

# A novel hexakis(tetrathiafulvalene) derivative: synthesis, structure and electrochemical properties

Christian A. Christensen,<sup>ab</sup> Martin R. Bryce,\*<sup>a</sup> Andrei S. Batsanov<sup>a</sup> and Jan Becher\*<sup>ab</sup>

<sup>a</sup> Department of Chemistry, University of Durham, Durham, UK DH1 3LE. E-mail: m.r.bryce@durham.ac.uk

<sup>b</sup> Department of Chemistry, Odense University, Campusvej 55 DK 5230 Odense M, Denmark

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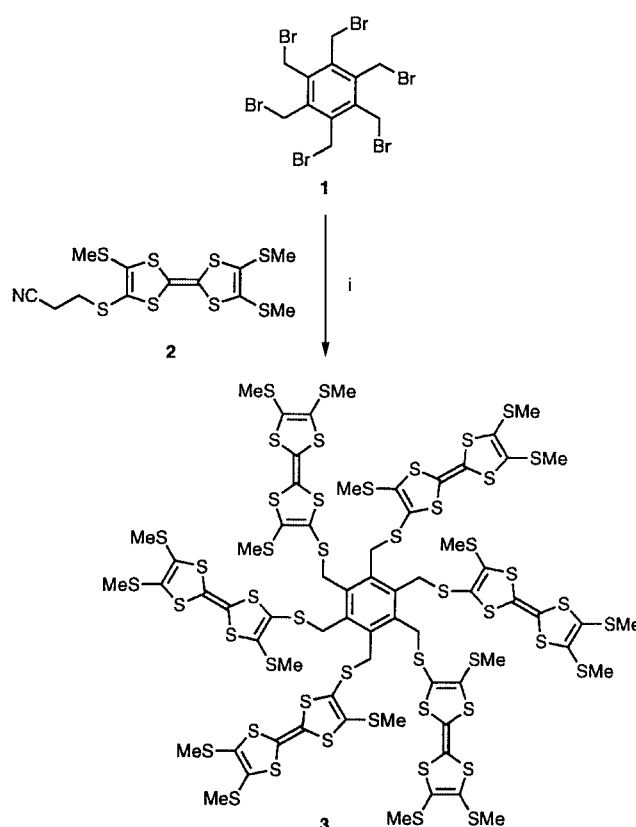
The hexakis(TTF) derivative **3** has been synthesised in 89% yield by six-fold reaction of the thiolate anion of reagent **2** with hexakis(bromomethyl)benzene: the solution electrochemistry of **3** shows sequential formation of the hexa-(radical cation) and the dodecacation species, and spectroelectrochemistry shows interacting radical cations; the X-ray crystal structure of **3** is reported.

Oligo(tetrathiafulvalene) (TTF) derivatives,<sup>1</sup> including dendrimers<sup>2</sup> and main-chain and side-chain polymers,<sup>3</sup> have received considerable attention recently. The two-step electrochemical oxidation of TTF,<sup>4</sup> to form sequentially the radical cation and dication, offers the prospect of controlled generation of oligo(radical cation) and oligo(dication) species, which may engage in intramolecular or intermolecular interactions, act as multi-electron redox switches,<sup>2e</sup> or modulate redox processes of organic guests incorporated within the oligo(TTF) host framework.<sup>5</sup> To date, all the pure TTF oligomers ( $n > 3$ ) which have been characterised have required multi-step syntheses. We now report the remarkably efficient synthesis of the novel hexakis(TTF) molecule **3** along with its X-ray crystal structure and solution electrochemistry.

Six-fold reaction of hexakis(bromomethyl)benzene **1**<sup>6</sup> with the thiolate anion of 4-(2-cyanoethyl)-4',5,5'-tris(methylsulfanyl)TTF **2**, which was generated using CsOH·H<sub>2</sub>O as described previously,<sup>7</sup> proceeded remarkably cleanly to afford the TTF hexamer **3** in 89% yield (Scheme 1).<sup>†</sup>

The X-ray crystal structure of **3**<sup>‡</sup> is shown in Fig. 1. As far as we are aware, no compound containing more than three TTF moieties has been structurally studied previously, and the structures of very few tris(TTF) compounds have been reported.<sup>8–11</sup> Molecule **3** has crystallographic C<sub>1</sub> symmetry. The central benzene ring is planar, with CH<sub>2</sub>-S bonds directed alternately above and below its plane. All three independent TTF moieties adopt a boat-like conformation: the inner dithiole rings are folded by 25.5, 29.6 and 13.2°, the outer ones by 18.4, 10.2 and 11.4°, with a small twist around the central C=C bond, by 6.3, 5.5 and 2.9°, respectively. Such flexibility and easy rotation around (exocyclic) C-S bonds may explain the fact that **3** forms a relatively dense crystal packing (21.6 Å<sup>3</sup> per non-H atom, cf. 22.8 and 22.1 Å<sup>3</sup> in monoclinic<sup>12</sup> and triclinic<sup>13</sup> polymorphs of MeS<sub>4</sub>TTF, respectively) with no significant cavities, while its poly-aryl analogues crystallise as clathrates, e.g. C<sub>6</sub>(CH<sub>2</sub>SPh)<sub>6</sub>·2CCl<sub>4</sub>,<sup>14a</sup> C<sub>6</sub>(CH<sub>2</sub>SO<sub>2</sub>CHMePh)<sub>6</sub>·4AcOH,<sup>14b</sup> C<sub>6</sub>(CH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>)<sub>6</sub>·1/2C<sub>30</sub>H<sub>50</sub><sup>14c</sup> and C<sub>6</sub>(CH<sub>2</sub>SCH<sub>2</sub>Ph)<sub>6</sub>·dioxane.<sup>14d</sup> Three of the six outer methyl groups in **3** are disordered between two positions each, indicating some residual looseness of the structure. There is no intramolecular S...S contact shorter than twice the van der Waals radius (3.60 Å)<sup>15</sup> of sulfur (excluding the contacts within the same TTF moiety) although each molecule participates in four significantly shorter intermolecular contacts.

Cyclic voltammetry (CV) of compound **3** (Fig. 2) showed two oxidation waves at  $E_1^{1/2}$  0.55 V and  $E_2^{1/2}$  0.88 V (vs. Ag/AgCl) typical of a tetra(alkylsulfanyl)TTF system.<sup>4b</sup> The first wave is reversible; the second wave is quasi-reversible. (The criterion applied for reversibility was a ratio of  $1.0 \pm 0.05$  for the intensities of the anodic and cathodic currents  $I_a/I_c$ , and no shift



Scheme 1 Reagents and conditions: i, CsOH·H<sub>2</sub>O, MeOH, DMF, 20 °C.

of the half wave potentials with varying scan rates between 50 and 500 mV s<sup>-1</sup>). There is no apparent interaction between the different TTF units. Thin layer CV was performed with the one-electron reduction peak of 2,3-dichloronaphthoquinone providing the internal reference, using procedures detailed previously.<sup>2d</sup> The number of electrons exchanged per oxidation

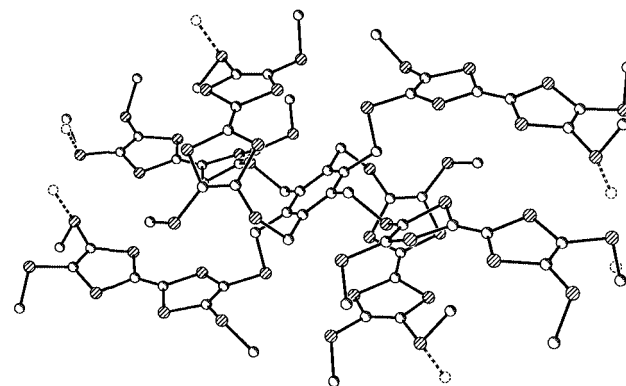


Fig. 1 Molecular structure of **3**, showing the disorder of the terminal methyl groups (H atoms are omitted).

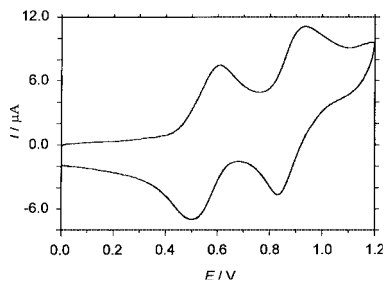


Fig. 2 Cyclic voltammogram of **3**.

wave was calculated to be  $6.0 \pm 0.5$ , which clearly suggests that complete oxidation occurs for all the TTF units. We note that in both CV and TLCV the reductive peak for the second redox couple ( $I_a/I_c = 0.8\text{--}0.9$ ) is slightly smaller than for the first wave, as observed previously for some other multi(TTF) systems,<sup>2d,16</sup> indicating an associated chemical reaction, or a marked conformational change, at the highest oxidation level of the molecule.

The spectroelectrochemistry of compound **3** is shown in Fig. 3 [compound **3** ( $10^{-4}$  M), BuNPF<sub>6</sub> ( $10^{-1}$  M), CHCl<sub>3</sub>]. The spectrum obtained at 0 V is consistent with neutral TTF units. On increasing the potential, as oxidation of the system proceeds, we see the concomitant emergence of the low energy absorption band of interacting TTF cation radicals ( $\pi$ - $\pi$  dimers)<sup>17</sup> at  $\lambda_{\text{max}}$  850 nm (Fig 3, spectrum at 0.65 V) along with a shoulder assigned to isolated (non-interacting) TTF cation radicals ( $\lambda_{\text{max}}$  480 nm). On further increasing the potential to form the fully oxidised species precipitation of material was observed in the cell, so the spectra of the +12 species could not be obtained. It is apparent, therefore, that the dense packing of TTF moieties in **3** favours intramolecular interactions of their cation radicals. This contrasts with previous less densely packed TTF units for which isolated TTF cation radicals are clearly detected in the UV-VIS absorption spectra.<sup>2c</sup>

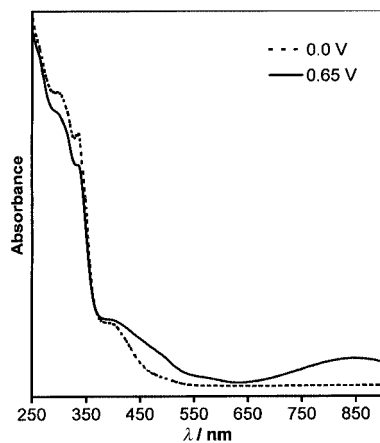


Fig. 3 Spectroelectrochemistry of **3**.

In summary, we report an extremely efficient one-pot synthesis of a hexakis(TTF) derivative **3**. This remarkably high-yielding six-fold reaction should make reagent **1** a suitable core unit for the convergent construction of higher TTF oligomers, including redox dendrimers, which are charged organic nanoparticles, relevant to miniaturisation in electronic materials.<sup>18</sup>

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## Notes and references

† To a stirred solution of **2** (0.427 g, 1.00 mmol) in dry degassed DMF (60 cm<sup>3</sup>) was added a solution of CsOH·H<sub>2</sub>O (0.185 g, 1.10 mmol) in dry MeOH (5 cm<sup>3</sup>). The solution was stirred under nitrogen at 20 °C for 1 h. Compound **1** (0.095 g, 0.150 mmol) was added and the reaction mixture was stirred at 20 °C for 16 h to afford an orange suspension which was poured onto water (400 cm<sup>3</sup>) and the orange precipitate was filtered off, washed with MeOH (10 cm<sup>3</sup>) and dried to afford analytically pure compound **3** (0.319 g, 89%), mp 214–215 °C. Recrystallisation from CS<sub>2</sub>-hexane afforded red prisms. Elemental analysis: calc. for C<sub>66</sub>H<sub>66</sub>S<sub>48</sub>: C, 33.05; H, 2.77. Found: C, 32.82; H, 2.62%;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 4.45 (s, 12H), 2.46 (s, 18H), 2.45 (s, 18H), 2.42 (s, 18H);  $m/z$  (ES) 2397.6 [M<sup>+</sup>], 1199.0 [M<sup>2+</sup>], 799.3 [M<sup>3+</sup>] (calc.: 2398.3, 1199.2, 799.4); CV  $E_{1/2}$  0.55 V;  $E_{2/2}$  0.88 V, CH<sub>2</sub>Cl<sub>2</sub>, Bu<sub>4</sub>NPF<sub>6</sub>, Pt electrode, vs. Ag/AgCl, scan rate 200 mV s<sup>-1</sup>.

‡ Crystal data for **3**: C<sub>66</sub>H<sub>66</sub>S<sub>48</sub>,  $M = 2398.1$ ,  $T = 120$  K, triclinic, space group  $P\bar{1}$  (No. 2),  $a = 10.799(3)$ ,  $b = 15.117(1)$ ,  $c = 16.732(5)$  Å,  $\alpha = 69.56(1)$ ,  $\beta = 76.88(1)$ ,  $\gamma = 77.89(1)^\circ$ ,  $U = 2467(1)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.614$  g cm<sup>-3</sup>, SMART 1K CCD area detector,  $\lambda = 0.71073$  Å (Mo-K $\alpha$ ), 22999 reflections (8659 unique,  $R_{\text{int}} = 0.017$ ) with  $2\theta = 50^\circ$ , semi-empirical absorption correction (SADABS: G. M. Sheldrick, 1997;  $T_{\text{max, min}} = 0.720, 0.591$ ), least squares refinement against  $F^2$  of all data (SHELXL97: G. M. Sheldrick, University of Göttingen, 1997), 541 variables,  $R = 0.028$  [7731 data,  $I > 2\sigma(I)$ ],  $wR(F^2) = 0.076$ ,  $\Delta\rho$  max./min. = 0.70, -0.35 e Å<sup>-3</sup>. CCDC 182/1528. See <http://www.rsc.org/suppdata/cc/a9/a909882h/> for crystallographic files in .cif format.

- Reviews: M. Adam and K. Müllen, *Adv. Mater.*, 1994, **6**, 439; T. Otsubo, Y. Aso and K. Takimiya, *Adv. Mater.*, 1996, **8**, 203; M. R. Bryce, W. Devonport, L. M. Goldenberg and C. Wang, *Chem. Commun.*, 1998, 945.
- (a) M. R. Bryce, W. Devonport and A. J. Moore, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1761; (b) C. Wang, M. R. Bryce, A. S. Batsanov, L. M. Goldenberg and J. A. K. Howard, *J. Mater. Chem.*, 1997, **7**, 1189; (c) C. A. Christiansen, L. M. Goldenberg, M. R. Bryce and J. Becher, *Chem. Commun.*, 1998, 509; (d) W. Devonport, M. R. Bryce, G. J. Marshall, A. J. Moore and L. M. Goldenberg, *J. Mater. Chem.*, 1998, **8**, 1361; (e) M. R. Bryce, P. de Miguel and W. Devonport, *Chem. Commun.*, 1998, 2565.
- S. Frenzel, S. Arndt, R. M. Gregorious and K. Müllen, *J. Mater. Chem.*, 1995, **5**, 1529; T. Yamamoto and T. Shimizu, *J. Mater. Chem.*, 1997, **7**, 1967; J. Roncali, *J. Mater. Chem.*, 1999, **9**, 1875.
- (a) S. Hünig, G. Kiesslich, H. Quast and D. Scheutzow, *Liebigs Ann. Chem.*, 1973, 310; (b) D. L. Lichtenberger, R. L. Johnston, K. Hinkelmann, T. Suzuki and F. Wudl, *J. Am. Chem. Soc.*, 1990, **112**, 3302.
- M. R. Bryce, W. Devonport and R. Katakya, unpublished results.
- J. Závada, M. Pánková, P. Holý and M. Tichý, *Synthesis*, 1994, 1132.
- J. Lau, O. Simonsen and J. Becher, *Synthesis*, 1995, 521.
- M. Fourmigué and P. Batail, *J. Chem. Soc., Chem. Commun.*, 1991, 1370.
- S. Yunoki, K. Takimiya, Y. Aso and T. Otsubo, *Tetrahedron Lett.*, 1997, **38**, 3017; M. Iyoda, M. Fukuda, S. Sasaki and M. Yoshida, *Synth. Met.*, 1995, **70**, 1171.
- P. Blanchard, N. Svenstrup, J. Rault-Berthelot, A. Riou and J. Becher, *Eur. J. Org. Chem.*, 1998, 1743.
- T. Akutagawa, Y. Abe, T. Hasegawa, T. Nakamura, T. Inabe, K. Sugiura, Y. Sakata, C. A. Christensen, J. Lau and J. Becher, *J. Mater. Chem.*, 1999, **9**, 2737.
- C. Katayama, M. Honda, H. Kumagai, J. Tanaka, G. Saito and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2272.
- H. Endres, *Z. Naturforsch., Teil B*, 1986, **41**, 1351.
- (a) A. D. U. Hardy, D. D. MacNicol and D. R. Wilson, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1011; (b) A. Freer, C. J. Gilmore, D. D. MacNicol and S. Swanson, *Tetrahedron Lett.*, 1980, **21**, 205; (c) A. Freer, C. J. Gilmore, D. D. MacNicol and D. R. Wilson, *Tetrahedron Lett.*, 1980, **21**, 1159; (d) A. D. U. Hardy, D. D. MacNicol, S. Swanson and D. R. Wilson, *J. Chem. Soc., Perkin Trans. 2*, 1980, 999.
- R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384.
- S. Booth, E. N. K. Wallace, K. Singhal, P. N. Bartlett and J. D. Kilburn, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1467.
- J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman and P. E. Seiden, *Phys. Rev. B*, 1979, **19**, 730.
- U. Simon, *Adv. Mater.*, 1998, **10**, 1487.

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