

Functionalised tetrathiafulvalenes: new applications as versatile π -electron systems in materials chemistry

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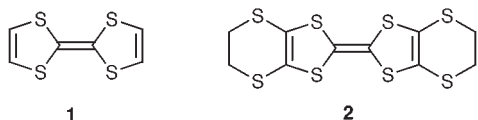
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Not only a component of molecular conductors! Tetrathiafulvalene (TTF) and its derivatives are versatile building blocks in many areas of materials chemistry. This article reviews the current role of substituted TTFs in cation sensors, liquid crystals, intramolecular charge-transfer and nonlinear optical materials, supramolecular switches and devices, and redox polymers (main-chain, side-chain and dendritic systems).

1 Historical perspective

The TTF molecule **1** is synonymous with the development of molecular organic metals,² the study of which was initiated in the early 1970s with the first observations of high electrical conductivity in a chloride salt of TTF,³ and metallic behaviour in the celebrated charge transfer (CT) complex TTF–TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane).⁴ Until recently, the reason for synthesising new TTF derivatives⁵ was almost invariably to obtain conducting and superconducting radical ion salts.⁶ In this respect bis(ethylenedithio)TTF (BEDT-TTF) **2** has emerged as the undisputed champion: all the TTF-based superconductors with $T_c > 10$ K are BEDT-TTF salts.⁷



The challenges of synthesising many TTF derivatives (especially unsymmetrical ones) in reasonable quantities hindered the development of TTF as a building block in the wider context of materials chemistry. This situation has changed recently with significant advances in synthetic TTF chemistry: (i) TTF itself is now available in 20 g batches from cheap starting materials;⁸ (ii) a lithiation/electrophilic substitution protocol provides substituted derivatives of TTF in high yields;⁹ (iii) selective protection/deprotection reactions of thiolate groups attached to the 1,3-dithiole-2-thione-4,5-dithiolate (dmit) system, and derived TTFs, readily yield multi-gram quantities of TTF building blocks;¹⁰ the thioalkyl substituents which this chemistry inevitably provides, slightly raise the oxidation potentials of the TTF system, but this is not a drawback for most purposes.

The unique combination of properties which make TTF such an interesting and versatile component of new materials have been stated recently.¹¹ To summarise, they are these:

(i) oxidation of the TTF ring system to the cation radical and dication species occurs sequentially and reversibly within a very accessible potential window (for unsubstituted TTF, $E_1^{1/2} = +0.34$ and $E_2^{1/2} = +0.78$ V, vs. Ag/AgCl in acetonitrile);

(ii) the oxidation potentials can be finely tuned by the attachment of electron-donating or electron-withdrawing substituents;

(iii) the TTF cation radical is thermodynamically very stable (due to a contribution from 6π -electron heteroaromaticity of the 1,3-dithiolium cation);

(iv) the UV–vis absorption spectra of TTF⁰, TTF^{+·} and TTF²⁺ are decisively different from one another: (only TTF²⁺ displays a fluorescence band, whereas TTF⁰ and TTF^{+·} do not exhibit any luminescence at all);

(v) TTF derivatives readily form dimers, highly-ordered stacks, or two-dimensional sheets, which are stabilised by intermolecular π – π interactions and non-bonded sulfur \cdots sulfur interactions;

(vi) TTF is stable to many synthetic transformations, although it is important to avoid strongly acidic conditions and strong oxidising agents.

It should also be mentioned that TTF is conformationally very flexible, with folding of the dithiole rings allowing its incorporation into strained cyclophane structures.¹² While these compounds have very interesting architectures and topologies, with increasing deformation of the fulvalenoid system π -conjugation is disrupted and the key property of reversible redox behaviour is lost.

This article focuses on new directions for TTF-based materials with the intention of demonstrating the widespread versatility and potential of TTF as a π -rich redox-active building block. Selected recent papers from a number of topics will be highlighted. Molecular conductors and magnets are excluded from this review as those areas have recently been covered comprehensively.⁶

2 Cation sensors, including self-assembled monolayers

This was one of the first topics, outside the arena of molecular metals, where functionalised TTFs were exploited. Macrocyclic ligands¹³ for which complexation of a neutral or ionic guest induces a change in the optical¹⁴ or redox¹⁵ properties of the system continue to attract great attention. Effective control and monitoring of host–guest binding is relevant to the development of ‘smart’ nanoscale sensors and molecular devices, while also addressing fundamental issues concerned with intermolecular recognition. Crown-annulated TTFs were first synthesised by Otsubo and Ogura¹⁶ and their metal-binding characteristics were explored by Becher *et al.*¹⁷ The presence of a metal cation within the crown cavity imposes an inductive effect on the polarisable TTF system resulting in a positive shift of the first oxidation potential as indicated by cyclic voltammetry (CV) experiments. For example, for compound **3** a shift of $E_1^{1/2} = 80$ mV for Na⁺ complexation within the S₂O₄ crowns has been observed in acetonitrile solution.^{17a} The second oxidation potential of the TTF is essentially unchanged and acts as a convenient internal reference. This is consistent with the expulsion of M⁺ after the first oxidation process. Cation binding in **3** has also been monitored by UV–vis spectroscopy.¹⁸ Fig. 1 shows that complexation of Ag⁺, Na⁺

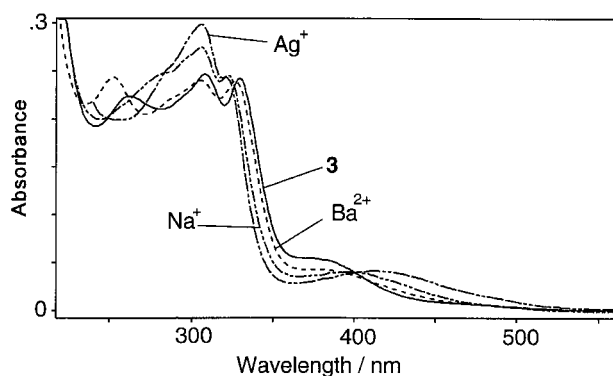


Fig. 1 Absorption spectra of compound **3** (2×10^{-5} M) in acetonitrile, and in the presence of $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (2.1×10^{-2} M), NaClO_4 (0.29 M) and $\text{Ba}(\text{ClO}_4)_2$ (0.7 M). Reprinted with permission from *J. Chem. Soc., Perkin Trans. 2*, 1996, 1587. Copyright (1996) by the Royal Society of Chemistry.

and Ba^{2+} results in a specific change in the electronic absorption spectrum of the TTF chromophore: the spectra of non-complexed and fully-complexed forms are shown.

Sallé *et al.* recently reported that the (*Z*) isomer of ligand **4** acts as a very selective Ag^+ sensor as monitored by CV and ^1H NMR titration experiments.¹⁹ The NMR data (a plateau in the shift of the signals from the CH_2S protons of the polythioether bridge after addition of 0.6 equivalents of AgCF_3SO_3) clearly suggest that a 1 : 1 complex is formed with the (*Z*) isomer only, which is the major isomer of compound **4** [the (*Z*)/(*E*) ratio is 60 : 40] (Fig. 2). A small positive shift in the E_1^{ox} value of **4** is also observed.

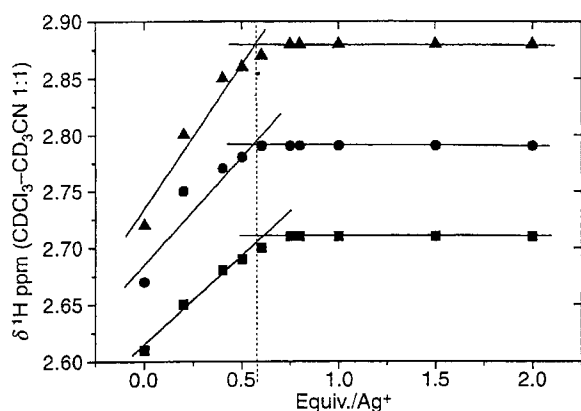
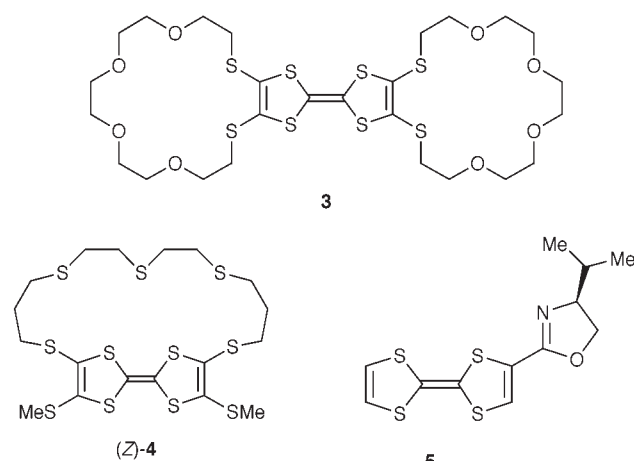
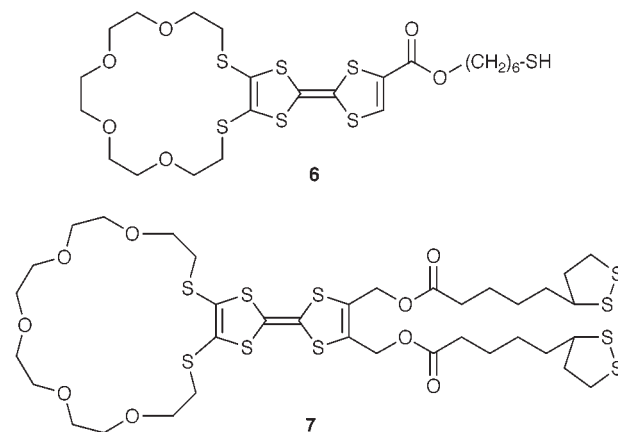


Fig. 2 ^1H NMR titration curve of the perturbation of the CH_2S protons of the polythioether bridge in (*Z*)-**4** upon addition of Ag^+ . Reprinted with permission from *Chem. Commun.*, 1999, 1417. Copyright (1999) by the Royal Society of Chemistry.

While these voltammetric and spectroscopic effects of metal binding with compounds **3**, **4** and analogues are small, they are highly reproducible and quantitative. For TTF derivatives to be practically useful as voltammetric sensors (in solution or thin films) larger potential shifts at low concentration of analyte are needed. For the chiral oxazoline derivative **5** the binding of palladium is believed to involve the nitrogen and a sulfur atom (*i.e.* a sulfur directly at the redox site, not in a peripheral macrocycle).²⁰ The shift in $E_1^{1/2}$ is, however, not significantly enhanced by this: it reaches a maximum $\Delta E = 70$ mV in the presence of 30 equivalents of $\text{Pd}(\text{OAc})_2$ ($E_2^{1/2}$ is essentially unchanged). Compound **5** has been used as a catalyst in asymmetric synthesis.²⁰

Self-assembled monolayers (SAMs) represent an attractive method for device fabrication, having the advantage of straightforward preparation and good stability.²¹ For SAMs of **6** adsorbed on platinum we observed the typical two-wave response of the TTF system.²² If the potential scanned was limited to the first wave (neutral/radical cation) the CV response was recorded for at least 1000 cycles, demonstrating remarkable stability of the SAM under those oxidative conditions. However, the electroactivity gradually decreased when the potential was scanned beyond the first oxidation.²³ Electrochemical recognition of metal cations by SAMs of **6** was clearly demonstrated with positive potential shifts upon metal binding, similar to those observed in solution, *e.g.* $\Delta E_1^{1/2}$ for Li^+ and $\text{K}^+ = 10\text{--}20$ mV; for Na^+ and $\text{Ba}^{2+} = 45\text{--}55$ mV and for $\text{Ag}^+ = 75\text{--}80$ mV.

New TTF SAMs have subsequently been reported by other workers.^{24,25} Notably, Echegoyen *et al.* reported cation recognition using very stable SAMs of compound **7** on gold.²⁵ The largest potential shifts were observed with Na^+ , *viz.* 60 and 55 mV for $E_1^{1/2}$, $E_2^{1/2}$, respectively (Fig. 3). The shift of $E_2^{1/2}$ (not observed with compounds **3–6**) was explained by surface aggregation or cooperativity effects between neighbouring crowns in the SAM.



3 Liquid crystalline derivatives

The propensity of TTF to form stacked structures and to transport charge makes it an attractive component of new mesogens relevant to liquid crystal (LD) display technologies.²⁶ TTF derivatives possessing LC properties²⁷ have recently been reported by three research groups. Cook *et al.* described compounds with one or two TTF substituent(s) attached to the discotic LC phthalocyanine core, *e.g.* compound **8**.²⁸ UV-vis absorption spectra suggested enhanced aggregation of the Pc ring system in **8**, compared to the parent Pc (lower intensity Q bands and increased absorption to the blue.) Polarised light microscopy and DSC data showed that **8** exhibits a mesophase between 73–97 °C, tentatively assigned as D_{hd} . UV-vis spectra of spin-coated films of **8** established that the supramolecular architecture can be changed by oxidation with iodine vapour

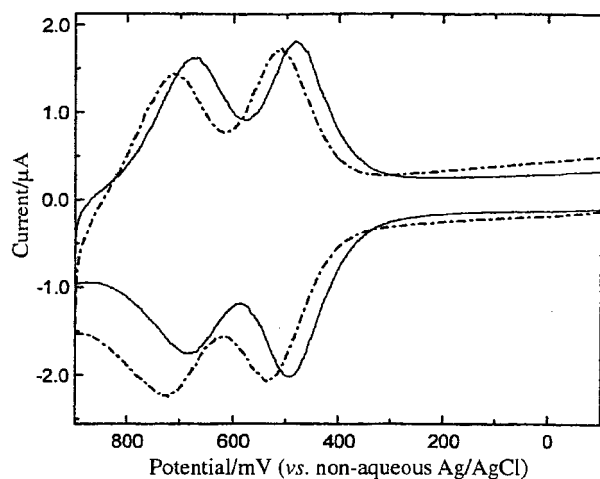


Fig. 3 CV of the SAM of compound **7** on gold in THF solution containing 0.1 M Bu_4NPF_6 in the absence (solid line) and presence (dashed line) of NaPF_6 (5.0 mM) at a scan rate of 400 mV s^{-1} . The potentials are vs. a non-aqueous Ag/AgCl reference electrode. Reprinted with permission from *Chem. Commun.*, 1999, 1493. Copyright (1999) by the Royal Society of Chemistry.

and heating to within the mesophase region. The attachment of two TTF units suppressed mesophase behaviour. A related symmetrical $\text{Pc}(\text{TTF})_8$ assembly with a different spacer group between the Pc core and TTF units did not exhibit LC properties.²⁹

Garín, Gorgues and coworkers attached mesogenic cyanobiphenyl units to the periphery of TTF through flexible spacers.³⁰ Compound **9** exhibits a nematic and smectic A phase. A schematic drawing of the proposed arrangement of **9** in the smectic A phase is shown in Fig. 4. An electrically-insulating charge-transfer salt (stoichiometry $9^{+} \cdot \text{I}_5^{-}$) has a nematic mesophase below 84°C .

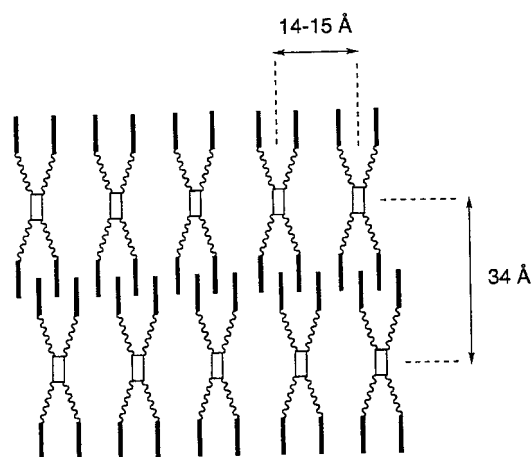
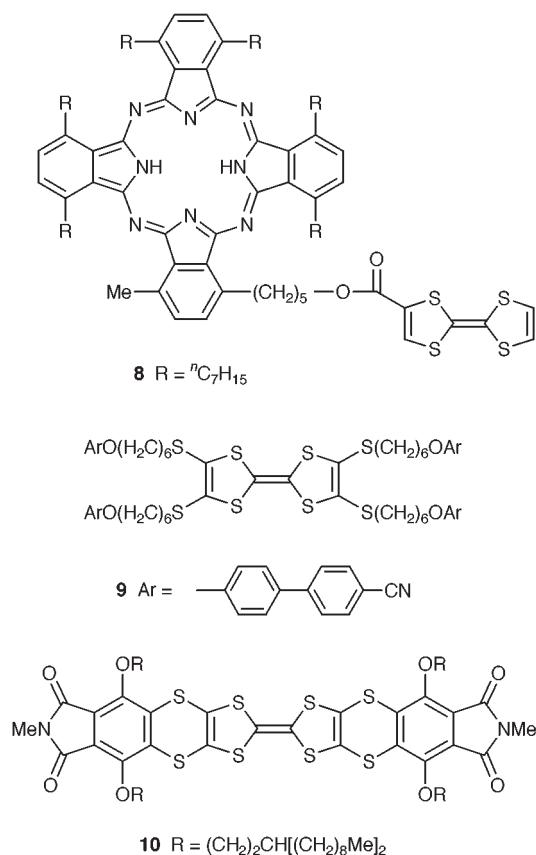


Fig. 4 Schematic drawing of the proposed arrangement of the smectic A mesophase of compound **9**. Reprinted with permission from *J. Mater. Chem.*, 1998, **8**, 881. Copyright (1998) by the Royal Society of Chemistry.

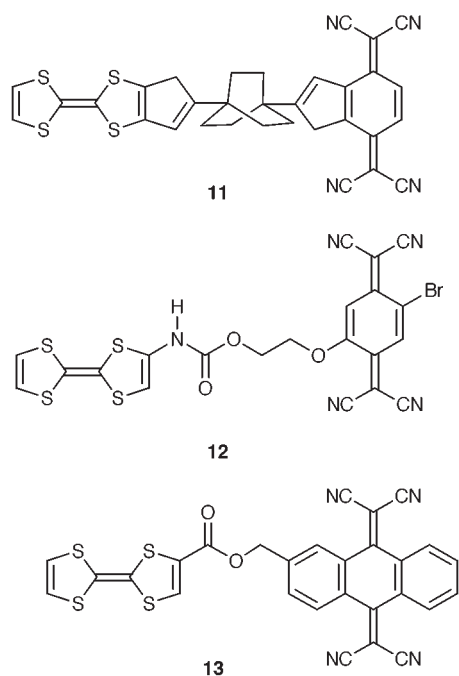
Bushby *et al.* have explored both calamitic and discotic mesogens based on the bis(phenylenedithio)TTF core, e.g. compound **10** displayed enantiotropic LC behaviour.³¹ p-Doping of **10** with SbCl_5 gave a conductivity value much lower than that normally found in doped discotics.³² Possible explanations given for this behaviour are that the cation radicals of **10** are highly localised and/or pinned by counterions, or that there is a major difference in geometry between neutral **10** and its radical cation, resulting in large local lattice distortions. (We note that the BEDT-TTF radical cation is usually more planar than in the neutral form).

4 Intramolecular charge-transfer and nonlinear optical materials

The covalent linkage of TTF to a π -acceptor moiety through a σ - or π -bonded bridge¹¹ offers considerable potential for the study of intramolecular charge transfer (ICT) processes in D-A molecules. Systems of this general type³³ are central to studies on chromophores for dyes, nonlinear optics, synthetic light-harvesting systems and theoretical aspects of charge transport at the molecular level. Aviram and Ratner's inspiring theoretical proposal in 1974³⁴ that molecular rectification might be observed in assemblies of the hypothetical TTF- σ -TCNQ molecule **11** sandwiched between two metal electrodes M_1 and M_2 in the architecture $\text{M}_1/\text{D}-\sigma-\text{A}/\text{M}_2$ has prompted several groups to explore the covalent linkage of TTF and TCNQ moieties. The synthetic challenge here is to prevent the irreversible formation of a stable (and usually insoluble) intermolecular CT complex, prior to the covalent coupling.

Compound **12** was the first TTF-TCNQ conjugate to be synthesised,³⁵ but the difficult synthetic route and problems with purification precluded detailed studies, although EPR and IR data suggested an ionic ground state. Compound **13** has recently proved to be straightforward to synthesise and purify, and amenable to detailed characterisation.³⁶ The TCNQ component in this molecule (TCNAQ: 11,11,12,12-tetracyanoanthraquinodimethane) is a substantially weaker acceptor than TCNQ [TCNAQ, $E_1^{1/2} = -0.285 \text{ V}$ (a two-electron wave) *cf.* TCNQ, $E_1^{1/2} = +0.130$ and $E_2^{1/2} = -0.290 \text{ V}$, in MeCN vs. SCE]; and in contrast to TCNQ (which is essentially planar) TCNAQ adopts a 'butterfly' conformation which will suppress intermolecular CT complex formation. In contrast to **12**, EPR (no signal) and IR data on powdered samples of **13** suggested a neutral ground state. Simultaneous electrochemistry and EPR (SEEPR) experiments provided qualitative evidence for intramolecular interaction of the TTF and TCNAQ moieties

in compound **13**. Model TTF and TCNAQ derivatives [*viz.* TTF-CO₂Me and TCNAQ-CH₂-O-C(O)Me, respectively] did not interact in solution when mixed in equimolar quantities. The SEEPR spectrum of diad **13** was significantly different from that of the two-component mixture under the same experimental conditions (Fig. 5), demonstrating that the spin density distribution in the cation radical of **13** was modulated intramolecularly by the adjacent TCNAQ moiety. Derivatives of TTF-spacer-TCNQ diads suitably functionalised to facilitate supramolecular alignment (either by LB or SA techniques) remain interesting targets to study further Aviram and Ratner's paradigm.



Cava, Metzger and coworkers have studied the TTF- σ -quinone diads **14** and **15**.³⁷ The latter compound is a derivative of the very strong donor bis(2,5-dimethylpyrrolo[3,4-*d*])TTF.

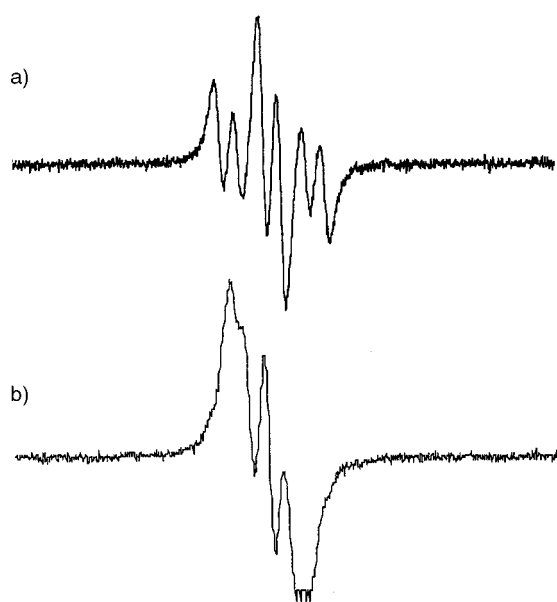
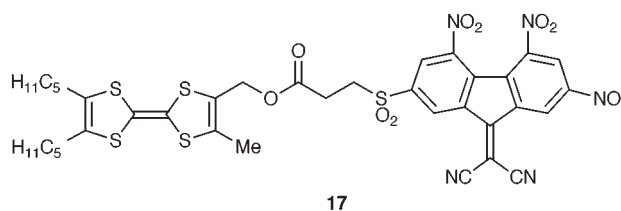
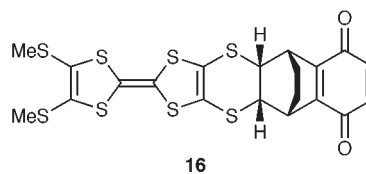
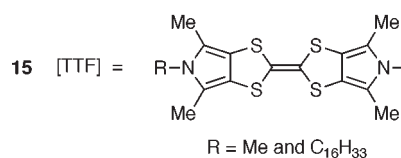
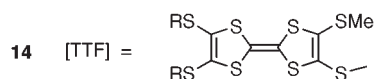
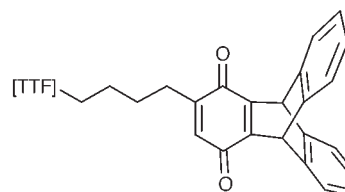


Fig. 5 SEEPR spectra in CH₂Cl₂: (a) mixture of TTF-CO₂Me and TCNAQ-CH₂-O-C(O)Me, both 10⁻³ M, +700 mV; (b) compound **13**, 10⁻³ M, +700 mV. Reprinted with permission from *J. Mater. Chem.*, 1998, **8**, 71. Copyright (1998) by the Royal Society of Chemistry.

The triptycene unit provides the steric bulk to prevent intermolecular CT complex formation: *N*-cyanoimine (DCNQI) analogues which would be stronger acceptors³⁸ could not be obtained. (Indeed, there appears to be no example of any TTF-quinone diad being converted into the corresponding DCNQI or TCNQ derivative).¹¹ While the CV data for **14** suggest non-interacting TTF and quinone moieties, the data for **15** are peculiar, in that remarkably large positive shifts (>400 mV in CH₂Cl₂) were observed for both TTF oxidation waves compared to a model compound, and the authors ascribed this effect to inductive electron withdrawal through the σ -chain of **15**. However, the potentials of the quinone reduction waves of **14** and **15** differ by only 40 mV, no CT band was discernible in the UV-vis spectra, and the chemical shifts of the carbonyl groups of **14** and **15** in the ¹³C NMR spectra are the same (within experimental error) and suggest a neutral quinone. One possible explanation for these anomalous CV data, which the authors do not mention³⁷, is that the bis(2,5-dimethylpyrrolo[3,4-*d*])TTF unit of **15** is inadvertently protonated or converted into its *S*-oxide derivative during the electrochemical experiments, thereby raising its oxidation potential without affecting the quinone moiety.

As a step towards controlling the distance and orientation between TTF and quinone moieties suitable for ICT, Becker, Khodorkovsky *et al.* synthesised the rigid diad **16**.³⁹ The UV-vis spectra in solution suggest there is a weak ICT interaction. CV data (which would be expected to be less sensitive) are consistent with non-interacting D and A moieties. X-Ray crystal structure analysis of **16** established a bent conformation for the molecule with the acceptor benzo-1,4-quinone moiety eclipsing the adjacent peripheral C=C bond of the TTF unit, with a close face-to-face separation of the D and A planes (3.29 Å).



We are currently studying the new TTF- σ -A system **17**.⁴⁰ The electron affinity of this 9-(dicyanomethylene)fluorene

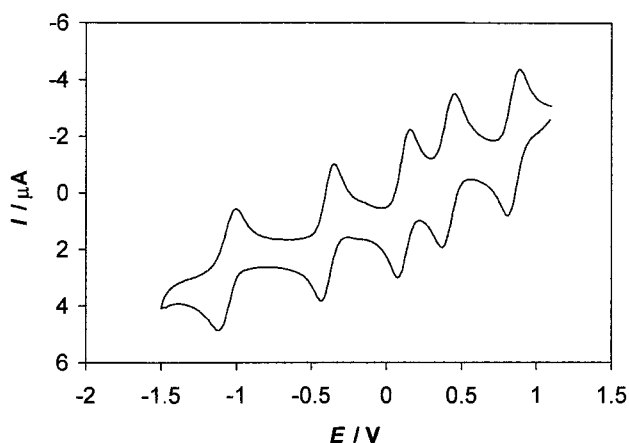
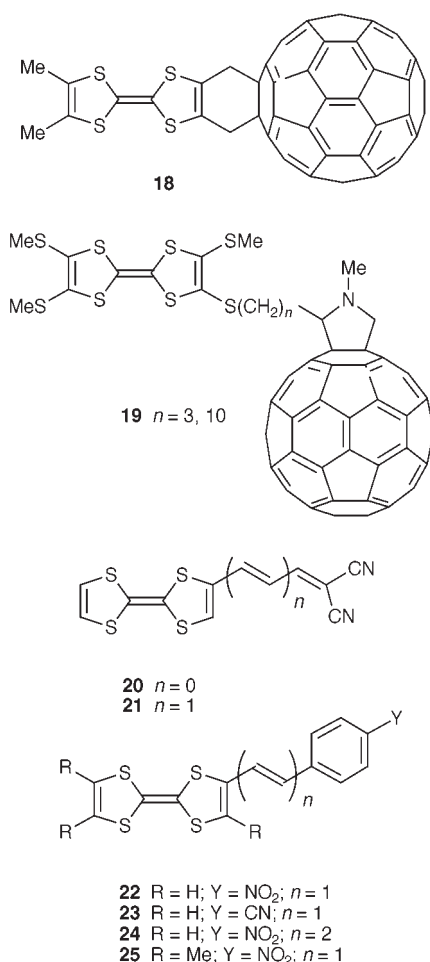


Fig. 6 CV of compound **17**: solvent CH_2Cl_2 , 20°C , electrolyte Bu_4NPF_6 , Pt electrode, versus Ag/AgCl, scan rate 100 mV s^{-1} . [From ref. 40].

derivative, as revealed by CV, approaches that of TCNQ: the 4,5-dipentyl substituents on the TTF moiety provide good solubility in organic solvents. The CV of compound **17** (Fig. 6) shows clean multi-stage redox behaviour with two TTF oxidation waves and three fluorene reduction waves observed.

Predictably, C_{60} has been studied as an acceptor component⁴¹ in TTF- C_{60} diads with both π - and σ -bonded spacers.⁴² Two in-depth studies have been reported recently. Rovira and coworkers established that photoinduced ICT in **18** led to the generation of a charge-separated state: the excited state of C_{60} was rapidly quenched by ICT from the dimethylTTF addend.^{42c} Metzger and coworkers studied TTF- C_{60} diads **19** which are linked by flexible spacers.^{42d} The electrochemical oxidation and reduction waves are the same as those of the



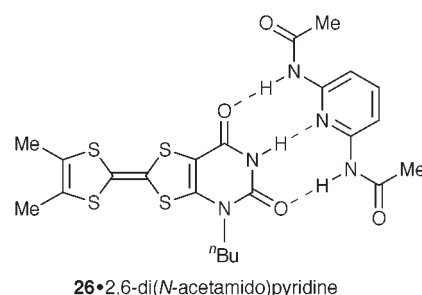
separate components and UV-vis data also indicate no appreciable CT in the ground state. Photoexcitation of **19** yields persistent EPR signals which the authors consider are more likely to arise from separate $\text{D}^{+\cdot}-\sigma\text{-A}$ and $\text{D}-\sigma\text{-A}^{\cdot-}$ species than from the excited state zwitterionic biradical $\text{D}^{+\cdot}-\sigma\text{-A}^{\cdot-}$. Stabilised charge-transfer states in the TTF-spacer-A diads remain a major goal.

TTF is emerging as a new π -donor in the field of second order NLO materials with reports from the groups of Garin and Martin that compounds **20** and **21** exhibit $\mu\beta(0)$ values of 35 and 234×10^{-48} esu, respectively.⁴³ Compounds **22** and **23** exhibit $\mu\beta(0)$ values of 135 and 115×10^{-48} esu, respectively.⁴⁴ (All these data were obtained using the EFISH technique).

Low energy ICT absorption bands are observed in the UV-vis spectra of **22-25**. Increasing the donor strength of the TTF unit in compound **25** predictably red shifts this band (**22**, λ_{max} 502 nm; **25**, 512 nm). The ICT band for **24** is, however, blue shifted by 15 nm (to λ_{max} 487 nm) relative to **22** by the insertion of an additional ethylenic bond. This effect is unusual, but does have precedent in other π -conjugated chains.⁴⁵ Thermal stability and processability issues need to be addressed before TTF-based NLO materials may be of practical value.

5 Supramolecular switches and devices

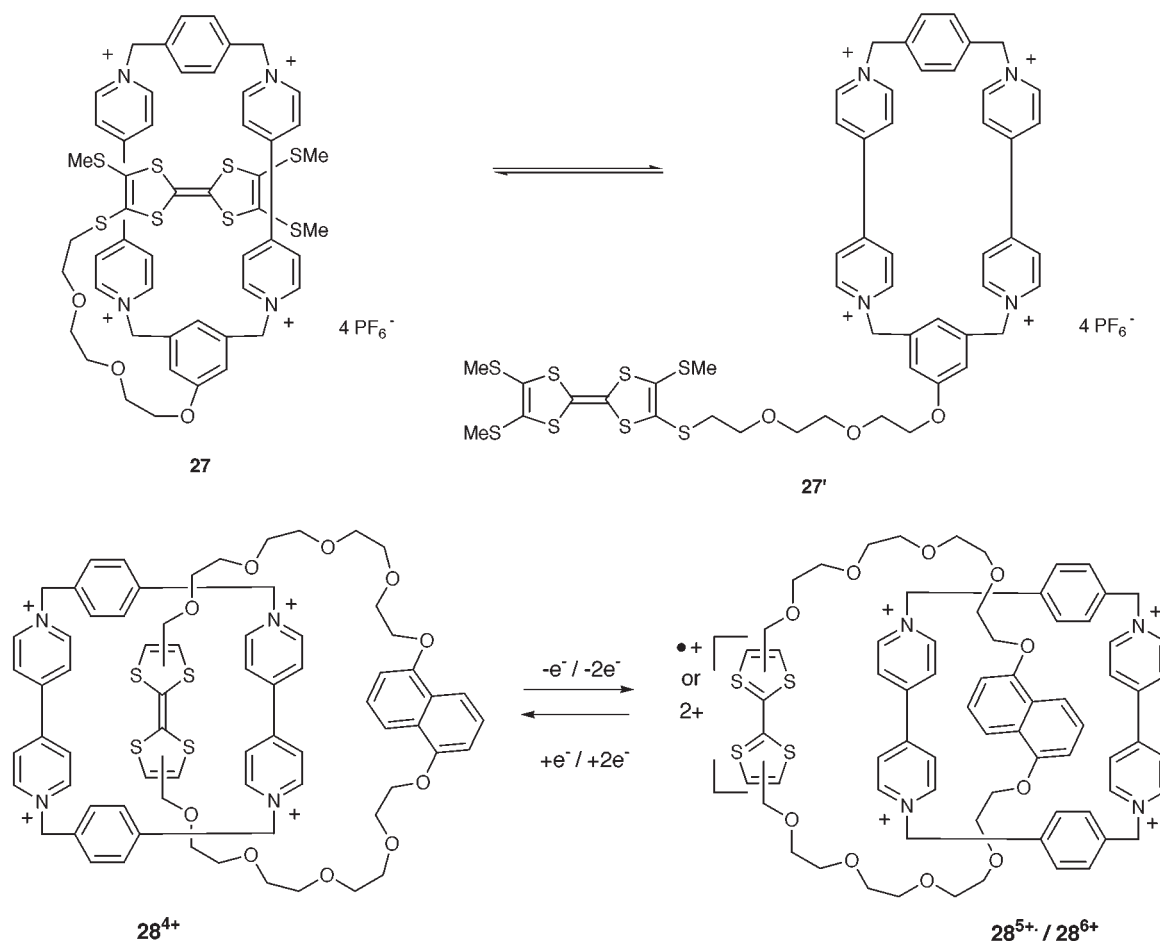
The reversible redox, intermolecular CT and hydrogen-bonding properties of TTF derivatives are attracting attention in the context of molecular/supramolecular systems which are prototype nanoscale devices, where the longer term aim is to recognise, store, process and read-out information at the molecular level.⁴⁶ Goldenberg and Neilands have studied TTF derivative **26** bearing a fused 2,4-dioxypyrimidine ring as a host system to which multi-H-bonding with a complementary 2,6-di(*N*-acetamido)pyridine guest results in a positive shift of TTF E_1^{ox} of 30 mV.⁴⁷ This is explained by an increase of the electron-acceptor properties of the pyrimidino moiety in response to the formation of H-bonds. Electron donation from the two carbonyl oxygens to the acetamido groups of the guest is the key interaction which affects the voltammetric response. These data are consistent with a small red shift in the absorption maximum of **26** (λ_{max} 406 nm) which is observed upon complexation. The behaviour of the E_2^{ox} wave in this system is complicated by an irreversible reaction of the dication.



Becher and coworkers⁴⁸ have exploited the 'self-complexing' ICT interaction of the TTF unit of **27** with a tethered cyclobis(paraquat-*p*-phenylene) π -acceptor⁴⁹ to obtain a thermally-controlled switch. Refluxing the green-coloured equilibrium solution (λ_{max} 785 nm) of **27** (complexed) and **27'** (decomplexed) caused almost complete disappearance of this ICT band, signifying conversion to the orange-coloured decomplexed form **27'**. Storing the solution at room temperature for ca. 20 h re-established the green colour. This cycle could be repeated with a small decrease in the equilibrium absorbance after each experiment.

The chemically- and electrochemically-switchable [2]catenane **28**⁴⁺ has been studied by Balzani, Stoddart and coworkers.⁵⁰ The molecule comprises two different π -elec-

tron-rich sites (*viz.* a disubstituted TTF⁵¹ and a 1,5-dioxy-naphthalene ring system). The former is located inside the cyclophane in **28**⁴⁺. However, chemical and/or electrochemical oxidation of the TTF unit into the cation radical or dication (*viz.* **28**⁵⁺ or **28**⁶⁺) leads to a circumrotation of the crown ether ring, and replacement of the TTF unit by the naphthalene system inside the cavity. This reversible process is accompanied by a colour change from green (**28**⁴⁺) to maroon (**28**^{5+·/6+}).



A more elaborate system which can be switched reversibly between three distinct states through the facile electrochemical manipulation of TTF's redox properties in the presence of two hosts with differing π -donor/ π -acceptor capabilities, *viz.* cyclobis(paraquat-*p*-phenylene) and 1,5-dinaphtho[38]crown-10 has been developed.⁵² A range of techniques established that the π -electron accepting TTF dication is bound within the macrocyclic polyether cavity. Neutral TTF (as an electron-donor guest) is complexed by the electron-acceptor paraquat cyclophane, and the TTF cation radical is not bound by either of the hosts. Electrochemical experiments revealed that the three-component mixture behaves as a reversible three-pole switch. Potential applications in electrochromic displays were noted as the three states have different colours and can be interconverted by changing the potential in an easily accessible range (from +0.3 to +0.8 V vs. SCE). Fluorescence of TTF²⁺ was noted.⁵²

6 Redox polymers

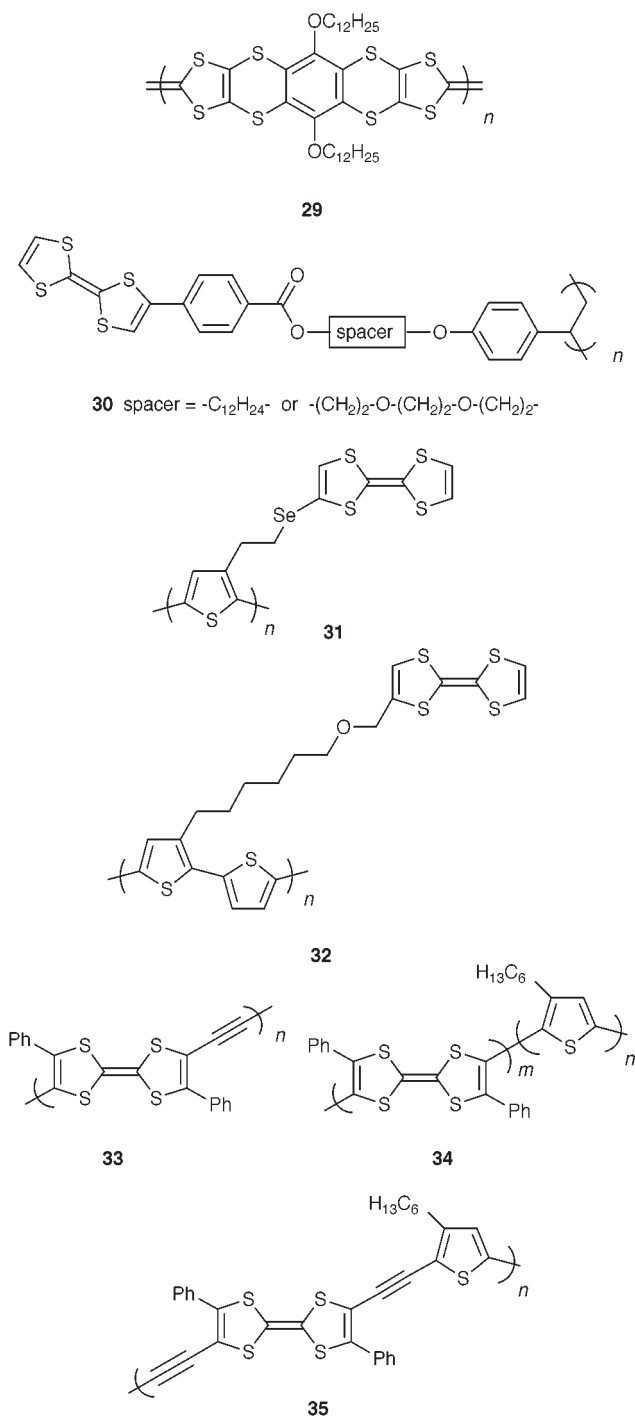
(a) Main-chain and side-chain systems

Motivated by attempts to improve the processability of TTF conductors, early work addressed the incorporation of TTF units into polymeric structures *via* condensation to conventional polyurethanes or polyamides *etc.*⁵³ Generally, these TTF

polymers were intractable or disordered, and although semiconducting materials were obtained upon doping, thorough characterisation was not reported. More recently, Müllen *et al.* synthesised a variety of main-chain, *e.g.* **29**, and side-chain, *e.g.* **30**, TTF polymers, some of which yielded free-standing processable films.⁵⁴ The possibility of inducing an LC phase and thereby raising conductivity values in TTF polymers was considered, but not achieved, in this study.

We synthesised a prototype TTF–thiophene derivative and proposed that long-range order in the electropolymerised hybrid poly(thiophene) might be modulated by π – π stacking of the pendant TTF units.⁵⁵ However, electropolymerisation did not proceed smoothly; the orange colour of the polymer **31** suggested a short conjugation length. We⁵⁶ and other groups^{57,58} have synthesised new TTF–thiophene hybrid monomers, and notable successes with polymerisation have been achieved by Roncali and coworkers⁵⁸ who pursued the idea that if stringent steric and electronic requirements could be met then electrical conductivity might be achieved by two parallel charge-transport mechanisms, *viz.* intrastack aromaticity migration along mixed-valence TTF stacks, and polaron/bipolaron conduction in the poly(thiophene) backbone.^{58c} Replacement of thiophene by bithiophene enabled polymerisation to proceed at a much lower potential; detailed spectroelectrochemical studies provided evidence for the occurrence of mixed-valence interactions among the pendant TTF units in **32**.^{58c} TTF, therefore, has potential as a side-chain substituent for electrogenerated polymers suitable for advanced electrode applications.⁵⁹

Main-chain polymeric TTF derivative **33** and poly(TTF–thiophene) systems **34** and **35** have been reported.⁶⁰ Extended π -conjugation in polymers **33** and **35** (compared to the precursor monomers and polymer **34**) is evident from a red



shift in their UV-vis absorption spectra: the ethynyl spacer unit relieves steric repulsion between the phenyl groups on the TTF units which would prevent coplanarity of adjacent TTFs in polymer **34**. Limited solubility of these polymers was noted and electroactivity of the TTF units was observed for cast films. Several redox waves were also observed on scanning to negative potentials, similar to other poly(aryleneethynylene) type systems. Iodine doping raised the conductivity of the polymers by *ca.* four orders of magnitude to *ca.* $10^{-3} \text{ S cm}^{-1}$.

(b) Dendritic systems: highly-charged organic nanoparticles

The study of dendrimers is a rapidly-expanding topic in macromolecular science.⁶¹ These materials possess well-defined, three-dimensional structural order, and their size and architecture are precisely regulated in their synthesis, providing unique molecular frameworks for the disposition of functional groups in predetermined spatial arrangements. In

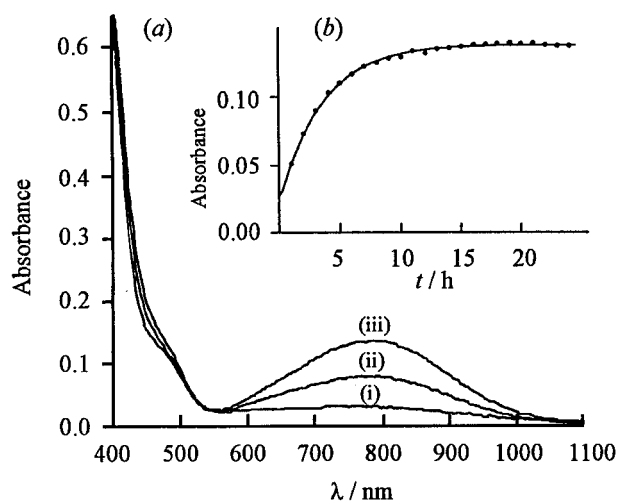


Fig. 7 (a) UV-Vis spectrum of the initially decomplexed **27'** in MeCN at (i) 0 h (ii) 3 h and (iii) 19 h. (b) Variation of the maximum absorbance (λ_{max} *ca.* 785 nm) of **27'** with time. Reprinted with permission from *Chem. Commun.*, 1998, 475. Copyright (1998) by the Royal Society of Chemistry.

the context of functional dendrimers, a variety of redox-active substituents (ferrocene, metalloporphyrins, metal-bipyridyls, *etc.*) have been built into the structures.⁶² 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. 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; and (v) mimics of biological redox processes.

We reported the first dendritic TTF derivatives comprising 12 TTF units at the periphery of an arylester dendrimer framework.⁶³ This convergent synthetic methodology has recently been adapted to provide the redox-switchable polyester 'co-block' $(\text{TTF})_4(\text{AQ})_2$ **36** and $(\text{TTF})_8(\text{AQ})_4$ dendrimers (AQ = anthraquinone).⁶⁴ The appeal of this system is that the CV reveals remarkably clean amphoteric switching between the +8, +4, 0, -2 and -4 redox states (Fig. 8). Such materials could find applications in the field of electrooptical switches, as these different redox states possess different UV-vis absorption spectra.

Other dendrimers which have TTF units placed at various levels within the structural hierarchy include a $(\text{TTF})_{13}$ system with *p*-xylyl groups as spacers,⁶⁵ and the $(\text{TTF})_{21}$ -glycol system **37**.⁶⁶ Thin layer CV studies on **37** show that all the TTF units undergo two, single-electron oxidations to produce the 42+ redox state. Spectroelectrochemical studies established that the

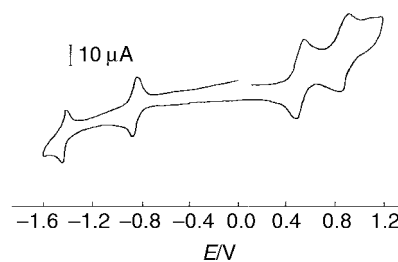
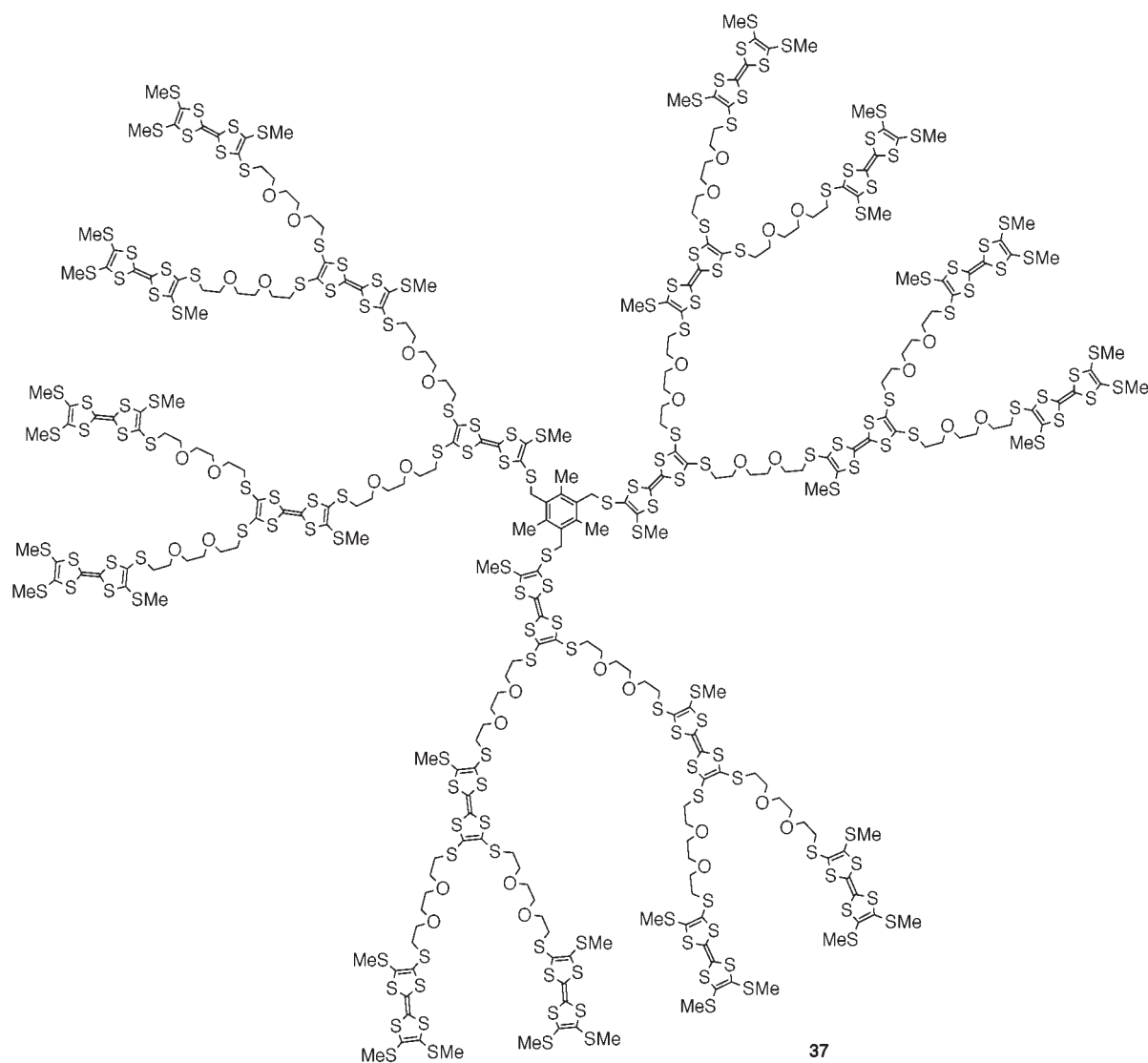
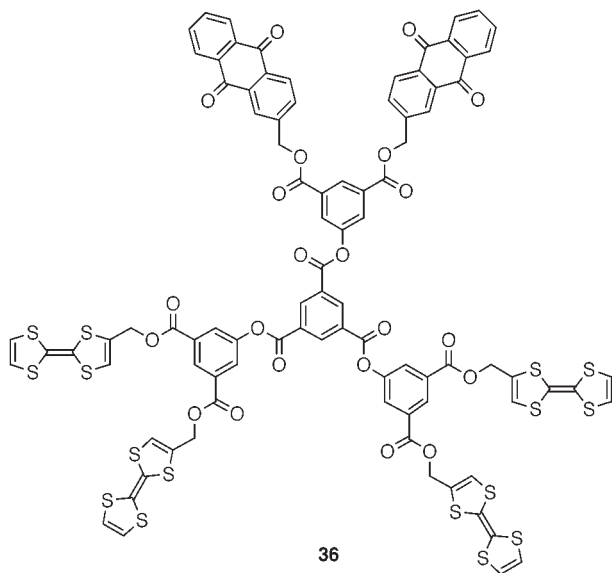


Fig. 8 CV of compound **36**: solvent MeCN, 20 °C, electrolyte Bu_4NPF_6 , Pt electrode, *versus* Ag/AgCl, scan rate 50 mV s^{-1} . Reprinted with permission from *Chem. Commun.*, 1998, 2565. Copyright (1998) by the Royal Society of Chemistry.



flexible glycol spacers facilitate intradendrimer interactions between partially-oxidised TTF units, which is relevant to the study of intradendrimer chemistry.⁶⁷ These TTF dendrimers represent highly-charged organic nanoparticles which offer scope for studies of charge transport within nanoscale systems.⁶⁸

7 Conclusion and outlook

It is now over 30 years since the parent molecule TTF was first unequivocally characterised,^{1a} leading to the development of organic metals, and hence organic superconductors. Ten years ago the T_c value for a BEDT-TTF superconductor was raised

to 12.8 K^{7a} and this has not been raised further, and there is a growing belief that this may be the limit for BEDT-TTF systems.⁶⁹ So while there is undoubtedly interesting and unexpected science to be uncovered by studying new molecular conductors with their novel electronic and magnetic properties, it is timely to apply the unique properties of the TTF molecule in other areas of organic materials chemistry. In particular the electrooptical and ICT properties of this chromophore are now the focus of increasing attention. Stabilised ICT states are proving to be an elusive target. Crucially, the synthetic chemistry to underpin these studies is now in place, and many versatile building blocks can be synthesised in multi-gram (even 20–50 g) quantities in a few days from cheap starting materials. This review article has sought to draw together different topics where TTF derivatives are being exploited. Much exciting work lies ahead in exploring the possibilities offered by TTF derivatives in materials chemistry!

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