ChemComm
FEATURE ARTICLE

Macromolecular tetrathiafulvalene chemistry

Martin R. Bryce,*† Wayne Devonport, Leonid M. Goldenberg and Changsheng Wang

Department of Chemistry, University of Durham, Durham, UK DH1 3LE

Recent developments in the functionalisation of tetrathiafulvalene (TTF) have enabled TTF units to be covalently linked into macromolecular systems. Convergent syntheses of dendrimers containing TTF units are presented, including a $(TTF)_{13}$ system in which TTF units are emplaced at all layers of the structural hierarchy. Thin layer cyclic voltammetry has established that the redox activity of TTF is retained in these macromolecules: sequential oxidation to the radical cation and dication occurs for all the TTF units, yielding highly-charged species in solution. Macromolecules comprising four and eight TTF units built around a phthalocyanine core are also described. These materials present novel architectures with the key property of multi-electron redox activity.

Tetrathiafulvalene—its molecular properties and functionalisation

Tetrathiafulvalene (TTF)[1,2] is famous as a π-electron donor in the field of organic molecular metals,[3] *e.g.* the complex TTF–TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane),[4] where the delocalised electrons responsible for conduction are derived from intermolecular charge transfer from TTF to the acceptor species. A few derivatives of TTF, notably bis(ethylenedithio)TTF (BEDT-TTF) form superconducting radical cation salts with closed shell anions,[5] *e.g.* the salt κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ which superconducts at temperatures below a T_c value of 11.5 K.[6] BEDT-TTF is also a component of interesting magnetic materials.[7]

In view of the unabated interest during the past 25 years in the molecular chemistry of TTF derivatives,[2,5] it is striking that TTF has rarely been incorporated into polymeric systems.[8] In this context, the key properties of TTF which make it an interesting building block are these: (i) oxidation of the TTF ring system to the radical cation and dication species occurs sequentially and reversibly at a very accessible potential window in a range of organic solvents (for unsubstituted TTF, $E_1^{\frac{1}{2}} = +0.34$ and $E_2^{\frac{1}{2}} = +0.78$ V *vs.* Ag/AgCl in MeCN); (ii) the oxidation potentials can be finely tuned by the attachment of appropriate substituents; (iii) the TTF radical cation is thermodynamically very stable (due to 6π-electron heteroaromaticity of the 1,3-dithiolium cation); (iv) TTF derivatives and their derived cation radicals readily form dimers, highly-ordered stacks, or two-dimensional sheets, which are stabilised by intermolecular π–π interactions and non-bonded sulfur ···sulfur interactions; and (v) TTF is stable to many synthetic transformations, although it is important to avoid strongly acidic conditions and oxidising agents.

Macromolecular aspects of TTF chemistry have been neglected primarily because of the synthetic challenge of obtaining suitably functionalised TTF derivatives in reasonable quantities. This barrier has recently been overcome with major progress in three important branches of synthetic TTF chemistry: (i) TTF can now be readily synthesised in 20 g batches;[9] (ii) methodology involving electrophilic substitution of lithiated TTF has been optimised to afford facile entry into a wide range of mono-substituted derivatives in high yield;[10] and (iii) selective protection/deprotection chemistry of the thiolate groups of the 1,3-dithiole-2-thione-4,5-dithiolate (dmit) system (and derived TTFs) has been developed, primarily by Becher and co-workers,[11] to provide multi-gram quantities of versatile building blocks for highly-functionalised TTF systems, including supramolecular architectures.[12]

Our work breaks new ground in the synthesis and redox properties of monodisperse macromolecules containing multi-TTF functionality, and this short review article will highlight progress in this area. At the outset our aim was to synthesise structurally well-defined multi-electron redox systems, exploiting the known solubility enhancement in highly-branched macromolecules (compared to their linear counterparts). A longer term aim is to combine the properties of TTF, which have been stated above, with the beneficial properties of polymers, such as film formation and processability. It should be noted that from a similar viewpoint other polymeric TTFs have been synthesised.[8] In earlier work, disubstituted TTFs were condensed to form polyamides,[8a] polyesters[8b] and polyurethanes,[8c] some of which were oxidised to radical cation systems. More recently, some well-defined main chain and side chain polymeric TTFs have been obtained,[8d–g] including some electrochemically polymerised systems.[8g]

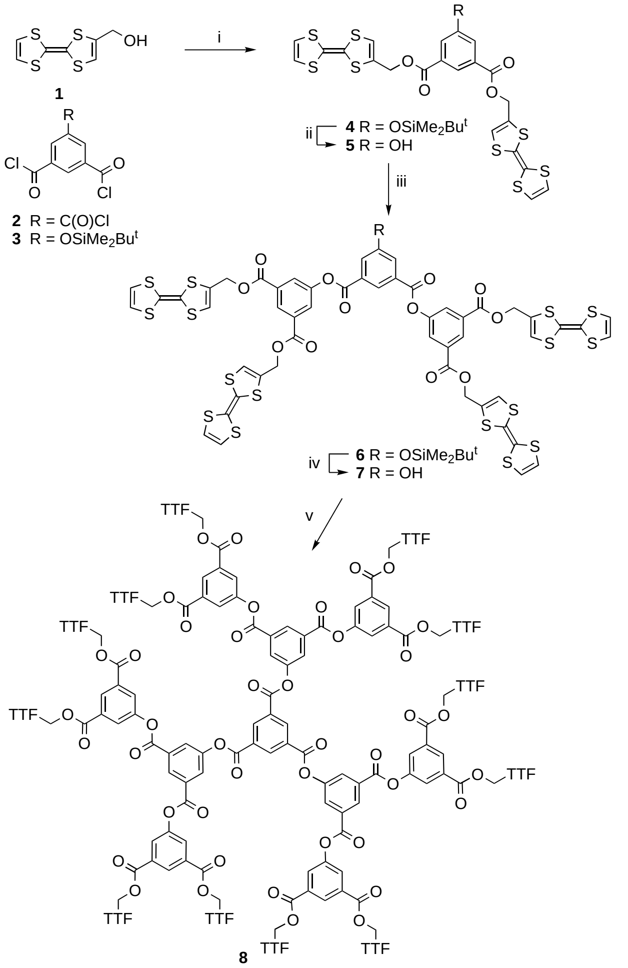
Constructing TTF dendrimers

The study of dendrimers, cascade molecules and related hyperbranched systems is a rapidly-expanding topic in macromolecular science.[13] These materials comprise a multifunctionalised core, from which radiate repeating layers of monomers with a branch occurring at each monomer unit. They possess well-defined, three-dimensional structural order, and their size and architecture is precisely regulated in their synthesis, providing unique molecular frameworks for the disposition of functional groups in predetermined spatial arrangements. Initial research into dendrimers focused on obtaining higher generation systems with large molecular weights, whereas nowadays the emphasis is mainly on systems which incorporate functional groups at the exterior surface of, or embedded within, the dendrimer framework.[14] In the context of functional dendrimers, a variety of redox-active substituents have been built into the structures.[15,16] These materials are relevant to the development of: (i) new electron-transfer catalysts; (ii) studies on the dynamics of electron transport at surfaces and within restricted reaction spaces; (iii) new materials for energy conversion (iv) electronic and photo-optical materials; (v) organic magnets; and (vi) mimics of biological redox processes. The redox groups may behave independently in multi-electron processes (*n* identical non-interacting electroactive centres giving rise to a single *n*-electron wave) or they may interact intra- or inter-molecularly, in which case overlapping or closely-spaced redox waves are observed at different potentials.

Synthesis of arylester TTF dendrimers

In the first phase of our work on multi-TTF macromolecules, we synthesised aryl ester dendrimers functionalised with peripheral TTF groups.[17] 4-(Hydroxymethyl)-TTF **1**, which is readily available in multi-gram quantities,[10a] served as a convenient starting material. A convergent strategy, based on a repetitive coupling/deprotection sequence, furnished dendrimer **8** comprising a 1,3,5-benzene triester core (derived from reagent **2**) and surface-functionalised with 12 TTF units. (In a convergent synthesis,[18] dendrimer construction begins at what will become the surface of the molecule, and progresses inwards *via* a series of dendron wedges of increasing size, several of which are attached to the core unit in the final step.) We used 5-(*tert*-butyldimethylsiloxy)isophthaloyl chloride **3**[19] as the functionalised reagent for the esterification reactions to build up successive generations.

The synthesis of the (TTF)$_{12}$ dendrimer **8** is shown in Scheme 1. The reaction of **1** with reagent **3** gave compound **4** (83% yield), deprotection of which (TBAF in THF at room temperature) afforded the bis(TTF) derivative **5** (85% yield) as a dendron wedge carrying the phenolic group as a reactive handle for further reactions. Following the same procedures that gave compounds **4** and **5**, reaction of 2 equiv. of alcohol **5** with reagent **3** yielded **6** (76% yield) and then (TTF)$_4$ dendron wedge **7** in 95% yield. Compound **7** reacted with the core reagent **2** to give the target dendrimer **8** in 48% yield.



Scheme 1 *Reagents and conditions*: i, NEt$_3$, **3**, CH$_2$Cl$_2$, 20 °C; ii, TBAF, THF, 20 °C; iii, DMAP, **3**, CH$_2$Cl$_2$, 20 °C; iv, TBAF, THF, 20 °C; v, DMAP–PhNMe$_2$, **2**, CH$_2$Cl$_2$, 35 °C

Within this series of macromolecules, stability decreased with increasing generation, so no attempts were made to assemble molecules of higher molecular weight than **8**. Macromolecule **8** is an oil which is readily soluble in polar organic solvents. It is reasonably stable to storage at < 0 °C; however, when stored at room temperature, even in the dark and under an argon atmosphere, it decomposed after a few days. ^{1}H NMR spectroscopy and plasma desorption mass spectra (PDMS) were entirely consistent with structure **8**. The energy-minimised conformation of compound **8** is shown in Fig. 1: it is notable that all the TTF groups are exposed and, therefore, are available to participate in redox processes. (The proviso must be made that the conformation may be very solvent dependent.) The instability of **8** is possibly due to the high density of ester groups in the interior of the molecule.

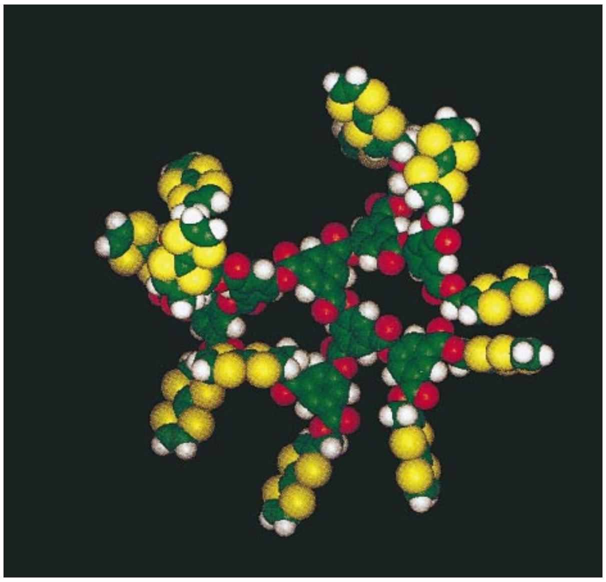


Fig. 1 Energy minimised conformation of **8**. Green = carbon; white = hydrogen; red = oxygen; yellow = sulfur.

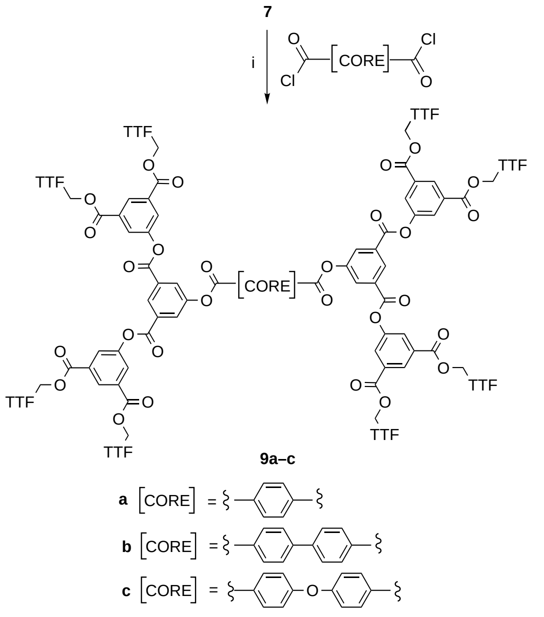
With a view to improving the stability of the (TTF)$_x$ aryl ester dendrimers, we changed from trifunctional to bifunctional core units, to obtain more ‘open’ structures. Thus, using terephthaloyl chloride, biphenyl-4,4′-dicarbonyl dichloride and 4,4′-oxydibenzoyl dichloride as core reagents, the series of (TTF)$_8$ systems **9a–c** was constructed.[17*b*,20] These three compounds were all stable upon storage at room temperature in air and daylight for at least one year. However, the compounds containing the benzene and biphenyl cores, *viz*. **9a** and **9b**, were only sparingly soluble in organic solvents, whereas analogue **9c**, with the more flexible biphenyl ether core unit, showed good solubility in polar organic solvents (*e.g*. acetone and CH$_2$Cl$_2$).

Synthesis of *p*-xylyl TTF dendrimers

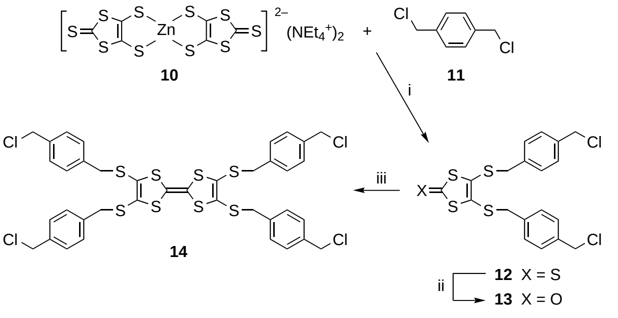
The use of entirely different building blocks afforded a second genre of TTF dendrimers, culminating in the synthesis of the macromolecule **21** comprising thirteen TTF units.[21] The special features of this work are that: (i) TTF units are emplaced at all layers of the structural hierarchy (unlike compounds **8** and **9**); and (ii) compound **14** was introduced as a new, readily-accessible (in multi-gram quantities) building block for TTF chemistry. The synthesis of **14** is shown in Scheme 3.

Zincate salt **10**,[22] which is a well-known precursor to the 1,3-dithiole-4,5-dithiolate dianion,[11*b*] reacted with α,α'-dichloro-*p*-xylene **11** to yield 4,5-disubstituted 1,3-dithiole-2-thione derivative **12** (60% yield) which was converted into the ketone **13** (84% yield) using mercuric acetate. Compound **14** was then synthesised in 78% yield by self-coupling of **13** in the presence of P(OEt)$_3$ under standard conditions,[23] and isolated as orange crystals. Compound **14** is our four-directional core reagent, and displacement of the benzylic chlorines of **14** by thiolate anions proved to be a facile process. For this purpose, we identified **20** as a suitable wedge from which a reactive thiolate anion could be generated, following the protocol developed by Becher *et al*. for related cyanoethyl-protected TTF-thiolate systems.[11]

Compound **16** was prepared in high yield by the literature route from **15**,[11*a*] and converted into ketone **17** (98% yield) using Hg(OAc)$_2$ (Scheme 4). Cross-coupling of equimolar



Scheme 2 *Reagents and conditions*: i, DMAP–PhNMe$_2$, **3**, CH$_2$Cl$_2$, 35 °C



Scheme 3 *Reagents and conditions*: i, acetone reflux; ii, Hg(OAc)$_2$, CHCl$_3$–AcOH, 20 °C; iii, P(OEt)$_3$, 120 °C

amounts of thione **12** and ketone **17**, in the presence of P(OEt)$_3$, gave compound **18** in an optimised yield of 45%. The benzylic chlorides of compound **18** were then displaced by the thiolate derived from compound **19** (prepared by direct analogy with **18**) to afford **20** in 74% yield. The caesium thiolate salt of **20** (4 equiv.) reacted cleanly with compound **14** to furnish the (TTF)$_{13}$ macromolecule **21** in 66% yield, as an air-stable yellow–brown solid, which was soluble in polar organic solvents. Compound **21** was characterised unambiguously by a combination of elemental analysis, MALDI TOF mass spectrometry [which showed the parent ion peak at *m/z* 7377 (M$^+$: calc. for $C_{314}H_{276}S_{104}$ = 7372)] and ^{1}H NMR spectroscopy.

Redox properties of (TTF)$_x$ dendrimers

An important aspect of this work was to evaluate the solution redox properties of these macromolecules, for which we have used a variety of electrochemical techniques, *viz.* cyclic voltammetry (CV) using conventional disc platinum electrodes, CV using platinum ultra-microelectrodes (UME CV), chronoamperometry (CA) and thin layer cyclic voltammetry (TLCV). CV data are collated in Table 1 for a selection of the new compounds, together with TTF and the model TTF phenyl ester derivative **22** for comparison.

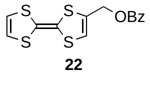


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Table 1 Solution electrochemical data obtained by CV[a]

Compound	Solvent	$E_{1}^{\frac{1}{2}}$/V	$E_{2}^{\frac{1}{2}}$/V
TTF	MeCN–CH$_2$Cl$_2$ (1 : 1)	0.34	0.71
TTF	PhCN	0.34	0.78
5	MeCN–CH$_2$Cl$_2$ (1 : 1)	0.42	0.81
7	MeCN–CH$_2$Cl$_2$ (1 : 1)	0.42	0.81
8	MeCN–CH$_2$Cl$_2$ (1 : 1)	0.43	0.86
9c	MeCN–CH$_2$Cl$_2$ (1 : 1)	0.41	0.83
14	PhCN	0.58	0.92
20	PhCN	0.57	0.90
21	PhCN	0.57	0.90
22	MeCN–CH$_2$Cl$_2$ (1 : 1)	0.41	0.83

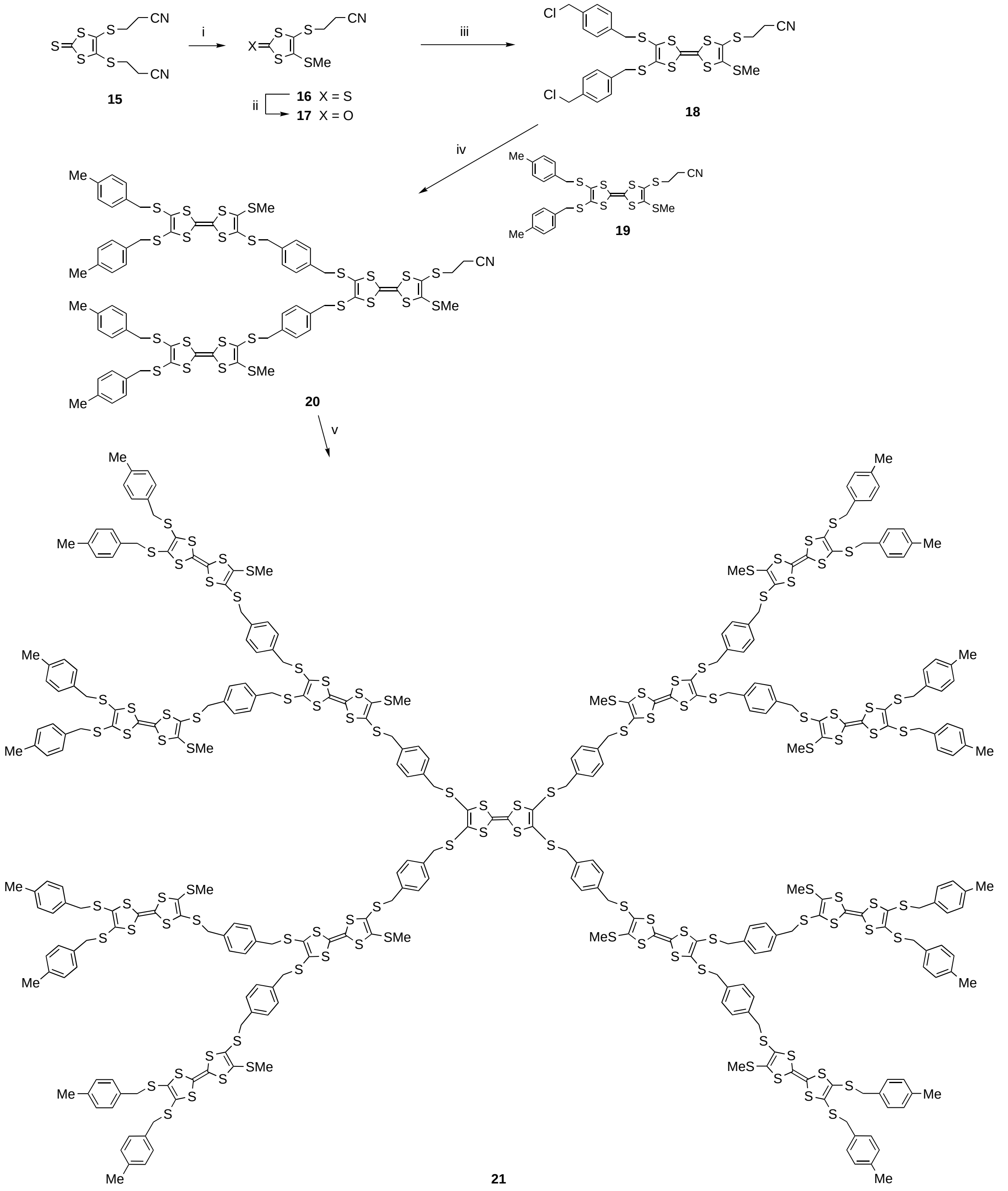
[a] Data were obtained at 20 °C under argon using a platinum working electrode (1.6 mm diameter) and a platinum wire counter electrode, compound (*ca.* 5×10^{-4} M), electrolyte = Bu$_4$N$^+$ PF$_6^-$ (0.1 M); scan rate = 100 mV s^{-1} *vs.* Ag/AgCl.

These experiments established that all the compounds exhibited two redox couples typical of the TTF system (*i.e.* the sequential formation of the TTF radical cation and the dication).[24] The direct attachment of an ester substituent to TTF (*i.e.* TTF-CO$_2$R) is known to raise both the first and second oxidation potentials:[10c,25] surprisingly, a quantitatively similar effect is observed for compound **22**. This substituent effect accounts for the increased oxidation potentials of multi-TTF systems **5**, **7**, **8** and **9c**, compared to TTF. The attachment of alkylsulfanyl substituents to TTF also raises the oxidation potential[24] (an additive effect has been noted for one, two and four alkylsulfanyl substituents)[26] and this gives rise to the consistent anodic shift in the values of E_1 and E_2 for compounds **14**, **20**, **21**, in which each TTF unit contains four alkylsulfanyl groups, relative to TTF under the same conditions. For the *p*-xylyl TTF systems **14**, **20** and **21**, the redox waves were reversible. Within the aryl ester series, reversibility was observed only with the mono- and bis-(TTF) derivatives **22** and **5**, respectively: for the higher oligomers **7**, **8** and **9c**, slightly increased peak separations at higher scan rates were observed, consistent with quasi-reversible behaviour.

A general trend with our aryl ester TTF macromolecules is that as the number of TTF units increases, the first redox wave broadens slightly and the second wave sharpens.[17b] Similar behaviour has been reported previously for TTF amides immobilised on RuO$_2$ or PtO$_2$ surfaces,[27] and the data can be explained by adsorption or precipitation on the electrode surface. The CV and UME CV of (TTF)$_{12}$ system **8**, which are representative, are shown in Figs. 2(*a*) and (*b*), respectively.

The electrochemistry of the stable macromolecules **9c** and **21** has been studied using TLCV techniques.[28] In contrast to conventional CV, in TLCV the current is not limited by the mass transport to the electrode. Integrating the voltammetric waves against the one-electron reduction peak of the internal standard 2,3-dichloronaphthoquinone (DCNQ) provides convincing evidence that complete oxidation occurs for all the TTF units in these compounds. We note that the second TTF oxidation wave is slightly narrower than the first wave, which could be due to adsorption phenomena. Fig. 2(*c*) shows the TLCV of compound **9c** in the presence of DCNQ. We have established that TLCV is the most reliable method for assessing the extent of oxidation of multi-TTF derivatives in solution.[17b,21] These macromolecules provide some of the first all-organic dendritic poly(radical cations) and poly(dications). Almost all other workers in the field decided to include metal centres as redox active species,[15] although naphthalene diimides have been attached to PAMAM dendrimers to form poly(radical anions),[29] and interior anthraquinone units have been studied.[30]

We have also studied the chemical oxidation of the stable (TTF)$_8$ macromolecule **9c**.[17b] UV–VIS Spectroscopy is a convenient method for monitoring the formation of TTF radical



Scheme 4 *Reagents and conditions*: i, CsOH.H_2O (1 equiv.), DMF–MeOH, 20 °C, followed by MeI; ii, $Hg(OAc)_2$, $CHCl_3$–AcOH, 20 °C; iii, **12**, $P(OEt)_3$, 125 °C; iv, **19**, CsOH·H_2O (1 equiv.), DMF–MeOH, then **18**, 20 °C; v, CsOH·H_2O, DMF–MeOH, then **14**, 20–80 °C

cations, which have a characteristic absorption band at λ_{max} 580 nm for unsubstituted TTF.[31] As mentioned earlier, oxidised TTF units can form dimers or stacks, and they display lower energy absorptions, *e.g.* 830 nm for $(TTF^{+\cdot})_2$ dimers.[31b] The UV–VIS spectrum for **9c** in CH_2Cl_2 showed significant changes upon addition of I_2 to the solution: new broad absorption bands appeared at λ_{max} 525 and 830 nm. The higher energy band is consistent with the formation of isolated (non-interacting) TTF radical cations, while the lower energy band suggests the existence of interacting dimers. Dilution studies established that the absorption coefficient of the latter band decreased with increasing dilution; it is, therefore, assigned to an intermolecular dimer band. These data provide evidence that the oxidised macromolecules self-associate in solution, by virtue of intermolecular interactions of their peripheral TTF radical cations. The relatively rigid and short aryl ester branching units in **9c** presumably disfavour intramolecular dimerisation.[32] Intermolecular self-association of dendrimers by hydrogen-bonding[33] or coordinative bonds[34] has also been reported recently.

A phthalocyanine core with pendant multi-TTF functionality

Prompted by our increasing knowledge of the synthesis and redox properties of TTF dendrimers possessing aryl ester and TTF cores, reported above, we have investigated closely related macromolecules with core units of increased complexity, *e.g.*

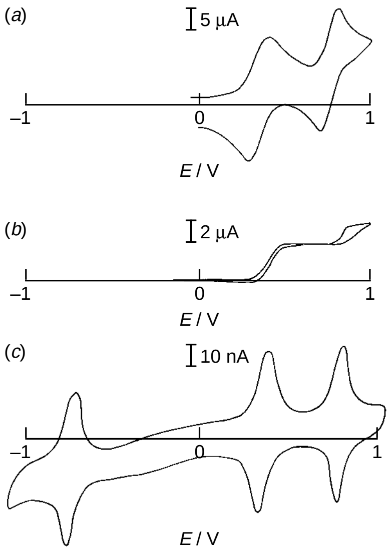


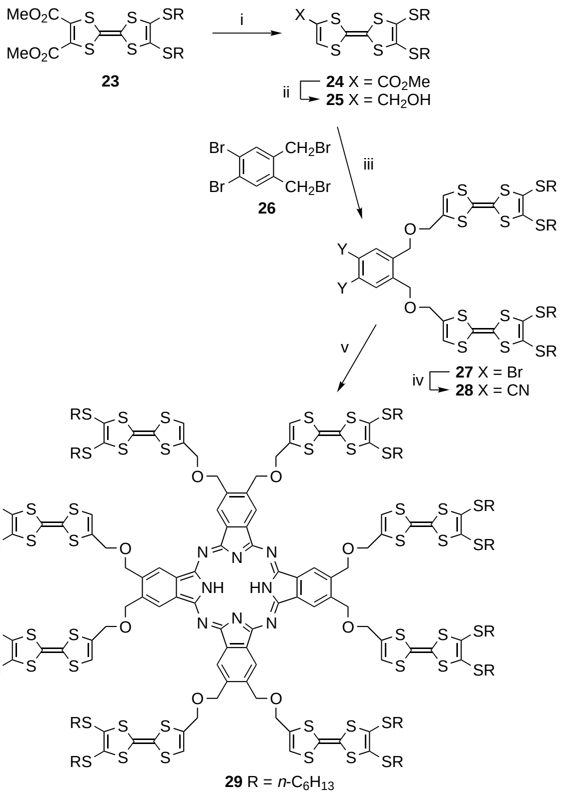
Fig. 2 Solution electrochemistry: (*a*) CV of **8** (solvent = MeCN, electrolyte = $Bu_4N^+PF_6^-$, Pt electrode, *vs.* Ag/AgCl, scan rate = 100 mV s^{-1}); (*b*) UME CV of **8** [solvent = MeCN–CH_2Cl_2 (1 : 1 v/v) electrolyte = $Bu_4N^+PF_6^-$, Pt electrode, *vs.* Ag/AgCl, scan rate = 20 mV s^{-1}]; (*c*) TLCV of **9c** (0.5×10^{-4} M) and 2,3-dichloronaphthoquinone (4.0×10^{-4} M) as internal reference (which gives rise to the wave at negative potential) in 1 M $Bu_4N^+PF_6^-$, solvent = CH_2Cl_2, *vs.* Ag/Ag$^+$, scan rate = 10 mV s^{-1}

phthalocyanines. It is envisaged that combining the versatile electrochemical, optical and coordination properties of phthalocyanines,[35] with the redox properties of pendant multi-TTF functionality should provide novel optoelectronic materials. In the longer term, the tendency of both phthalocyanines and TTFs to self-assemble by face-to-face π–π stacking, and the potential for coordinatively linking metallophthalocyanines to form stable polymers, might be harnessed to afford nanometer-sized molecular wires and cables, which could be electronically and/ or ionically conducting.[36]

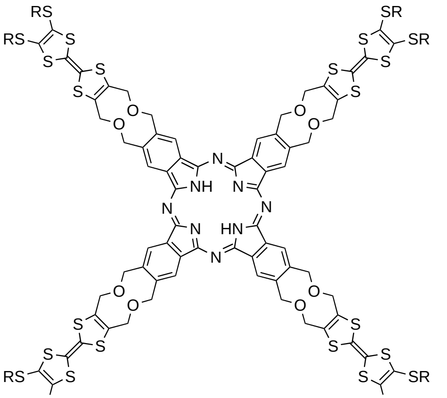
Synthesis of prototype Pc-(TTF)$_8$ and Pc-(TTF)$_4$ systems

The simplest methodology to symmetrically substituted phthalocyanines involves tetramerisation of a phthalonitrile precursor.[37] We, therefore, targeted compound **28**, with peripheral hexylsulfanyl substituents to impart solubility.[38] The synthesis is shown in Scheme 5.[39] TTF derivative **23** was obtained in 63% yield from readily available 1,3-dithiole half-units by cross-coupling methodology. One of the ester substituents on **23** was removed by treatment with LiBr in HMPA at 80 °C,[40] to afford monoester derivative **24** (88% yield) which was reduced with DIBAL-H to yield the alcohol derivative **25** (86% yield). The alkoxide ion of **25** (2 equiv.) reacted with 2,3-dibromo-4,5-di(bromomethyl)benzene **26** to yield the bis(TTF) system **27** (64% yield) which upon reaction with CuCN in DMF at 140 °C produced phthalonitrile derivative **28** (28% yield), this being the most problematical step in the whole Scheme. Tetramerisation of **28** to furnish the Pc-(TTF)$_8$ derivative **29** (56% yield) was achieved upon reaction with lithium pentanolate in pentanol at 125 °C. Analogous chemistry gave the Pc-(TTF)$_4$ system **30**.[39]

Compounds **29** and **30** were both isolated as dark green solids, which were soluble in a range of organic solvents (*e.g.* $CHCl_3$, CS_2, CH_2Cl_2 and toluene) but insoluble in alcohols, MeCN and DMF. Spectroscopic data, elemental analysis and MALDI TOF mass spectra were entirely consistent with the proposed structures.



Scheme 5 *Reagents and conditions*: i, LiBr, HMPA, 80 °C; ii, DIBAL-H, THF, −78 to 20 °C; iii, NaH, THF, 40 °C, then **26**, 20 °C; iv, CuCN, DMF, 140 °C; v, lithium pentanolate, pentanol, 125 °C



30 R = *n*-C_6H_{13}

Spectroscopic and electrochemical studies

Evidence for supramolecular aggregation of **29** and **30** was obtained from ^1H NMR and UV–VIS spectroscopic studies.[39] The ^1H NMR spectra of **29** and **30** at 20 °C in $CDCl_3$ gave broad signals with no fine structure: ^{13}C NMR spectra were obtained at 50 °C in $CDCl_3$ and the signals for compound **29** were much sharper than those for compound **30**, suggesting that the latter compound is more aggregated in this solvent at the relatively high concentration of the NMR sample. No ESR signals were observed for either compound, suggesting that the broad NMR spectra were not due to radical impurities.

UV–VIS spectra of compounds **29** and **30** dissolved in a mixture of toluene and pyridine (99 : 1 v/v) at 20 °C are shown in Fig. 3. The split Q-band, which is characteristic of a metal-free phthalocyanine, is observed at λ_{max} 665 and 700 nm (for compound **29**) and at λ_{max} 674 and 709 nm (for compound **30**). The additional broader hypsochromically-shifted band at λ_{max} 636 (for **29**) and 648 (for **30**) is indicative of aggregated species.[36a]

The luminescence emission from compounds **29** and **30** was found to be of very low intensity and fell in the same spectral region as that of unsubstituted metal-free phthalocyanines.

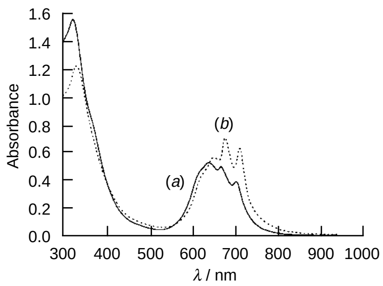


Fig. 3 UV–VIS spectra of (*a*) **29** (1.18×10^{-5} M) and (*b*) **30** (1.44×10^{-5} M) in toluene–pyridine (99 : 1 v/v)

Fluorescence quantum yields were $< 10^{-4}$ and $1.7 \pm 0.3 \times 10^{-4}$ for **29** and **30**, respectively. These values are very much lower than that obtained for a metal-free Pc lacking the TTF moieties, *cf.* Bu_4PcH_2 (Φ = 0.50). We demonstrated that the fluorescence from Bu_4PcH_2 is efficiently quenched by the addition of TTF to the solution: in toluene the rate constant for this process was found to be diffusion controlled, $k_Q(1.1 \pm 0.1) \times 10^{10}$ $dm^3\ mol^{-1}\ s^{-1}$. Quenching in the tethered compounds **29** and **30** is, therefore, ascribed to rapid intramolecular electron transfer between the excited singlet state of the Pc core and a peripheral (neutral) TTF acting as an electron donor group. It will be interesting to explore if the fluorescence can be switched on when the TTF units are oxidised.

Solvent-dependent CV data were obtained for systems **29** and **30**. In PhCN, compound **29** exhibits the expected two TTF redox waves at $E_1^{\frac{1}{2}}$ +0.50 and $E_2^{\frac{1}{2}}$ +0.87 V (*vs.* Ag/AgCl) together with a third irreversible oxidation peak at +1.18 V (the corresponding reduction is not seen on the reverse sweep), and on the cathodic sweep a reduction peak is observed at $E^{\frac{1}{2}}$ −0.51 V. Based on literature precedents,[41] we assign these additional redox waves to a single-electron oxidation and reduction, respectively, of the phthalocyanine core unit. The electrochemistry of **30** was qualitatively similar to **29**, although the redox waves of the Pc unit were more discernable in CH_2Cl_2 than in PhCN, and they are clearly seen in the differential pulse voltammogram (DPV). The CV and DPV for **30** in CH_2Cl_2 are shown in Figs. 4(*a*) and (*b*), respectively.

Based on the CV peak current for compounds **29** and **30**, we suggest that all the TTF units are oxidised, although for compound **29** especially, the second TTF wave was less intense than the first wave. The solvent dependency of the electrochemistry and the UV–VIS spectra of these compounds suggests that the conformation and/or extent of aggregation vary considerably with the solvent. We have obtained qualitatively similar data for a pyrazinoporphyrazine system with eight appended TTF groups.[42]

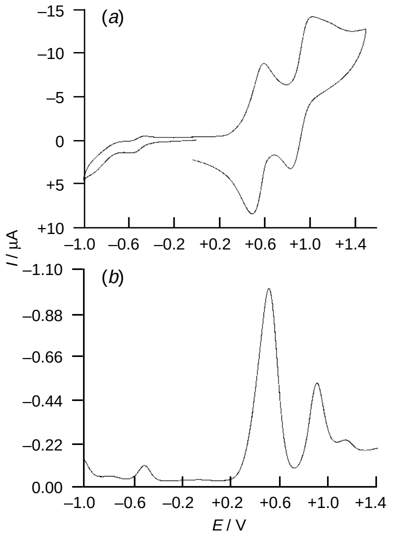


Fig. 4 (*a*) Cyclic voltammogram of **30** in CH_2Cl_2. Pt disc working electrode, 1.6 mm diameter; Pt wire counter electrode, *vs.* Ag/AgCl. Supporting electrolyte = 0.1 M $Bu_4N^+PF_6^-$; scan rate = 100 mV s^{-1}. (*b*) Differential pulse voltammogram of **30** in CH_2Cl_2: sample width = 8 ms; pulse amplitude = 50 mV; pulse width = 10 ms; pulse period = 200 ms; electrodes as Fig. 4(*a*).

Conclusions and future prospects

It is intended that this article will reinforce the fact that TTF is an interesting building block for covalent attachment into a variety of macromolecular assemblies. The synthesis of these multi-TTF systems would have been virtually impossible prior to the recent developments in synthetic methodology which have made available the functionalised TTF starting materials in multi-gram quantities. The materials described herein are tractable and amenable to unambiguous characterisation by standard spectroscopic, mass spectrometric and analytical techniques: they also possess aesthetically pleasing structures. If insolubility of the TTF system is a problem, this can be readily overcome by attachment of alkylsulfanyl chains (*e.g.* compound **29**). This substitution slightly raises the oxidation potential, which for our compounds generally has the added benefit of increased stability to acids and oxidising agents.

These materials present novel macromolecular architectures, with controlled emplacement of TTF groups, and our attention has focused on establishing their multi-electron redox activity. This work paves the way for combining the unique properties of the TTF molecule, which have fascinated scientists in the field of molecular solid state chemistry for over 25 years, with the beneficial properties of polymers, such as film formation and processability, to provide new optoelectronic materials.

Our results suggest interesting targets for future synthetic studies. Unsymmetrical systems, *i.e.* macromolecules constructed by the attachment of different wedges to the core units, are unexplored: in particular, combinations of different substituted TTF units with a strong gradient of redox properties, or π-donor and π-acceptor wedges within the same dendrimer structure, could lead to vectoral electron transport. The study of intra- and inter-dendrimer π–π stacking interactions of oxidised TTF units also promises to be a fruitful line of research.

We thank the EPSRC for funding (W. D. and C. W.) and the Royal Society for financial support (L. M. G.).

Martin Bryce was born in Sutton Coldfield, UK in 1953. He obtained a BSc from Wolverhampton Polytechnic and a DPhil from York University, under the supervision of Drs P. Hansen and J. M. Vernon. He was a postdoctoral fellow with Professor L. Weiler (University of British Columbia) and Professor R. W. Alder (University of Bristol). He was appointed as a Senior Demonstrator at Durham University in 1981, and subsequently as a Lecturer, Senior Lecturer, Reader and Professor of Chemistry (in 1995). In 1988 he was a Visiting Scientist at the Univesity of California, Santa Barbara, working in Professor Wudl's group. He has received the Bader Award and the Interdisciplinary Award from the Royal Society of Chemistry, and a Nuffield Foundation Research Fellowship. His research interests embrace the synthesis of new organic materials with unconventional electrical, optical and magnetic properties, supramolecular chemistry and new synthetic methodology.

Wayne Devonport was born in Barnsley, UK in 1970. He obtained his BSc from Bradford University, and a PhD from Durham University for work on the synthesis of TTF dendrimers. He then held a postdoctoral post at IBM, San Jose, and is currently employed as a research chemist at the Cabot Corporation, near Boston, USA. His research interests focus on well-defined surface modifications by organic and polymeric substrates.

Leonid Goldenberg was born in Zaporozh'e, Ukraine in 1957. He obtained his PhD for work on TTF salts at the Institute of

Chemical Physics of the USSR Academy of Sciences in Chernogolovka, where he is currently a Senior Research Fellow. He has recently been a visiting scientist at Durham University, working on organic thin films and the electrochemistry of charge-transfer materials.

Changsheng Wang was born in Hebei, China in 1963. He obtained his PhD for work on heterocyclic synthesis at Nankai University, China. He joined the faculty of Tsinghua University in 1988 and is currently working at Durham University with Professor Bryce on dendrimer and polymer synthesis.

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† E-mail: m.r.bryce@durham.ac.uk

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