

# Synthesis and electrochemistry of a tetrathiafulvalene (TTF)<sub>21</sub>-glycol dendrimer: intradendrimer aggregation of TTF cation radicals

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The convergent synthesis of a TTF-glycol dendrimer is reported: thin layer cyclic voltammetric studies on (TTF)<sub>21</sub> system **11** show that all the TTF units undergo two single-electron oxidations to produce the 42+ redox state spectroelectrochemical studies establish that there are intradendrimer interactions between partially-oxidised TTF units.

The study of dendrimers is a burgeoning topic.<sup>1</sup> These macromolecules possess well-defined, three-dimensional structural order, and they provide unique frameworks for placing functional groups in predetermined spatial arrangements in a polymeric structure. In the context of functional dendrimers,<sup>2</sup> a variety of redox-active groups have been incorporated into the structures.<sup>3</sup>

Tetrathiafulvalene (TTF) dendrimers should be very interesting materials as the TTF system possesses a unique combination of properties,<sup>5</sup> viz. (i) oxidation to the cation radical and dication species occurs sequentially and reversibly, (ii) the oxidation potentials can be finely tuned by substituents on the TTF ring system, (iii) TTF cation radicals are thermodynamically very stable, and (iv) oxidised TTF units have a high propensity to form dimers or higher aggregates. A large number of multi-TTF derivatives<sup>5</sup> and some main- and side-chain polymeric TTFs<sup>6</sup> are known, but dendrimeric TTFs are largely unexplored.<sup>7</sup> Here we present the synthesis of a novel (TTF)<sub>21</sub> dendrimer with TTF units placed at peripheral sites and within the branches of the structure, and we report the electrochemistry and spectroelectrochemistry of this polymer. Glycol chains were incorporated into the branches to impart solubility in organic solvents, and air stability, and to provide a flexible structure to facilitate interactions between the TTF units.

The synthesis of dendrimer **11** uses a convergent strategy, with the caesium salts of TTF thiolate anions (Scheme 1) (generated by the *in situ* deprotection of their cyanoethyl derivatives)<sup>8</sup> as key intermediate species in the iterative steps. Compound **1** was deprotected by reaction with CsOH, and the resulting dithiolate reacted *in situ* with glycol derivative **2** to yield compound **3** in 63% yield. Cross-coupling of thione **3** with ketone **4**<sup>8b</sup> in the presence of P(OEt)<sub>3</sub> gave the TTF derivative **5** in 67% yield. Halogen exchange to yield diiodide **6** (NaI, 84% yield) was followed by reaction of **6** with 2 equiv. of the thiolate anion derived from **7**,<sup>8c</sup> to afford tris(TTF) system **8** in 77% yield. In an iterative procedure, the thiolate anion derived from **8** (2 equiv.) reacted with **6** to furnish the heptakis(TTF) dendron wedge **9** in 79% yield. Finally, the thiolate anion derived from **9** (3 equiv.) smoothly displaced the benzylic bromides of the core reagent **10** to furnish the dendrimer **11** possessing 21 TTF units (75% yield) as an air-stable, orange toffee-like solid, which has good solubility in a range of organic solvents (*e.g.* CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF, toluene, dichlorobenzene and CS<sub>2</sub>) and was insoluble in water.<sup>‡</sup>

The solution electrochemistry of **11** in CH<sub>2</sub>Cl<sub>2</sub> was studied using thin layer cyclic voltammetric (TLCV) techniques in which the current is not limited by mass transport to the electrode.<sup>9</sup> Integrating the voltammetric waves against the one-electron reduction peak of the internal standard 2,3-dichloronaphthoquinone (DCNQ) provided clear evidence that

complete oxidation occurs for all the TTF units, thus ultimately generating the 42+ oxidation state of the dendrimer.<sup>§</sup> We note that the second TTF oxidation wave was slightly narrower than the first wave, which was probably due to adsorption phenomena. Fig. 1 shows the TLCV of **11** in the presence of DCNQ.

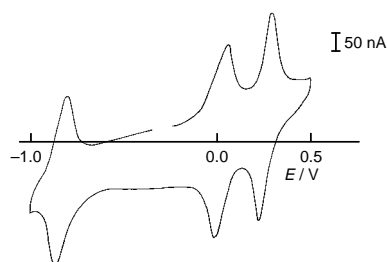


Fig. 1 TLCV of dendrimer **11** ( $0.5 \times 10^{-4}$  M) and DCNQ ( $1.05 \times 10^{-3}$  M) in Bu<sub>4</sub>NClO<sub>4</sub> (1 M)/CH<sub>2</sub>Cl<sub>2</sub> solution, vs. Ag/Ag<sup>+</sup>, scan rate 2 mV s<sup>-1</sup>

The spectroelectrochemistry of dendrimer **11** is shown in Fig. 2. The spectrum obtained at 0 V [Fig. 2(a)] is consistent with neutral TTF units; upon oxidation at 0.7 V, the characteristic absorptions of TTF cation radicals are seen: the new band at  $\lambda_{\text{max}}$  425 nm is assigned to isolated (non-interacting) TTF cation radicals, while the absorption at  $\lambda_{\text{max}}$  800 nm is diagnostic of interacting TTF cation radicals ( $\pi$ - $\pi$  dimers).<sup>10</sup> On increasing the potential [Fig. 2(c)], as oxidation of the system proceeds the higher energy absorption decreases in intensity while there is a concomitant increase in the lower energy absorption, suggesting more of the partially-oxidised TTF units are now dimerised. Even when the spectrum was obtained at the threshold potential for oxidation, both bands were always present, which suggests that the cation radicals interact even when they are present in very low concentration: we therefore assign this to an intradendrimer interaction, achieved due to the flexibility of the glycol spacers. To the best of our knowledge, this is the first observation of  $\pi$ - $\pi$  interactions (either intra- or inter-molecular) in oxidised dendrimers. This is timely in the light of studies of  $\pi$ - $\pi$  stacking at the periphery of functionalised PAMAM dendrimers,<sup>12</sup> and the intermolecular self-association of dendrimers mediated by hydrogen bonding<sup>13</sup> or coordinative bonds.<sup>14</sup>

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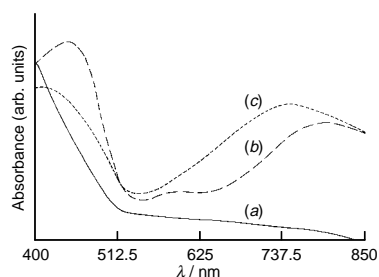
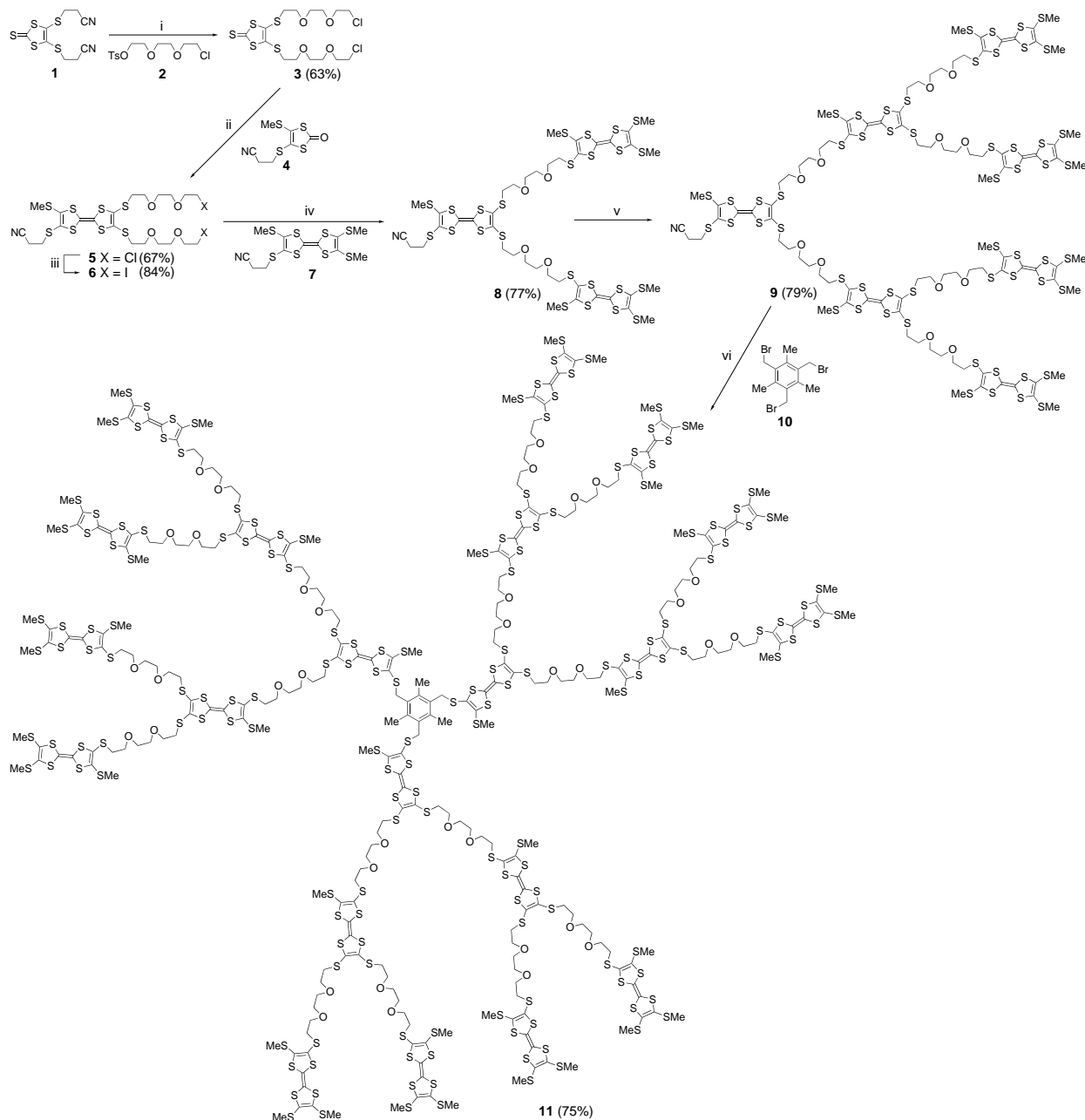


Fig. 2 Spectroelectrochemistry of **11** at (a) 0.0, (b) 0.7 and (c) 1.0 V



**Scheme 1** Reagents and conditions: *i*, **2** (2 equiv.), CsOH·H<sub>2</sub>O, MeCN, reflux, 17 h; *ii*, **4**, P(OEt)<sub>3</sub>, 120 °C, 5 h; *iii*, NaI, acetone, reflux, 3 d; *iv*, **7** (2 equiv.), CsOH·H<sub>2</sub>O, DMF, room temp., 16 h; *v*, **6** (0.5 equiv.), CsOH·H<sub>2</sub>O, DMF, room temp., 16 h; *vi*, **10** (0.33 equiv.), CsOH·H<sub>2</sub>O, DMF, room temp.

## Notes and References

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‡ All new compounds gave satisfactory <sup>1</sup>H NMR spectra, mass spectra (FAB, plasma desorption or MALDI-TOF) and analytical data.

§ Allowing for the very small quantities of compound used and the large number of TTF groups present, we estimate that these data are accurate to within ±2 electrons for each TTF wave of compound **11**. CV data obtained in both CH<sub>2</sub>Cl<sub>2</sub> and MeCN solutions gave two reversible redox waves at *E*<sub>1</sub><sup>1/2</sup> +0.56 and *E*<sub>2</sub><sup>1/2</sup> +0.86 V vs. Ag/AgCl.

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