL), and the mixture was thoroughly Ar-degassed. Then [PdCl₂(PPh₃)₂] (10 mg, 0.014 mmol) and diisopropylamine

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(1.5 mL) were added under Ar-degassing. Finally, CuI (3 mg, 0.016 mmol) was added, and the mixture was stirred for 3 h. Then Et₂O (300 mL) was added, and the organic phase was washed with H₂O (250 mL) and saturated aqueous NH₄Cl (250 mL), dried (MgSO₄), and concentrated in vacuo. Column chromatography (SiO₂, CH₂Cl₂/cyclohexane, 2:1) afforded **10** (74 mg, 29%) as an orange oily solid. ¹H NMR (300 MHz, CDCl₃): δ = 0.88 (m, 12 H), 1.27 (br s, 56 H), 1.70–1.76 (m, 8 H), 4.24 (t, 6.8 Hz, 4 H), 4.29 (t, 6.5 Hz, 4 H), 7.62 (s, 4 H), 7.63 (d, 8.8 Hz, 4 H), 8.21 (d, 8.8 Hz, 4 H). ¹³C NMR (75 MHz, CDCl₃): δ = 14.1, 22.7, 25.7, 25.8, 28.3, 29.2 (× 2), 29.3, 29.5 (× 3), 31.9, 67.1, 67.3, 93.4, 97.3, 105.8, 123.7, 126.9, 129.8, 130.6, 131.6, 132.7, 135.5,

144.3, 146.9, 158.9, 159.5. HR-FT-MALDI-MS (DHB): Calcd for $C_{74}H_{96}N_2O_{12}S_4$: 1332.5846 (M⁺); Found: 1332.5833. Elemental analysis: Calcd for $C_{74}H_{96}N_2O_{12}S_4$ (1333.82): C, 66.64; H, 7.25; N, 2.10; S, 9.61; Found: C, 66.84; H, 7.33; N, 2.15; S 9.55.

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