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Electrochemically controlled interactions between TTF-based dendrimers and an electron-rich oligomer†

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Received (in Cambridge, UK) 7th October 2002, Accepted 1st November 2002
First published as an Advance Article on the web 18th November 2002

Electrochemically controlled interactions have been shown to occur between TTF containing dendrimers 1 and 2 and the electron-rich oligomer 3.

Dendrimers incorporating electro-active units have been the focus of a number of investigations in recent years in endeavours to produce novel systems with interesting supramolecular, advanced materials and biomimetic applications.[1] In particular, the introduction of redox-active units at the periphery or core of dendrimer architectures has proved fertile ground for studying host–guest complexation[2] and the effect of dendrimer shell encapsulation on redox properties.[3] Although a wide variety of redox active units have been incorporated into dendrimer frameworks, systems functionalised with tetrathiafulvalene (TTF)[4] are particularly promising in view of the possibility of exploiting the multi-stage redox states of the TTF moiety (TTF^0, $TTF^{+\cdot}$, TTF^{2+}) as a versatile handle for modulating intermolecular recognition processes. Therefore, it is remarkable that the electrochemically controlled host–guest complexation of TTF based dendrimers has not been more widely explored.[4d] Here, we report the electrochemically controlled interactions between dendrimers **1** and **2**[4f] and the electron rich oligomer **3**[5] (Fig. 1).

The electrochemical properties of dendrimers **1** and **2** were studied using cyclic voltammetry (CV).[6] These studies revealed remarkably simple redox behaviour for both systems. In particular, there was no evidence for shielding of the inner TTF units, as only two oxidation waves were observed, indicating that complete oxidation of all TTF units occurs by applying the appropriate potential ($\mathbf{1}^{9+\cdot}$ and $\mathbf{2}^{21+\cdot}$ were formed at $E^1_{1/2}$ = 0.55 V whilst $\mathbf{1}^{18+}$ and $\mathbf{2}^{42+}$ were formed at $E^2_{1/2}$ = 0.86 V) (Fig. 2).[7] The addition of an excess of oligomer **3** to a solution of dendrimers **1** or **2**, resulted in a small (~ −5 mV) negative shift in the half-wave potential for the radical cationic states of these systems, indicating a slight stabilisation of the $\mathbf{1}^{9+}$and $\mathbf{2}^{21+\cdot}$ species *via* electrochemically generated supramolecular interactions.[8] However, more dramatic changes were apparent for the $\mathbf{1}^{18+}$ and $\mathbf{2}^{42+}$ redox waves upon the addition of oligomer **3**, as a significant decrease in the peak currents (~40%) was observed. This further supports complex formation between the oxidised dendrimers and polymer **3**, indicating interactions between the macromolecular species decrease the diffusion rate of the redox-active dendrimers to the working electrode surface.[9] Furthermore, the slightly larger negative shifts in the half-wave potentials (~ −15 mV) observed for the $\mathbf{1}^{18+}$ and $\mathbf{2}^{42+}$ states following the addition of oligomer **3**, indicate stronger interactions occur than those observed for the $\mathbf{1}^{9+\cdot}$ and $\mathbf{2}^{21+\cdot}$ states. It is noteworthy that similar cyclic voltammetry data have been reported for the electrochemically controlled decomplexation of TTF^{2+} from within the cavity of the electron rich macrocycle 1,5-dinaphtho[38]crown-10.[10] Therefore, by analogy, our data are consistent with the macromolecular complex undergoing a fast, reversible decomplexation when dendrimers $\mathbf{1}^{18+}$ or $\mathbf{2}^{42+}$ are first reduced.[11]

We have also investigated the electrochemically controlled complexation of dendrimers **1** and **2** with 1,4-dimethoxybenzene. Similar negative shifts in the half-wave potentials for the radical cation and fully oxidised states of the dendrimers were obtained to those observed upon the addition of oligomer

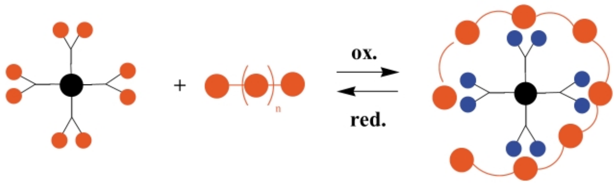

Fig. 1 Schematic representation of the electrochemically controlled complexation between dendrimers **1** and **2** with oligomer **3**.

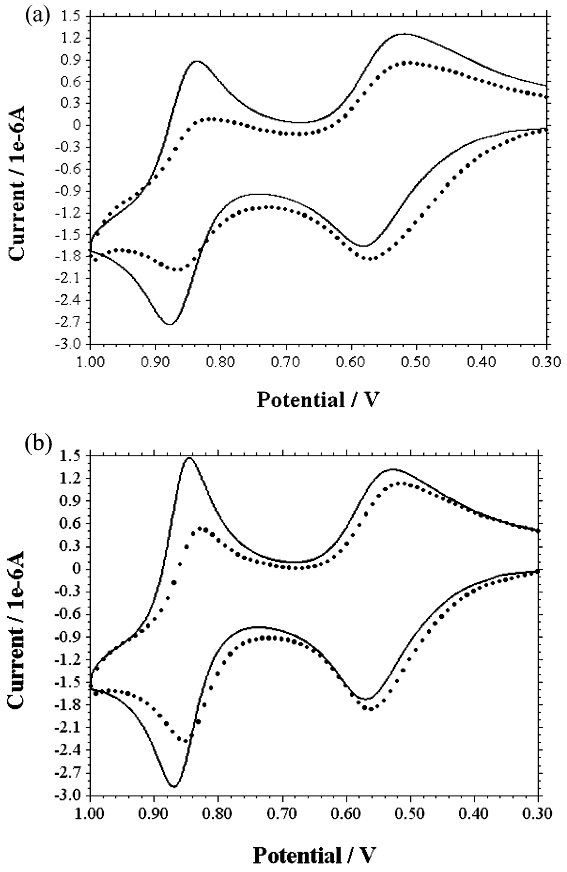

Fig. 2 CV data for (a) dendrimer **1** and (b) **2** (~ 10^{-5} M) recorded in the absence (—) of and in the presence (···) of an excess of oligomer **3** (~ 10^{-3} M).

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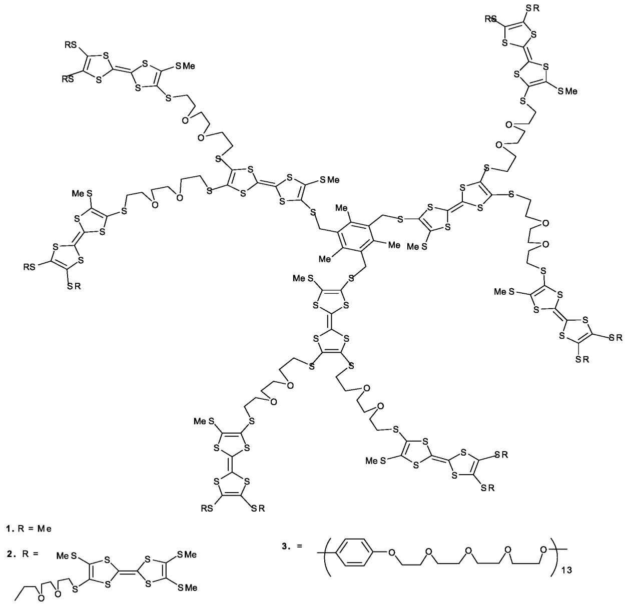
† Electronic supplementary information (ESI) available: CV data for dendrimers **1** and **2**. See http://www.rsc.org/suppdata/cc/b2/b209765f/

DOI: 10.1039/b209765f



3, indicating that electrochemically controlled supramolecular interactions occur. However, a decrease in the peak currents for the $\mathbf{1}^{18+}$ and $\mathbf{2}^{42+}$ states was not observed, indicating the overall change in the effective diffusion coefficient for these systems is smaller than that obtained following the addition of oligomer **3** (see ESI†). This result is expected as strong interactions between dendrimers $\mathbf{1}^{18+}$ and $\mathbf{2}^{42+}$ and 1,4-dimethoxybenzene are entropically unfavourable.

To provide further evidence for the electrochemically controlled interactions between **2** and **3** we have investigated the fluorescence spectroscopy of oligomer **3** in the presence of the neutral and oxidised dendrimer, with the expectation that the electron-deficient $\mathbf{2}^{21+\cdot}$ and $\mathbf{2}^{42+}$ states would quench the emission of the oligomer upon complexation (Fig. 3).[12] Indeed, the fluorescence spectra of oligomer **3** measured in the presence of approximately one equivalent of dendrimer $\mathbf{2}^{21+\cdot}$ or $\mathbf{2}^{42+}$ revealed a significant quenching (~40%) in the emission spectra of the oligomer (Fig. 3).[13] Interestingly, the $\mathbf{2}^{21+\cdot}$ and $\mathbf{2}^{42+}$ species appear to be equally efficient in quenching the oligomer's fluorescence.

In conclusion, we have established that electrochemical oxidation of dendrimers **1** and **2** can trigger supramolecular interactions with 1,4-dimethoxybenzene and its oligomer **3**. Moreover, the electrochemically controlled supramolecules display some degree of reversibility. We are currently exploring the redox controllable architectures formed between related oligomers and dendrimers to provide novel devices and biomimetic systems, and the results of these investigations will be reported in due course.

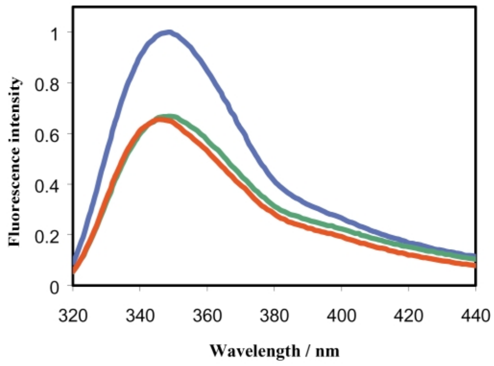


Fig. 3 Fluorescence emission spectra of oligomer **3** (~10^{-5} M) recorded in the presence of **2** (~10^{-5} M) (blue) and electrochemically generated $\mathbf{2}^{21+\cdot}$ (red) and $\mathbf{2}^{42+}$ (green) states, λ_{ex} = 300 nm.

We acknowledge support from the EPSRC (FMAD), The EPSRC National Mass Spectrometry Service Centre, Swansea, and the The Royal Society. We thank Professor A. E. Kaifer for helpful comments relating to the electrochemical characterisation of these systems.

Notes and references

1 For examples of recent reviews of electro-active dendrimers, see: (*a*) M. R. Bryce and W. Devonport, *Advances in Dendritic Macromolecules*, ed. G. R. Newkome, JAI Press, London, 1996, vol. 3, p. 115; (*b*) V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc Chem. Res.*, 1998, **31**, 26; (*c*) D. K. Smith and F. Diederich, *Chem. Eur. J.*, 1998, **4**, 1353; (*d*) A. E. Kaifer and M. Gómez-Kaifer, *Supramolecular Electrochemistry*, Wiley-VCH, Weinheim, 1999, p. 207; (*e*) D. Astruc, J. C. Blais, E. Cloutet, L. Djakovitch, S. Rigaut, J. Ruiz, V. Sartor and C. Valerio, *Dendrimers II, Top. Curr. Chem.*, 2000, **210**, 229; (*f*) A. Juris, *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley-VCH, Weinheim, 2001, vol. 3, p. 655; (*g*) S. Hecht and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2001, **40**, 79; (*h*) S. M. Grayson and J. M. J. Fréchet, *Chem. Rev.*, 2001, **101**, 3819; (*i*) C. B. Gorman and J. C. Smith, *Acc. Chem. Res.*, 2001, **34**, 60.

2 For examples, see: (*a*) R. Castro, I. Cuadrado, B. Alonso, C. M. Casado, M. Morán and A. E. Kaifer, *J. Am. Chem. Soc.*, 1997, **119**, 5760; (*b*) B. González, C. M. Casado, B. Alonso, I. Cuadrado, M. Morán, Y. Wang and A. E. Kaifer, *Chem. Commun.*, 1998, 2569; (*c*) C. M. Cardona, T. M. McCarley and A. E. Kaifer, *J. Org. Chem.*, 2000, **65**, 1857.

3 For examples, see: (*a*) P. J. Dandliker, F. Diederich, M. Gross, C. B. Knobler, A. Louati and E. M. Sanford, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1739; (*b*) R. Toba, J. M. Quintela, C. Peinador, E. Román and A. E. Kaifer, *Chem. Commun.*, 2001, 857; (*c*) D. L. Stone, D. K. Smith and P. T. McGrail, *J. Am. Chem. Soc.*, 2002, **124**, 856.

4 For examples of TTF containing dendrimers, see: (*a*) M. R. Bryce, W. Devonport and A. J. Moore, *Angew. Chem., Int. Ed.*, 1994, **33**, 1761; (*b*) C. Wang, M. R. Bryce, A. S. Batsanov, L. Goldenberg and J. A. K. Howard, *J. Mater. Chem.*, 1997, **7**, 1189; (*c*) W. Devonport, M. R. Bryce, G. J. Marshallsay, A. J. Moore and L. M. Goldenberg, *J. Mater. Chem.*, 1998, **8**, 1361; (*d*) C. A. Christensen, L. M. Goldenberg, M. R. Bryce and J. Becher, *Chem. Commun.*, 1998, 509; (*e*) M. R. Bryce, P. de Miguel and W. Devonport, *Chem. Commun.*, 1998, 2565; (*f*) C. A. Christensen, M. R. Bryce and J. Becher, *Synthesis*, 2000, **12**, 1695; (*g*) F. Le Derf, E. Levillain, G. Trippé, A. Gorgues, M. Sallé, R.-M. Sebastían, A.-M. Caminade and J.-P. Majoral, *Angew. Chem., Int. Ed.*, 2001, **40**, 224.

5 (*a*) G. J. Owen and P. Hodge, *Chem. Commun.*, 1997, 11; (*b*) P. Hodge, P. Monvisade, G. J. Owen, F. Heatley and Y. Pang, *New. J. Chem.*, 2000, **24**, 703.

6 All electrochemical experiments were performed using a CH120A electrochemical workstation. The electrolyte solution was prepared from recrystallised Bu_4NPF_6 using spectroscopic grade dichloromethane and acetonitrile (3 : 1 v/v) (0.1 M) and purged with nitrogen prior to use. A three-electrode configuration was used with a Pt working electrode, a Ag/AgCl reference electrode and a platinum wire as the counter electrode. Scan rate = 100 mV s^{-1}. *T* = 21 °C.

7 Integration of the voltammetric waves against the one-electron oxidation peak of a decamethylferrocene internal standard provided evidence for the formation of the $\mathbf{1}^{9+\cdot}$, $\mathbf{1}^{18+}$, $\mathbf{2}^{21+\cdot}$ and $\mathbf{2}^{42+}$ states.

8 ^{1}H NMR spectroscopy ($CDCl_3/CD_3CN$ 3 : 1) studies revealed negligible interactions between the neutral dendrimers and **3**.

9 A similar decrease in peak current is often observed in the cyclic voltammograms of encapsulated redox-active units. For a review, see: C. M. Cardona, S. Mendoza and A. E. Kaifer, *Chem. Soc. Rev.*, 2000, **29**, 37.

10 For an example of an electrochemically reversible complex formed between the TTF^{2+} and an electron rich macrocycle displaying similar electrochemical data, see: P. R. Ashton, V. Balzani, J. Becher, A. Credi, M. C. T. Fyfe, G. Mattersteig, S. Menzer, M. B. Nielsen, F. M. Raymo, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 3951.

11 Repeated electrochemical cycling (> 10 scans) resulted in a decrease in the peak currents for the radical cationic waves presumably due to the formation of an irreversible tangled aggregate.

12 H. A. de Cremiers, G. Clavier, F. Ilhan, G. Cooke and V. M. Rotello, *Chem. Commun.*, 2001, 2232.

13 Excitation wavelength = 300 nm, 5 nm band pass on both excitation and emission monochromators. Spectra were recorded in a 0.1 M solution of Bu_4NPF_6 in spectroscopic grade dichloromethane and acetonitrile (3 : 1 v/v).