ARTICLE

OBC
www.rsc.org/obc

New strategies and building blocks for functionalised 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives, including pyrrolo-annelated derivatives and π-extended systems with intramolecular charge-transfer †‡

Christian A. Christensen,[a] Martin R. Bryce,*[a] Andrei S. Batsanov[a] and Jan Becher[b]

[a] *Department of Chemistry, University of Durham, Durham, UK DH1 3LE. E-mail: m.r.bryce@durham.ac.uk*

[b] *Department of Chemistry, Odense University, Campusvej 55, DK 5230 Odense M, Denmark*

Received 12th November 2002, Accepted 12th December 2002
First published as an Advance Article on the web 24th January 2003

A range of new functionalised 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (TTFAQ) derivatives have been synthesised from the key di(halomethyl) building blocks, 10-[4,5-bis(bromomethyl)-1,3-dithiol-2-ylidene]-anthracene-9(10H)-one **10**, 10-[4,5-bis(chloromethyl)-1,3-dithiol-2-ylidene]anthracene-9(10H)-one **11** and 9-[4,5-bis(chloromethyl)-1,3-dithiol-2-ylidene]-10-[4,5-bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-9,10-dihydro-anthracene **18**. A Diels–Alder strategy comprising trapping of the transient exocyclic diene **19**, which is derived from **18**, with 1,4-naphthoquinone leads to the aromatised TTFAQ anthraquinone system **21**. Horner–Wadsworth–Emmons olefination of **21** with the anion generated from reagent **22** gave the fused bis(TTFAQ) structure **23**. Pyrrolo-annelated derivatives **30**–**34** have been obtained in a sequence of reactions from compound **10**. Mono-formylation of the pyrrole ring of **32** and **33** under Vilsmeier conditions gave **35** and **36** which upon reaction with 2,4,5,7-tetranitrofluorene gave the donor–π-acceptor diads **38** and **39**. Cyclic voltammetry (CV) in solution for all the TTFAQ derivatives shows the typical quasi-reversible two-electron oxidation wave of the TTFAQ core at potentials which vary slightly depending on the substituents. For example, the value of E^{ox} is raised by the electron withdrawing anthraquinone and tetranitrofluorene units of **21** and **38**, respectively. The CV of the conjugated TTFAQ dimer **23** showed two, two-electron oxidation waves corresponding to the sequential formation of $\mathbf{23}^{2+}$ and $\mathbf{23}^{4+}$ (ΔE^{ox} = 130 mV) providing evidence for a significant intramolecular electronic interaction, *i.e.* the dication $\mathbf{23}^{2+}$ acts as a conjugated donor–π-acceptor diad, thereby raising the oxidation potential of its partner TTFAQ unit. Spectroelectrochemical studies on **23** support this explanation. A strong intramolecular charge transfer band at λ_{max} 538 nm is seen in the UV-Vis spectra of the TTFAQ–π-tetranitrofluorene diads **38** and **39**. The X-ray crystal structures are reported for compounds **30**, **33** and **34**. The pyrrolo–TTFAQ moiety adopts a saddle-shape with the central ring of the dihydroanthracene moiety folded along the C(9)**. . .**C(10) vector in each case. Significant intermolecular interactions are observed in the structures.

Introduction

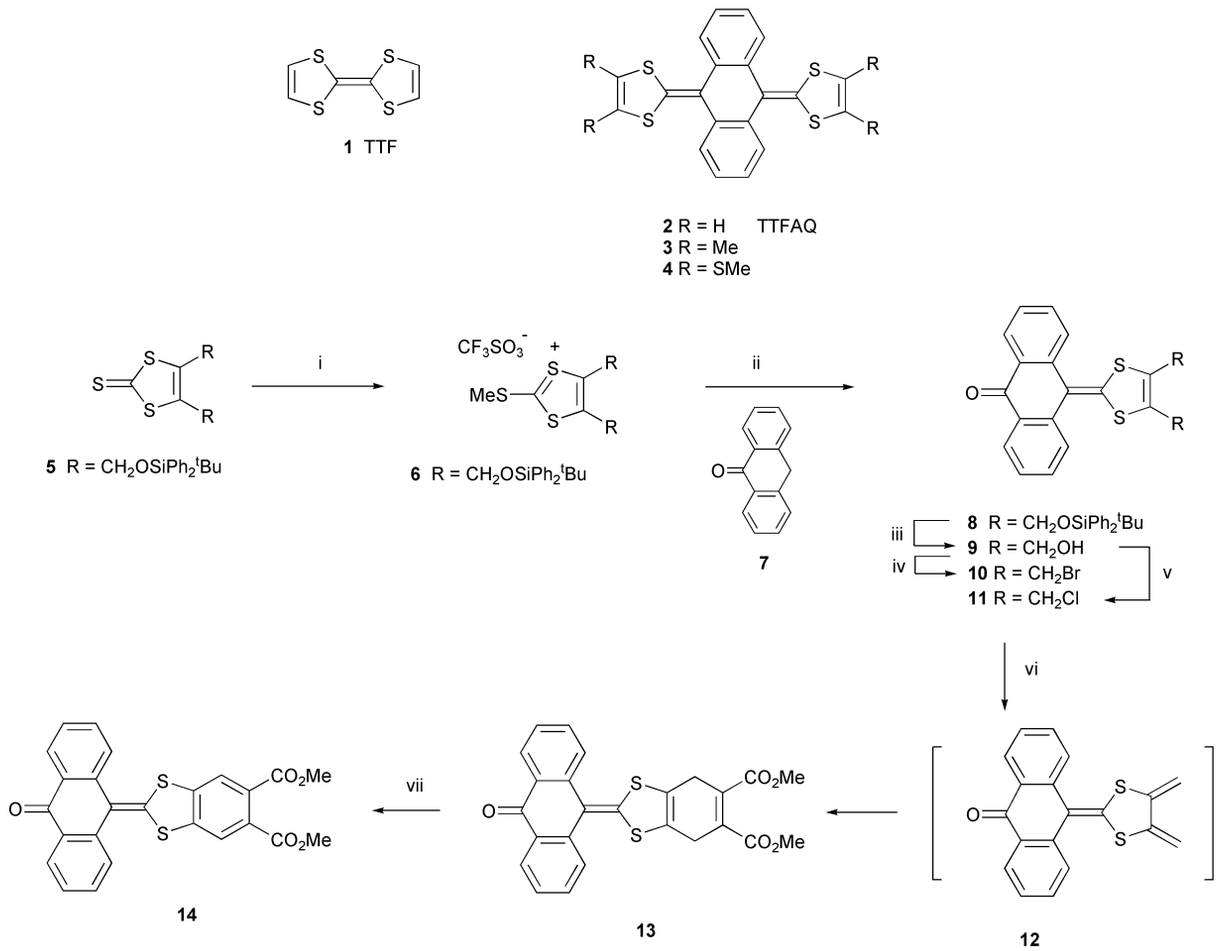
The anthraquinone-derived "extended TTF" (TTF = tetrathiafulvalene **1**) π-electron donor unit 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene **2**[1] (herein abbreviated to TTFAQ) offers a unique combination of redox and structural properties which are very different from those of TTF. Solution electrochemical studies[2] have established that whereas TTF **1** undergoes two, reversible, one-electron oxidation waves, system **2** undergoes a single, two-electron oxidation process to yield a thermodynamically stable dication [E^{ox} +0.30 − +0.40 V (*vs* Ag/AgCl in MeCN) depending upon the substituents present]. This redox process, which is electrochemically quasi-reversible and chemically reversible, is accompanied by a dramatic conformational change,[3] as shown by X-ray crystallographic studies on **3**,[3a] $\mathbf{3}^{2+}$,[3a] **4**[3b] and $\mathbf{4}^{2+}$.[3c] The neutral molecules are saddle-shaped comprising a concave cavity and a folded anthracenediylidene unit, whereas in the dications the anthracene ring system becomes planar and aromatic, with bond lengths similar to anthracene itself, and the hetero-aromatic 1,3-dithiolium cations are almost orthogonal to this plane. These structures are supported by theoretical studies on **2** which show that the saddle shape arises from steric hindrance between the sulfur atoms and the hydrogen atoms at the *peri* sites.[2b] Calculated energies predict that the HOMO in **2** lies slightly below that of TTF **1**, and these data support the experimental evidence that the two, one-electron oxidations of **2** coalesce under the same oxidation wave.[2b] The cation radical of system **2** is a transient species which has been generated by flash photolysis[3c] and pulse radiolysis experiments.[4] This fascinating interplay of redox and conformational properties has led to derivatives of **2** being employed as building blocks for charge-transfer salts,[3a,5] nonlinear optical materials,[6] multi-stage redox assemblies,[7] cyclophanes,[8] dendrimers[9] and compounds for photosynthetic models.[4a,7c,10]

Derivatives of **2** have generally been prepared by two-fold Horner–Wadsworth–Emmons olefination of the appropriate anthraquinone starting material with 1,3-dithiole-phosphonate reagents,[11] or by stepwise reactions on anthrone.[11b,12] Lithiation of the dithiole ring(s) of **2** (or, more efficiently the di- or trimethyl derivatives)[13] followed by trapping with electrophiles provides a means of attaching other substituents, *e.g.* -CO_2Me, -C(S)NHMe and -SC(O)Ph.

Herein we report new functionalised TTFAQ derivatives obtained from key di(halomethyl) building blocks **10**, **11** and **18**, including a Diels–Alder strategy using the transient exocyclic diene **19**.[14] Most notably the π-extended systems **21** and **23**, and pyrrolo-annelated derivatives **30**–**36** and **38**–**39** have been obtained. Solution electrochemical studies and X-ray crystallographic data are also reported.

† This paper is Molecular Saddles Part 10. For Part 9 see reference 5c.
‡ Electronic supplementary information (ESI) available: NOE spectra for compound **23**. See http://www.rsc.org/suppdata/ob/b2/b211153p/

DOI: 10.1039/b211153p



Scheme 1 *Reagents and conditions:* i, MeOTf, CH_2Cl_2, 20 °C; ii, pyridine–AcOH; iii, Bu_4NF, THF, 20 °C, iv, PBr_3, DMF, 0 °C to 20 °C; v, $SOCl_2$, DMF, 0 °C to 20 °C; vi DMAD, KI, 18-crown-6, PhMe, 100 °C; vii, DDQ, PhMe, 100 °C.

Results and discussion

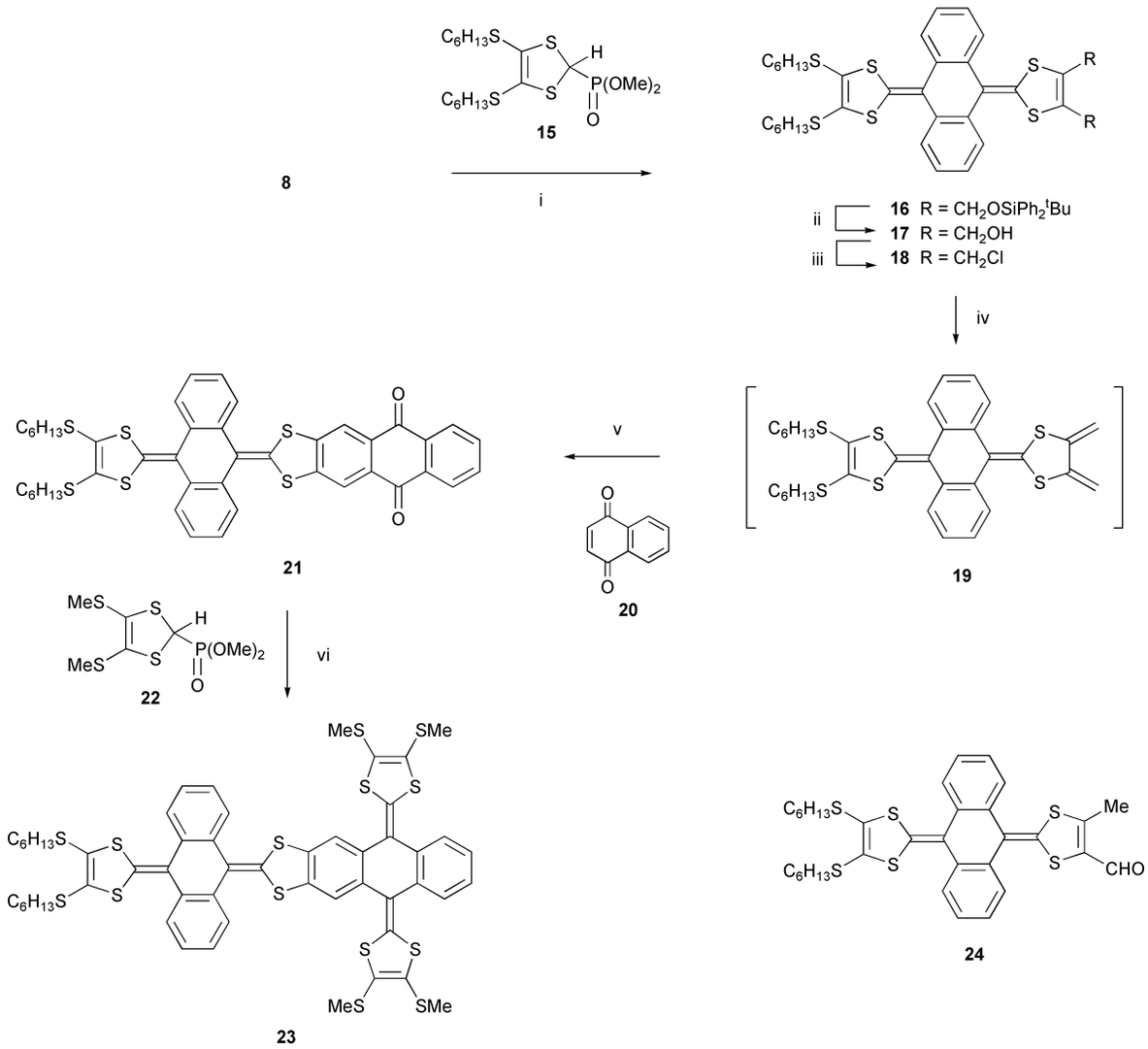
Generation and trapping of exocyclic dienes 12 and 19

Reactions of the anion of anthrone with 1,3-dithiolium cations are known to proceed readily to yield 10-(1,3-dithiol-2-ylidene)anthracene-9(10*H*)-one derivatives[15] which can function as precursors to unsymmetrical TTFAQ systems.[11b,12] Following this strategy, the bis-DPTBS protected diol **5**[16] was methylated using methyl triflate to give the unstable salt **6** which was sufficiently pure (^{1}H NMR evidence) for immediate reaction with anthrone **7** in the presence of pyridine and acetic acid to yield product **8** in 91% overall yield from thione **5** (Scheme 1). As a model for subsequent TTFAQ systems we initially explored the conversion of **8** into the exocyclic diene **12**. Other reports have addressed related reactions of TTF[17] and 1,3-dithiole-2-one derivatives.[11c] Deprotection of compound **8** with tetrabutylammonium fluoride gave the di(hydroxymethyl) derivative **9** (84% yield) which was brominated using PBr_3 in DMF to give the di(bromomethyl) derivative **10** (89% yield). Similarly di(chloromethyl) derivative **11** was obtained using $SOCl_2$ in DMF (83% yield). Both compounds **10** and **11** are shelf-stable yellow solids.

Derivative **11** was tested as a diene precursor using the conditions of Müllen *et al*[17d] and Gorgues *et al*.[17c] with dimethyl acetylenedicarboxylate (DMAD) as the dienophile for *in situ* trapping. A mixture of **11**, potassium iodide, 18-crown-6 and DMAD was heated in dry toluene at 100 °C until all compound **11** was consumed and two new products were obtained (TLC evidence): these were presumably the adduct **13** and the derived aromatised product **14**. Separation of these was not attempted; instead the mixture was converted cleanly into **14** as the sole product (61% yield from **11**) by addition of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and further heating (Scheme 1). These experiments established that the transient diene **12** could be efficiently generated and trapped *in situ*.

We next turned to the analogous diene **19** (Scheme 2) with the hexylsulfanyl substituents chosen to enhance the solubility of the derived TTFAQ systems. Horner–Wadsworth–Emmons olefination of **8** with the anion generated from reagent **15**[18] (LDA at –78 °C) gave compound **16** (77% yield) which upon deprotection gave the diol **17** (88% yield). Conversion of **17** into di(chloromethyl) derivative **18** was achieved using either $SOCl_2$ in CCl_4 (10% yield) or, more efficiently, by reaction with PPh_3 in a mixture of CCl_4 and MeCN[19] (optimised 66% yield). (No reaction occurred in neat CCl_4). Formation of aldehyde **24** in this transformation has been discussed previously:[14] its formation was suppressed when as high a concentration of reactants as possible was used. By analogy with the generation of **12** described above, diene **19** was generated *in situ* and trapped with 1,4-naphthoquinone **20** followed by aromatisation with DDQ to yield the black crystalline product **21** (63% yield) comprising a rigid donor–π-acceptor system. Reaction of **21** with the anion generated from reagent **22**[18] gave the fused bis-(TTFAQ) structure **23** as a yellow powder in 88% yield. To ensure reaction of both carbonyl groups of **21**, an excess of **22** (10 equivalents) was used, as noted by Gorgues *et al* for similar reactions.[20] The solubility of **23** in organic solvents was considerably greater than that of its precursor **21**. Concurrent with our initial report on the synthesis of **21**,[14] Herranz and Martín described the generation of an analogue of **19** (possessing SMe substituents instead of SC_6H_{13}) from the corresponding di(bromomethyl) precursor and its trapping with C_{60} (25% yield).[21]

Previous studies have shown that the TTFAQ unit flips in



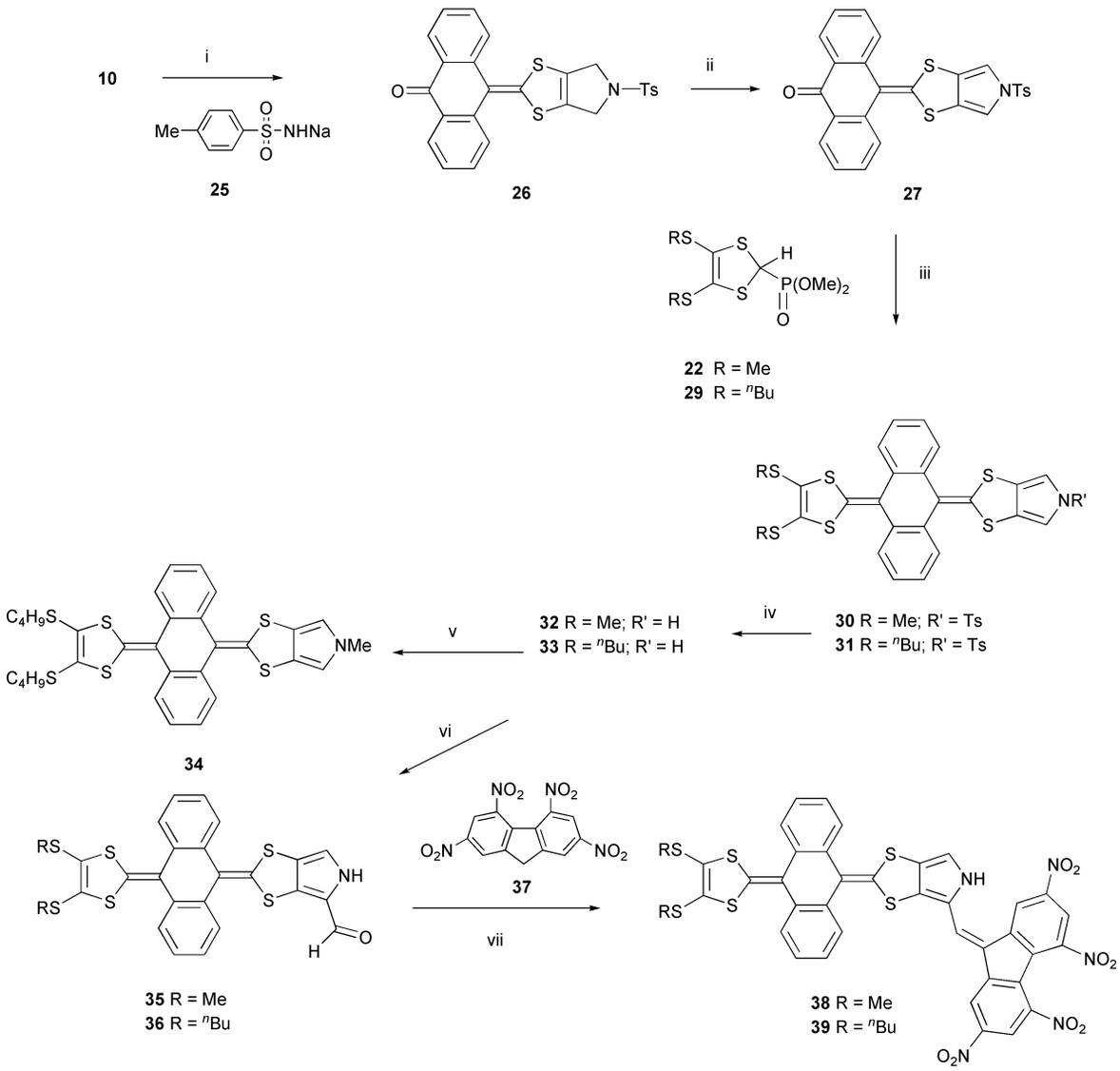
Scheme 2 *Reagents and conditions:* i, LDA, THF, −78 °C to 20 °C; ii, Bu_4NF, THF, 20 °C; iii, PPh_3, CCl_4, MeCN, 80 °C; iv, KI, 18-crown-6, PhMe, 90 °C; v, DDQ, PhMe, 90 °C; vi, LDA, THF, −78 °C to 20 °C.

solution between two different saddle conformations.[13c] The ^{1}H NMR spectrum of **23** (Fig. 1a) is, therefore, complicated by the fact that the two TTFAQ units are joined in a rigid and locked fashion. They have no possibility to rotate relative to each other, hence the molecule can adopt two different conformations, one where each TTFAQ moiety is flipped up [(up, up) = (down, down)] and another where one moiety is up and the other is down [(up, down) = (down, up)] which explains the two pairs of singlets observed for the two non-equivalent SMe groups. The larger pair integrated to *ca.* four protons for each singlet, whereas the smaller pair integrated to two protons for each singlet, consistent with twelve protons for the four SMe groups. Also the aromatic multiplets at 7.80 and 7.72 ppm integrated to *ca.* 0.6 and 1.4 protons, respectively, and two triplets were seen for the terminal Me groups of the hexylsulfanyl chains, which also integrated in a *ca.* 1 : 2 ratio. This suggests that **23** is approximately twice as long in one conformation as in the other. Oxidation of **23** to its tetracation $\mathbf{23}^{4+}$ was achieved with iodine in $CDCl_3$ to afford a red precipitate, the ^{1}H NMR spectrum of which in $(CD_3)_2SO$ is shown in Fig. 1b. This spectrum is simplified compared to that of neutral **23** because $\mathbf{23}^{4+}$ consists of planar moieties free to rotate with respect to each other, and hence due to the symmetry of the tetracation only one SMe singlet is seen, integrating to 12H. Also, the multiplets and the singlet in the aromatic region of the spectrum now all have integrals divisible by two, and the two triplets arising from the terminal methyl groups of the hexylsulfanyl chains have collapsed into one triplet integrating to 6H. An NOE experiment further proved the existence of two conformers of **23**. (See the Electronic supplementary information).

Pyrrolo-annelated TTFAQ derivatives

By analogy with pyrrolo–TTF syntheses,[22] we recognised that di(bromomethyl) derivative **10** could serve as a precursor to pyrrolo-annelated TTFAQ derivatives. An extension of the π-system of TTFAQ in this way would be novel and could provide interesting solid state structures. Furthermore, the pyrrole unit should give new reactive sites for the attachment of functional groups. Accordingly, the dihydropyrrolo derivative **26** was prepared in 82% yield by reaction between **10** and two equivalents of sodium tosylamide **25** (1 equiv. of **25** reacts with the HBr which is formed) (Scheme 3). Oxidation of **26** to the pyrrolo derivative **27** was achieved using DDQ in refluxing chlorobenzene (92% yield). Reaction of **27** with reagents **22** and **29** (as described above for the synthesis of **16**) cleanly afforded TTFAQ derivatives **30** and **31**, respectively, in 86–91% yields. Detosylation of **30** and **31** using sodium methoxide gave compounds **32** and **33** as yellow solids in high yields: they have good solubility in a range of organic solvents and can be synthesised on a multi-gram scale.

The potential for *N*-functionalisation of the pyrrolo–TTFAQ system was demonstrated in the clean conversion of **33** into **34** (97% yield) upon deprotonation with sodium hydride in DMF, followed by reaction with iodomethane. High-yielding mono-formylation of **32** and **33** was achieved by analogy with



Scheme 3 *Reagents and conditions:* i, MeCN–DMF, 80 °C; ii, DDQ, PhCl, reflux; iii, LDA, THF, −78 °C to 20 °C; iv, NaOMe, MeOH, THF, reflux; v, NaH, DMF, 20 °C, then MeI, DMF, 20 °C; vi, $POCl_3$, DMF, 20 °C; vii, DMF, 20 °C.

pyrrolo–TTF,[23] upon reaction with phosphorus oxychloride and DMF under standard Vilsmeier conditions to give **35** and **36**, respectively. To demonstrate that the aldehyde group of **35** and **36** can serve as a reactive 'handle' for further functionalisation, a condensation reaction with 2,4,5,7-tetranitrofluorene **37**[24] in DMF gave the π-extended donor–acceptor diad molecules **38** and **39** as black powders in 80 and 87% yields, respectively. The butylsulfanyl chains of the latter greatly increased the solubility in organic solvents, compared to its methylsulfanyl analogue **38**. The ^{1}H NMR spectra of both **38** and **39** displayed two sets of broad peaks as a result of the ability of the molecules to adopt two different conformations, as described for compound **23** above.

Solution electrochemical and UV-Vis spectroscopic properties

Solution electrochemical properties of the TTFAQ derivatives were studied by cyclic voltammetry (CV) and the data are collated in Table 1. All the derivatives show the typical quasi-reversible two-electron oxidation wave of the TTFAQ core[2] at potentials which vary slightly depending on the substituents which are attached to the dithiole rings. For example, the value of E^{ox} is raised (*i.e.* the TTFAQ dication is destabilised) by the electron withdrawing chloromethyl groups in **18**, and, more notably by the anthraquinone unit of donor–acceptor diad **21**; for this compound a reversible one-electron reduction wave of the anthraquinone moiety was also observed. An increase in the oxidation potential when electron withdrawing groups are attached has precedent in TTFAQ–C_{60} diads studied by Martín and Herranz,[21] and rigid TTF–quinone triads studied by Frenzel and Müllen.[25] The relatively high oxidation potential of compound **16** is harder to explain; it is raised by 90 mV compared to compound **17** and ΔE (defined as $E^{ox}_{pa} - E^{ox}_{pc}$) is the highest (310 mV) in this series. This is possibly due to steric effects of the bulky DPTBS groups.

The CV of the conjugated TTFAQ dimer **23** showed two, well-resolved, two-electron oxidation waves (ΔE^{ox} = 130 mV) (Fig. 2). The difference in oxidation potentials for the two TTFAQ moieties in **23** cannot be explained by their different substituents, rather it is more likely to be due to a significant intramolecular electronic interaction, as seen for other TTFAQ–donor diads (donor = TTF or ferrocene) with conjugative links.[2c,d] Whichever TTFAQ unit in **23** is oxidised first will become a good electron acceptor, and thus the dication $\mathbf{23}^{2+}$ acts as a conjugated donor–π–acceptor diad,[26] thereby raising the oxidation potential of the second (neutral) TTFAQ unit in the molecule.

Spectroelectrochemical studies were performed on compound **23** (Fig. 3). Upon oxidation to the dication $\mathbf{23}^{2+}$ the UV-Vis spectrum resembles the sum of the spectra for neutral **4** and $\mathbf{4}^{2+}$. However, the broad band at λ_{max} 540 nm extends to 840 nm, whereas for $\mathbf{4}^{2+}$ there is no absorption beyond 600

Table 1 Cyclic voltammetric data[a]

Compound	E^{ox}_{pa} /V	E^{ox}_{pc} /V	E^{red}_{pc} /V	E^{red}_{pa} /V
16	0.54	0.23	—	—
17	0.45	0.32	—	—
18	0.58	0.48	—	—
21	0.71	0.61	−0.85 (1e)	−0.79 (1e)
23	0.54 (E_1), 0.67 (E_2)	0.45 (E_1), 0.62 (E_2)	—	—
30	0.63	0.45	—	—
31	0.66	0.46	—	—
32	0.50	0.35	—	—
33	0.49	0.34	—	—
34	0.50	0.32	—	—
35	0.55	0.48	—	—
36	0.58	0.47	—	—
38	0.63	0.42	−0.41 (1e)[b]	—
39	0.64	0.45	−0.41 (1e)[b]	—

[a] Data recorded *vs.* Ag/AgCl; compound *ca.* 1×10^{-3} M, electrolyte 0.1 M Bu_4NPF_6 in CH_2Cl_2, 20 °C, scan rate 100 mV s^{-1}. All waves are two-electron processes, unless otherwise designated. [b] Irreversible.

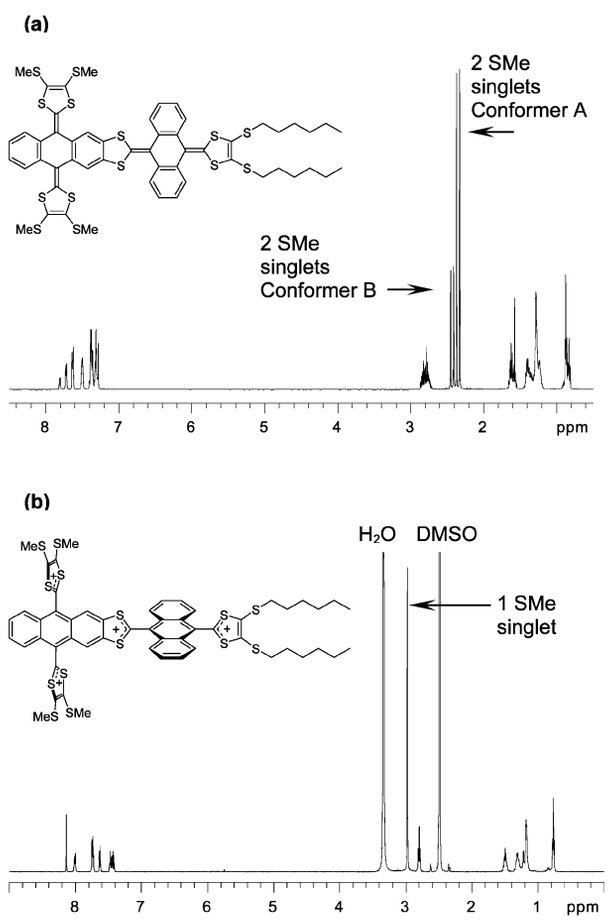


Fig. 1 ^{1}H NMR spectra of (a) **23** in $CDCl_3$; (b) $\mathbf{23}^{4+}$ in $(CD_3)_2SO$.

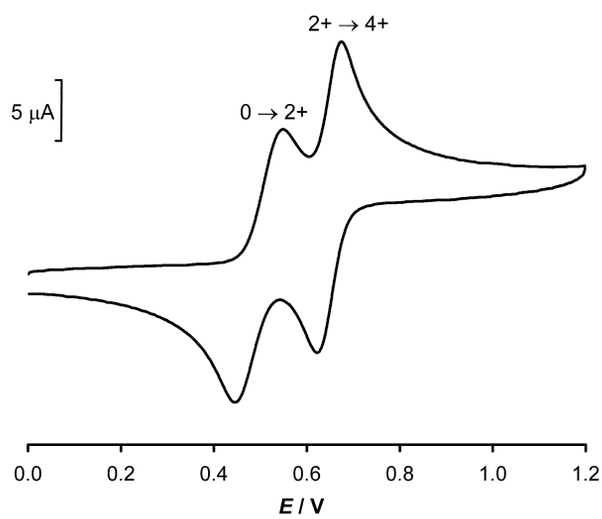


Fig. 2 Cyclic voltammogram of compound **23** under the conditions stated in Table 1.

nm.[3c] This could indicate the presence of a charge-transfer (CT) band in $\mathbf{23}^{2+}$ overlaid with the characteristic $TTFAQ^{2+}$ absorption (λ_{max} 500 nm). The CT band at λ_{max} 650 nm is clearly seen to collapse upon further oxidation by which the donor–π-acceptor system $\mathbf{23}^{2+}$ is destroyed. Since no intermolecular CT band was seen upon oxidation of **4** to $\mathbf{4}^{2+}$,[3c] we assign the CT band of $\mathbf{23}^{2+}$ as being intramolecular as a result of conjugative interaction between the two redox active moieties. For the oxidation of both **23** and $\mathbf{23}^{2+}$ isosbestic points indicate the clean formation of $\mathbf{23}^{2+}$ and $\mathbf{23}^{4+}$, respectively. The spectra of both $\mathbf{23}^{2+}$ and **23** could be fully recovered upon sequential reduction of $\mathbf{23}^{4+}$ showing that the λ_{max} 650 nm band is not due to decomposition products.

The donor–π-acceptor diads **38** and **39** are black powders, with an intensely dark red appearance in solution, clearly different from the yellow TTFAQ precursors **35** and **36**. The UV-Vis absorption spectra of **38** and **39** were almost identical (see Fig. 4 for **39**). In addition to the two bands typical of TTFAQ derivatives (λ_{max} 357 and 428 nm) a lower energy band was present at λ_{max} 538 nm. The intensity of this band, relative to the two higher energy bands, was independent of concentration, and is thus assigned to an intramolecular CT band. Similar ICT bands have been observed for other conjugatively linked donor–π-tetranitrofluorene molecules.[24b,27]

X-Ray crystal structures of compounds 30, 33 and 34

The molecular structures and conformations of **33** and **34** are similar (Fig. 5). The TTFAQ core of the molecule adopts the usual saddle-shape,[3a,3b,5b,13c] with the central ring of the dihydroanthracene moiety folded along the C(9)...C(10) vector by 39.5° and 38.1°, respectively, while the inclination between the two benzene rings is slightly larger (50.6° and 43.6°, respectively). The pyrrole ring and the adjacent S(1) and S(2) atoms are co-planar within experimental error, and since both dithiole rings are folded inward along the S(1)...S(2) and S(3)...S(4) vectors, respectively, (by 14.8° and 14.7° in **33** and by 14.1° and 11.9° in **34**) the S(3)C(21)C(22)S(4) plane forms a slightly acute angle (82.0° in **33** and 84.5° in **34**) with the pyrrole ring system. In both structures the *n*-butyl chain at the S(5) atom is disordered between two conformations in a 10 : 1 (**33**) or 2 : 1 (**34**) ratio. The major component and the other (ordered) *n*-butyl chain adopt the planar all-*trans* conformations and lie practically parallel to the pyrrole ring. Two molecules, related *via*

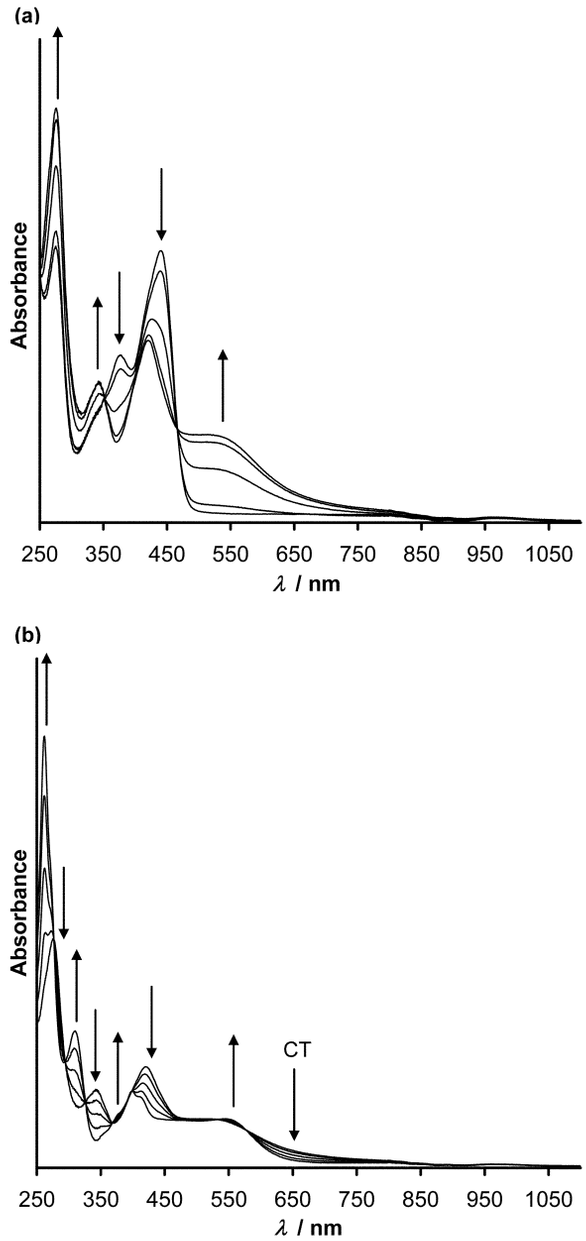


Fig. 3 UV-VIS-NIR Spectroelectrochemistry of compound **23** in CH_2Cl_2. (a) Oxidation to form $\mathbf{23}^{2+}$; (b) oxidation to form $\mathbf{23}^{4+}$. (Note the collapse of the CT band at 650 nm).

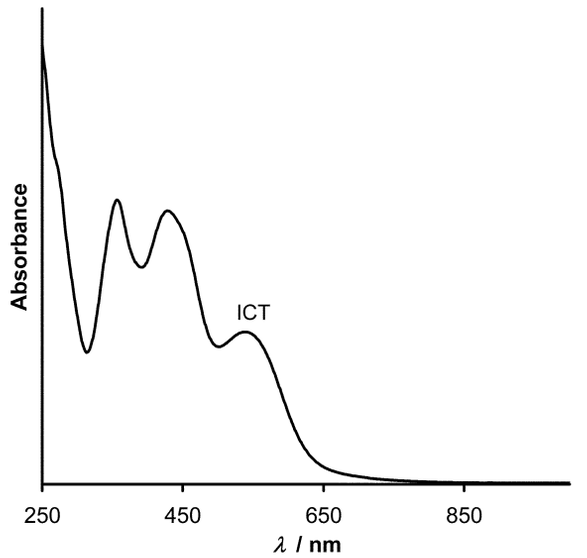


Fig. 4 UV-VIS absorption spectrum of compound **39** in CH_2Cl_2.

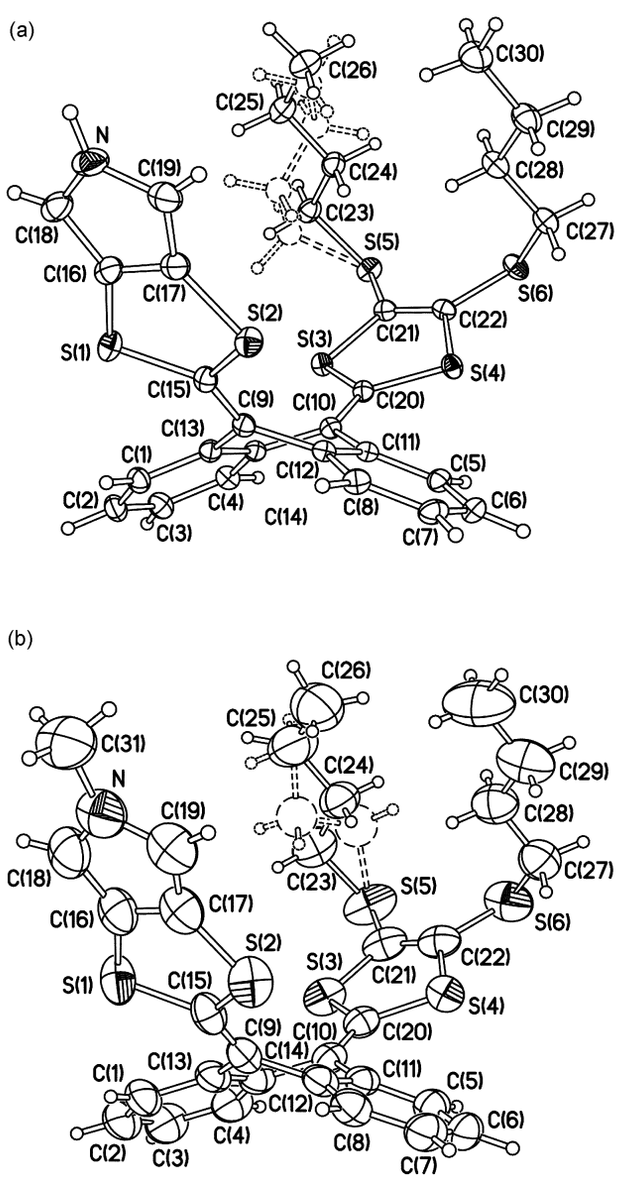


Fig. 5 X-Ray molecular structures of (a) compound **33** and (b) compound **34** showing thermal ellipsoids at the 50% probablity level.

an inversion centre, form a typical pseudo-dimer[3a,3b,5b,13c,14] in which *n*-butyl chains of one molecule are engulfed between the pyrrole ring and *n*-butyl chains of the other, their separations corresponding to normal van der Waals distances.[28] The shortest intradimer contacts are S(6)**. . .**N′ of 3.43 Å in **33** and 3.54 Å in **34**, and it is noteworthy that the NH group in **33** forms no hydrogen bond.

Packing of the dimers in **33** and **34** is different. In the triclinic structure **33**, all the dimers have the same orientation and form a succession of layers (Fig. 6a). Within a layer, each dimer interacts with four others through two face-to-face contacts between dithiole rings and two face-to-face contacts between dithiole–pyrrole systems; the shortest contact distances S**. . .**S 3.63–3.73 Å and S**. . .**C 3.54–3.61 Å are close to the sums of the van der Waals radii (S, 1.81 Å; C, 1.77 Å).[28] In the monoclinic structure **34**, the dimers are arranged in rows, parallel to the *x* axis, but dimers in adjacent layers have non-parallel (herringbone) orientations (Fig. 6b). Thus face-to-face contacts of dithiole rings exist only within the row; the shortest distances therein (S**. . .**S 3.73 and S**. . .**C 3.69–3.72 Å) are comparable to those in **33**. The molecular geometry of **33** and **34** can be compared with six

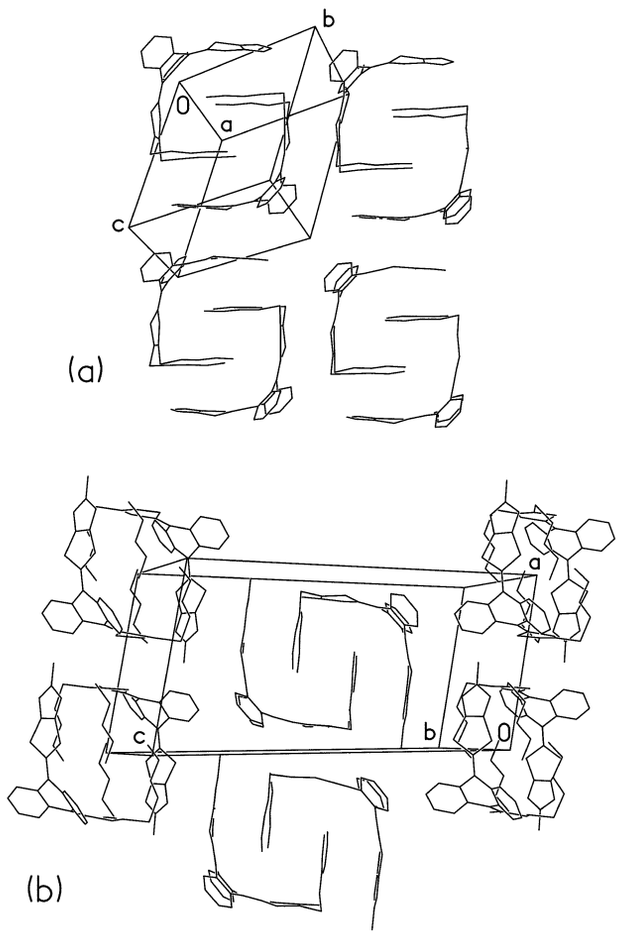


Fig. 6 Crystal packing of (a) compound **33** and (b) compound **34**.

structurally characterised pyrrolo-annelated TTF derivatives[29] (all with *N*-alkyl substituents) which have both the pyrrole ring and the N atom bonding essentially planar. Even when the molecule is sterically strained, as in some *N,N*-cyclophane derivatives, the bis(pyrrolo–TTF) system folds only along the S**. . .**S vectors of the dithiole rings. Structures of such TTF systems with an SO_2Ph substituent at the N atom are unknown, but **30** can be compared with *N*-(benzenesulfonyl)pyrrole and a number of its derivatives[30] some of which display small but significant non-planarity of the N atom with the sum of bond angles being 350–356°.

The asymmetric unit of **30** comprises two molecules (A and B) of broadly similar, but not identical, conformation (Fig. 7). The dihydroanthracene moiety is folded along the C(9)**. . .**C(10) vector by 39.0° (A) and 40.0° (B) into two practically planar moieties, and both dithiole rings are folded inwards. In molecule A the folding along the S(1)**. . .**S(2) and S(3)**. . .**S(4) equals 11.6° and 15.2°; the corresponding angles in B are 17.4° and 7.3°. Thus, the angle between the S(1)C(16)C(17)S(2) and S(3)C(21)C(22)S(4) planes is reduced to 76.0° in both independent molecules. Whilst in **33** and **34** the pyrrole ring with immediately adjacent atoms comprise a planar system, in **30** (molecule A) the ring is folded along the C(18). . .C(19) vector by 2.7° and the N–S bond tilts out of the C(18)NC(19) plane by 20.6° (in molecule B by 2.4° and 13.5°, respectively). As expected,[30] the E–N–S–C torsion angles (E is the $p\pi$(N) orbital direction) are small *viz*. 9.5(2)° in A and 15.1(2)° in B. However, the orientation of the benzene ring is not the expected one: the torsion angles N–S–C–C of 62.1(2)° (A) and 62.6(2)° (B) are far from the 90° expected for C_s molecular symmetry.

Each of the independent molecules and its own inversion equivalent form a mutually engulfing dimer. In contrast with structures **33** and **34**, where the molecular cavity is occupied by

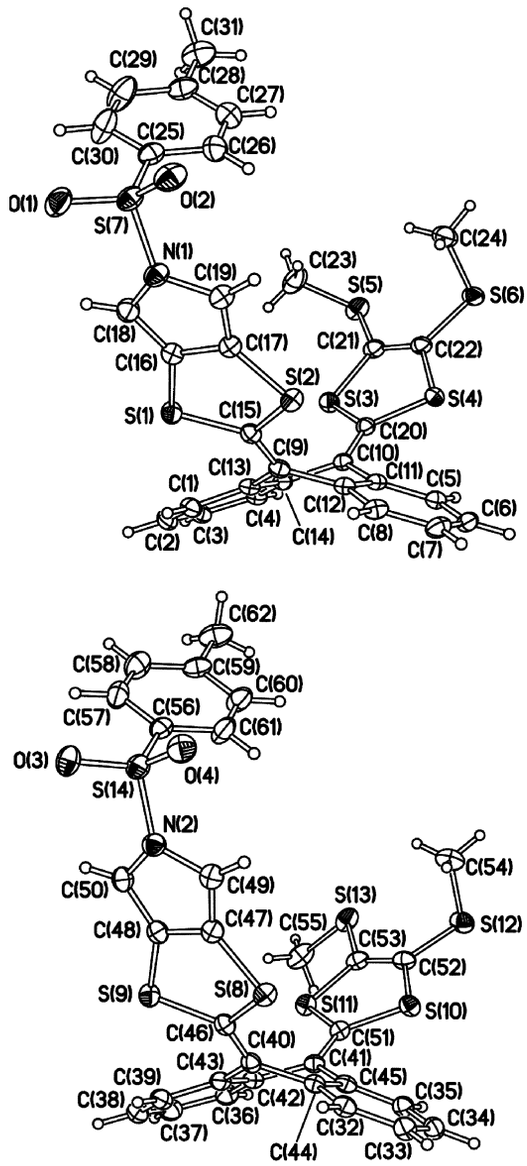


Fig. 7 Two independent molecules of **30** in the crystal structure.

the long *n*-butyl chains, in **30** the dithiole ring itself and its methylsulfanyl substituents are accommodated therein, with short intradimer contacts S(2)**. . .**S(5^{ii}) 3.59 Å and S(8)**. . .**S(13^{iii}) 3.60 Å for A and B, respectively. Dimers of each type, related by the *a–b* translation, contact by their dithiole–pyrrole systems in a face-to-face fashion, thus forming an infinite chain (Fig. 8). The contact between BB^{iii} dimers is rather close: the dithiole–pyrrole systems overlap in a nearly eclipsed manner (pyrrole over dithiole ring, and *vice versa*) with the interplanar separation of 3.52 Å. For AA^{ii} dimers the separation is larger (3.66 Å) and there is a large lateral shift between the fused systems. The chains can also be described as combining into a layer, parallel to the (1 −1 0) plane. Thus, pronounced intermolecular π–π interactions were indeed observed in the crystal structures of **30**, **33** and **34**, as a consequence of the extension of the π-system of one of the 1,3-dithiole rings.

In conclusion, a range of new TTFAQ derivatives has been obtained, using the di(halomethyl) compounds **10**, **11** and **18** as key reagents which are available in synthetically-useful quantities. Their derived products display interesting redox and structural properties, and TTFAQ–π-acceptor systems (acceptor = anthraquinone, $TTFAQ^{2+}$ and tetranitrofluorene) have been characterised. These compounds are versatile redox-active systems, and by virtue of their synthetic utility and molecular electronic properties these TTFAQ derivatives

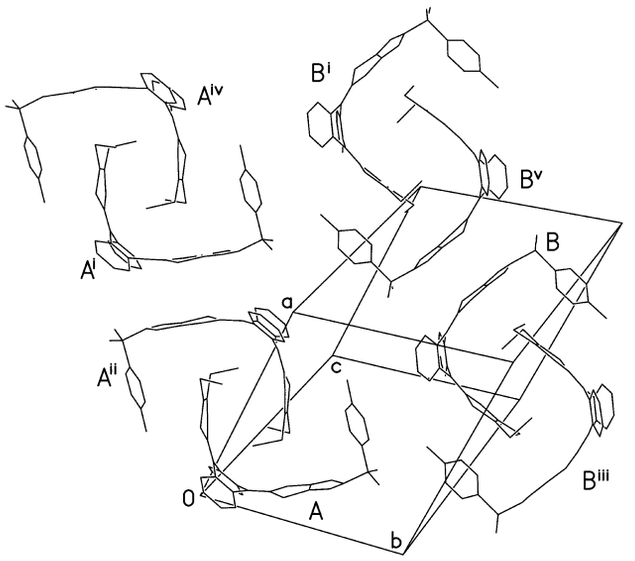


Fig. 8 Crystal packing of **30**. Symmetry operations: (i) $x + 1, y - 1, z$; (ii) $1 - x, -y, -z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $2 - x, -y - 1, -z$; (v) $1 - x, 1 - y, 1 - z$.

should continue to attract attention among the organic and materials chemistry communities.

Experimental

General procedures and equipment

These are the same as those reported previously.[9]

4,5-Bis(*tert*-butyldiphenylsiloxymethyl)-2-methylsulfanyl-1,3-dithiolium trifluoromethanesulfonate (6)

Compound **5**[16] (28.50 g, 42.47 mmol) was dissolved in dry degassed dichloromethane (200 cm^3) and stirred under argon at room temperature. Methyl triflate (5.00 cm^3, 44.18 mmol) was added in one portion and the stirring was continued for 1 h, whereupon the solution changed from yellow to almost colourless. Concentration *in vacuo* afforded a pale yellow salt **6**, which was used without further purification, mp 90–91 °C. ^{1}H NMR ($CDCl_3$): δ 7.57–7.52 (8 H, m), 7.44–7.35 (12 H, m), 4.66 (4 H, s), 3.17 (3 H, s), 1.04 (18 H, s).

10-[4,5-Bis(*tert*-butyldiphenylsiloxymethyl)-1,3-dithiol-2-ylidene]anthracene-9(10*H*)-one (8)

Salt **6** (from 28.50 g, 42.47 mmol of **5**) and anthrone **7** (8.24 g, 42.4 mmol) were dissolved in a 3 : 1 (v/v) mixture of pyridine–acetic acid (400 cm^3) and stirred under argon at 60 °C for 3 h and then at 120 °C for another 3 h. The dark red mixture was concentrated under reduced pressure, redissolved in dichloromethane (500 cm^3), washed with water (2 × 400 cm^3) and brine (400 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed (silica gel, dichloromethane–hexane, 3 : 1 v/v) affording **8** as an orange powder (32.00 g, 91% from **5**), mp 128−129 °C (from chloroform–methanol). ^{1}H NMR ($CDCl_3$): δ 8.32 (2 H, d, J = 8.0 Hz), 7.93 (2 H, d, J = 8.0 Hz), 7.67−7.63 (2 H, m), 7.59−7.56 (8 H, m), 7.46–7.30 (14 H, m), 4.19 (s, 4 H), 1.02 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 183.6, 143.9, 139.1, 135.5, 132.4, 131.5, 130.5, 129.9, 129.2, 127.8, 127.0, 126.3, 126.1, 116.6, 59.0, 26.6, 19.2. MS (PD): m/z = 831.2 (theory: 831.2). Anal. calcd. for $C_{51}H_{50}O_3S_2Si_2$ (MW 831.24): C, 73.69; H, 6.06. Found C, 73.45; H, 6.22.

10-[4,5-Bis(hydroxymethyl)-1,3-dithiol-2-ylidene]anthracene-9(10*H*)-one (9)

To a stirred solution of **8** (32.00 g, 38.50 mmol) in dry tetrahydrofuran (200 cm^3) was added a solution of tetrabutylammonium fluoride (115 cm^3 of a 1.0 M solution in tetrahydrofuran, 115 mmol) over 15 min. Stirring under argon at room temperature was continued for 2 h, whereupon water (500 cm^3) was added to afford a red precipitate. The precipitate was filtered, washed with water (40 cm^3) and methanol (3 × 40 cm^3), and dried in vacuum over phosphorus pentoxide to give **9** as an orange powder sufficiently pure for further reaction (11.48 g, 84%). Compound **9** could be recrystallised from ethanol–hexane to give small red needles, mp 245−247 °C (decomp.). ^{1}H NMR (DMSO-d_6): δ 8.13 (2 H, d, J = 7.6 Hz), 7.94 (2 H, d, J = 7.6 Hz), 7.78 (2 H, t, J = 7.6 Hz), 7.50 (2 H, t, J = 7.6 Hz), 5.61 (2 H, t, J = 5.6 Hz), 4.33 (4 H, d, J = 5.6 Hz). ^{13}C NMR ($CDCl_3$): δ 182.1, 144.5, 138.4, 132.3, 130.6, 129.5, 126.5, 126.44, 126.43, 115.6, 56.0. MS (EI): m/z (%) 354 (45, M$^+$), 336 (100). Calcd. for $C_{19}H_{14}O_3S_2$: 354.03844. HRMS (EI): 354.03791 (−1.5 ppm).

10-[4,5-Bis(bromomethyl)-1,3-dithiol-2-ylidene]anthracene-9(10*H*)-one (10)

Compound **9** (11.40 g, 32.16 mmol) was dissolved in dry *N*,*N*-dimethylformamide (150 cm^3) and stirred at 0 °C under argon. Phosphorus tribromide (9.07 cm^3, 96.50 mmol) was added *via* syringe over 5 min, accompanied by a colour change from red to yellow–orange. Stirring at 0 °C was continued for 30 min followed by another 2 h at room temperature, after which a yellow precipitate was formed. Methanol (500 cm^3) was added to precipitate the remaining product, whereupon the reaction mixture was filtered. The yellow precipitate was washed with water (30 cm^3) and methanol (3 × 30 cm^3), and dried in a vacuum over phosphorus pentoxide to give **10** as a yellow powder sufficiently pure for further reaction (13.76 g, 89%), mp 228−230 °C (from dichloromethane–hexane, decomp.). ^{1}H NMR ($CDCl_3$): δ 8.27 (2 H, d, J = 7.2 Hz), 7.82 (2 H, d, J = 7.6 Hz), 7.67 (2 H, t, J = 7.6 Hz), 7.46 (2 H, t, J = 7.6 Hz), 4.23 (4 H, s). ^{13}C NMR ($CDCl_3$): δ 183.5, 138.6, 137.8, 131.9, 130.7, 129.6, 127.3, 127.1, 126.1, 119.4, 21.3. MS (EI): m/z (%) 482 (4, [M + 4]$^+$), 480 (7, [M + 2]$^+$), 478 (4, M$^+$), 320 (100). Anal. calcd. for $C_{19}H_{12}Br_2OS_2$ (MW 480.24): C, 47.52; H, 2.52. Found C, 47.70; H, 2.53.

10-[4,5-Bis(chloromethyl)-1,3-dithiol-2-ylidene]anthracene-9(10*H*)-one (11)

To a stirred solution of **9** (0.210 g, 0.59 mmol) in dry *N*,*N*-dimethylformamide (7 cm^3) at 0 °C under argon was added thionyl chloride (0.211 g, 1.78 mmol) dropwise *via* syringe, whereupon the colour changed from dark red to pale brown. The reaction mixture was stirred for 30 min, whilst slowly warming to room temperature, and diluted with dichloromethane (100 cm^3). The organic phase was washed with water (3 × 100 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by column chromatography (silica gel, dichloromethane–hexane, 2 : 1 v/v) afforded **11** as small yellow crystals (0.192 g, 83%), mp 230 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.27 (2 H, d, J = 8.0 Hz), 7.83 (2 H, d, J = 8.0 Hz), 7.67 (2 H, t, J = 7.5 Hz), 7.46 (2 H, t, J = 7.5 Hz), 4.36 (4 H, s). ^{13}C NMR ($CDCl_3$): δ 183.5, 138.6, 138.2, 131.9, 130.7, 129.3, 127.3, 127.0, 126.1, 119.6, 36.1. MS (EI): m/z (%) 394 (2, [M + 4]$^+$), 392 (5, [M + 2]$^+$), 390 (6, M$^+$), 208 (100). Anal. calcd. for $C_{19}H_{12}Cl_2OS_2$ (MW 391.34): C, 58.31; H, 3.09. Found C, 58.35; H, 3.05.

Compound 14

Compound **11** (0.115 g, 0.294 mmol), dimethyl acetylenedicarboxylate (0.14 cm^3, 0.167 g, 1.18 mmol), potassium iodide (0.146 g, 0.882 mmol) and 18-crown-6 (0.233 g, 0.882 mmol) were dissolved in dry toluene (70 cm^3) and stirred under argon at 100 °C for 2 h, in which time the colour changed from yellow to brown. DDQ (0.133 g, 0.588 mmol) was added to the reaction mixture, which was stirred for another 1 h at 100 °C.

The mixture was diluted with dichloromethane (200 cm^3), washed with an aqueous 0.5% sodium thiosulfate solution (3 × 200 cm^3) and water (200 cm^3), dried ($MgSO_4$) and filtered through a short silica column, eluting with dichloromethane–toluene, 1 : 1 v/v. The filtrate was concentrated *in vacuo* and the residue purified by column chromatography (silica gel, dichloromethane–ethyl acetate, 95 : 5 v/v) affording **14** as small golden needles (0.082 g, 61%), mp >250 °C. ^{1}H NMR ($CDCl_3$): δ 8.26 (2 H, d, J = 7.8 Hz), 7.90 (2 H, d, J = 7.8 Hz), 7.69 (2 H, t, J = 7.5 Hz), 7.60 (2 H, s), 7.49 (2 H, t, J = 7.5 Hz), 3.89 (6 H, s). ^{13}C NMR ($CDCl_3$): δ 183.6, 166.8, 138.7, 138.6, 137.8, 131.9, 131.0, 130.2, 127.5, 127.3, 126.3, 121.3, 121.2, 52.9. MS (EI): *m*/*z* (%) 460 (100, M^+). Anal. calcd. for $C_{25}H_{16}O_5S_2$ (MW 460.52): C, 65.20; H, 3.50. Found C, 64.80; H, 3.44.

9-[4,5-Bis(*tert*-butyldiphenylsiloxymethyl)-1,3-dithiol-2-ylidene]-10-[4,5-bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (16)

To a solution of the phosphonate ester **15**[18] (1.35 g, 3.05 mmol) in dry tetrahydrofuran (100 cm^3) at −78 °C under argon was added lithium diisopropylamide (2.23 cm^3 of a 1.5 M solution in cyclohexane, 3.35 mmol) *via* syringe and the resultant cloudy yellow mixture was stirred for 2 h. Compound **8** (2.11 g, 2.54 mmol) was added to the mixture as a solid, against a positive pressure of argon, which afforded an orange suspension. The suspension was stirred at −78 °C for another 2 h, whereupon it was allowed to slowly attain room temperature overnight. Evaporation of the solvent gave a red residue which was dissolved in dichloromethane (200 cm^3), washed with water (200 cm^3) and brine (200 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography (silica gel, dichloromethane–hexane, 1 : 3 v/v) afforded **16** as a yellow foam (2.26 g, 77%), mp 56–58 °C. ^{1}H NMR ($CDCl_3$): δ 7.72−7.70 (2 H, m), 7.60−7.56 (10 H, m), 7.39–7.28 (16 H, m), 4.18 (2 H, d, J = 12.8 Hz), 4.11 (2 H, d, J = 13.2 Hz), 2.88–2.73 (4 H, m), 1.65–1.58 (4 H, m), 1.41–1.34 (4 H, m), 1.31–1.23 (8 H, m), 1.01 (18 H, s), 0.87 (6 H, t, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 135.54, 135.52, 135.3, 134.7, 133.8, 132.6, 132.5, 130.4, 129.8, 128.4, 127.7, 126.1, 126.0, 125.7, 125.4, 125.2, 123.4, 121.1, 59.1, 36.2, 31.3, 29.7, 28.2, 26.6, 22.5, 19.2, 14.0. UV-vis (CH_2Cl_2): λ_{max} (lg ε) 366 (4.19), 438 (4.43) nm. MS (PD): *m*/*z* = 1148.6 (theory: 1149.9). Anal. calcd. for $C_{66}H_{76}O_2S_6Si_2$ (MW 1149.88): C, 68.94; H, 6.66. Found C, 68.86; H, 6.73.

9-[4,5-Bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-10-[4,5-bis(hydroxymethyl)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (17)

Compound **16** (2.21 g, 1.93 mmol) was dissolved in dry tetrahydrofuran (25 cm^3) and stirred under argon at room temperature. A solution of tetrabutylammonium fluoride (5.78 cm^3 of a 1.0 M solution in tetrahydrofuran, 5.78 mmol) was added dropwise *via* syringe over 15 min, inducing a colour change from yellow to light brown. Further stirring for 1.5 h, followed by addition of a few drops of water (0.1 cm^3) and evaporation of the solvent afforded a brown residue which was dissolved in dichloromethane (200 cm^3), washed with water (200 cm^3) and brine (200 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography using a short column (silica gel, dichloromethane until no more traces of by-products were visible on the column, then dichloromethane–ethyl acetate, 2 : 1 v/v) afforded **17** as a yellow solid (1.14 g, 88%), mp 110–111 °C. ^{1}H NMR ($CDCl_3$): δ 7.62–7.55 (4 H, m), 7.28–7.26 (4 H, m), 4.27–4.17 (4 H, m), 2.93 (2 H, t, J = 5.6 Hz), 2.80–2.75 (4 H, m), 1.63–1.56 (4 H, m), 1.40–1.33 (4 H, m), 1.29–1.24 (8 H, m), 0.87 (6 H, t, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 134.8, 134.5, 131.9, 131.4, 129.9, 126.1(2C), 125.9, 125.5, 125.1, 123.1, 122.6, 56.8, 36.2, 31.3, 29.6, 28.2, 22.5, 14.0. UV-vis (CH_2Cl_2): λ_{max} (lg ε) 269 (4.24), 364 (4.20), 432 (4.45) nm. MS (PD): *m*/*z* = 672.2 (theory: 673.1). Anal. calcd. for $C_{34}H_{40}O_2S_6$ (MW 673.08): C, 60.67; H, 5.99. Found C, 60.51; H, 5.99.

9-[4,5-Bis(chloromethyl)-1,3-dithiol-2-ylidene]-10-[4,5-bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (18)

To a solution of **17** (0.600 g, 0.891 mmol) in dry degassed acetonitrile (10 cm^3) was added dry carbon tetrachloride (3.0 cm^3) and triphenylphosphine (0.701 g, 2.67 mmol) whereupon the reaction was stirred under argon at 80 °C for 20 min, in which time the colour changed from yellow to dark brown. The reaction mixture was cooled to room temperature and immediately filtered through a plug of silica, eluting with ethyl acetate, to remove the brown baseline material. The yellow solution was concentrated *in vacuo* and the product was triturated with cyclohexane to give a yellow solid which was filtered off, washed with methanol and dried, affording **18** as a yellow powder (0.415 g, 66%), mp 97–99 °C. ^{1}H NMR ($CDCl_3$): δ 7.61–7.58 (4 H, m), 7.32–7.30 (4 H, m), 4.31 (4 H, s), 2.86–2.74 (4 H, m), 1.65–1.59 (4 H, m), 1.42–1.36 (4 H, m), 1.30–1.26 (8 H, m), 0.87 (6 H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ 134.7, 134.6, 131.9, 129.0, 128.8, 126.5, 126.2 (2C), 125.4, 125.2, 123.9, 122.5, 36.5, 36.3, 31.3, 29.6, 28.2, 22.5, 14.0. UV-vis (CH_2Cl_2): λ_{max} (lg ε) 361 (4.21), 430 (4.47) nm. MS (ES): *m*/*z* (%) = 712 (16, $[M+4]^+$), 710 (84, $[M+2]^+$), 708 (100, M^+). Calcd. for $C_{34}H_{38}Cl_2S_6$: 708.06749. HRMS (ES): 708.06777 (+0.4 ppm).

Compound 21

Compound **18** (0.100 g, 0.141 mmol), naphthoquinone **20** (0.089 g, 0.563 mmol), potassium iodide (0.070 g, 0.423 mmol) and 18-crown-6 (0.112 g, 0.423 mmol) were dissolved in dry toluene (40 cm^3) and stirred under argon at 90 °C for 5 h, in which time the colour changed from yellow to dark brown. DDQ (0.128 g, 0.563 mmol) was added to the reaction mixture, which was stirred for another 4 h at 90 °C. The colour changed to red–brown and a black precipitate formed. The mixture was diluted with dichloromethane (200 cm^3), washed with aqueous 0.5% sodium thiosulfate solutions (3 × 200 cm^3) and water (200 cm^3), dried ($MgSO_4$) and filtered through a short silica column, eluting with dichloromethane–toluene, 1 : 1 v/v. Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane–hexane, 1 : 1 v/v) afforded **21** as shiny black–red crystals (0.070 g, 63%), mp 229–230 °C. ^{1}H NMR ($CDCl_3$): δ 8.28–8.26 (2 H, m), 8.08 (2 H, s), 7.80–7.77 (2 H, m), 7.73–7.70 (2 H, m), 7.65–7.63 (2 H, m), 7.39–7.37 (4 H, m), 2.84–2.71 (4 H, m), 1.62–1.53 (4 H, m), 1.39–1.32 (4 H, m), 1.28–1.21 (8 H, m), 0.83 (6 H, t, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 181.9, 143.7, 134.9, 134.4, 134.2, 133.2, 132.7, 131.4, 128.7, 127.2, 127.0, 126.3, 126.22, 126.19, 125.5 (2C), 122.1, 118.8, 36.2, 31.2, 29.6, 28.1, 22.5, 14.0. UV-vis (CH_2Cl_2): λ_{max} (lg ε) 350 (4.55), 427 (4.50) nm. MS (EI): *m*/*z* (%) = 792 (M^+, 78), 502 (100). Calcd. for $C_{44}H_{40}O_2S_6$: 792.13526. HRMS (EI): 792.13524 (+0.0 ppm).

Compound 23

To a stirred solution of compound **22**[18] (0.183 g, 0.60 mmol) in dry tetrahydrofuran (50 cm^3) at −78 °C under argon was added lithium diisopropylamide (0.44 cm^3 of a 1.5 M solution in cyclohexane, 0.66 mmol) and the resultant cloudy yellow mixture was stirred for 2 h at −78 °C. Compound **21** (0.045 g, 0.057 mmol) was dissolved in dry tetrahydrofuran (100 mL) with sonication and added to the reaction mixture *via* syringe over 1 h. The reaction mixture was stirred at −78 °C for another 1 h, whereupon it was allowed to slowly attain room temperature for 12 h. Evaporation of the solvent afforded a red residue which was dissolved in dichloromethane (100 cm^3), washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (silica gel, dichloromethane–hexane, 1 : 1 v/v) afforded an orange powder which was purified using a short column (silica gel, carbon disulfide) to give **23** as a yellow powder (0.058 g, 88%), mp 154–156 °C. ^{1}H NMR ($CDCl_3$):

δ 7.80–7.78 (0.6 H, m), 7.71–7.69 (1.4 H, m), 7.62–7.60 (2 H, m), 7.49–7.47 (2 H, m), 7.38–7.27 (8 H, m), 2.85–2.71 (4 H, m), 2.43 (1.9 H, s), 2.39 (1.9 H, s), 2.35 (4.1 H, s), 2.31 (4.1 H, s), 1.63–1.54 (4 H, m), 1.41–1.31 (4 H, m), 1.29–1.20 (8 H, m), 0.85 (4.1 H, t, J = 7.0 Hz), 0.81 (1.9 H, t, J = 7.0 Hz). UV-vis (CH_2Cl_2): λ_{max} (lg ε) 275 (4.74), 377 (4.51), 440 (4.73) nm. MS (ES): m/z (%) 1187 (100, $[M+K]^+$), 1171 (31, $[M+Na]^+$), 1148 (28, M^+). Calcd. for $C_{54}H_{52}S_{14}$: 1148.0159. HRMS (ES): 1148.0148 (−1.0 ppm).

Generation and ^{1}H NMR spectrum of the tetracation 23^{4+}

To half the volume of the NMR sample of **23** was added a solution of iodine (excess) in $CDCl_3$ to give a red precipitate which was filtered, dried *in vacuo*, dissolved in DMSO-d_6 and the ^{1}H NMR spectrum of $\mathbf{23}^{4+}$ was recorded. ^{1}H NMR (DMSO-d_6): δ 8.15 (2 H, s), 8.03–8.01 (2 H, m), 7.76–7.74 (4 H, m), 7.65–7.64 (2 H, m), 7.50–7.43 (4 H, m), 2.99 (12 H, s), 2.81 (4 H, t, J = 7.5 Hz), 1.54–1.47 (4 H, m), 1.35–1.29 (4 H, m), 1.23–1.17 (8 H, m), 0.78 (6 H, t, J = 7.0 Hz).

10-{4,6-Dihydro-*N*-tosylpyrrolo[3,4-*d*]-1,3-dithiol-2-ylidene}-anthracene-9(10*H*)-one (26)

Sodium tosylamide **25**[31] (2.68 g, 13.9 mmol) was suspended in dry acetonitrile (50 cm^3) and stirred under argon at 80 °C. Compound **10** (3.33 g, 6.93 mmol) was dissolved in a minimum of dry *N*,*N*-dimethylformamide (200 cm^3) stirred at 80 °C and transferred to the sodium tosylamide suspension over 10 min using a double ended needle and a positive pressure of argon. The dark brown reaction mixture was stirred for another 5 min at 80 °C before being cooled to 0 °C, using an ice bath, and concentrated under reduced pressure. To the residue was added water (150 cm^3) and the mixture was extracted with dichloromethane (3 × 100 cm^3). The combined organic phases were dried ($MgSO_4$), filtered through a plug of silica and concentrated *in vacuo*. Column chromatography (silica gel, dichloromethane until two minor by-products were off the column, then dichloromethane–ethyl acetate, 95 : 5 v/v) afforded **26** as an orange powder (2.77 g, 82%), mp 218–220 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.21 (2 H, d, J = 7.5 Hz), 7.76 (2 H, d, J = 8.0 Hz), 7.68 (2 H, d, J = 8.0 Hz), 7.61 (2 H, t, J = 7.5 Hz), 7.42 (2 H, t, J = 7.5 Hz), 7.30 (2 H, d, J = 8.5 Hz), 4.25 (4 H, s), 2.39 (3 H, s). ^{13}C NMR ($CDCl_3$): δ 183.4, 147.8, 144.3, 138.5, 133.3, 131.8, 130.6, 130.1, 127.3, 127.2, 127.1, 126.3, 126.0, 121.0, 52.4, 21.5. MS (EI): m/z (%) 489 (14, M^+), 91 (100). Calcd. for $C_{26}H_{19}NO_3S_3$: 489.05271. HRMS (EI): 489.05200 (−1.5 ppm).

10-{*N*-Tosylpyrrolo[3,4-*d*]-1,3-dithiol-2-ylidene}anthracene-9(10*H*)-one (27)

To a suspension of **26** (8.70 g, 17.8 mmol) in chlorobenzene (200 cm^3) was added DDQ (4.84 g, 21.3 mmol) and the mixture was refluxed for 1 h. The reaction mixture was cooled to room temperature and reduced to 50 mL *in vacuo*. The resulting suspension was chromatographed (silica gel column, dichloromethane) to give **27** as a yellow powder (7.98 g, 92%), mp 250–251 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.21 (2 H, d, J = 7.5 Hz), 7.90 (2 H, d, J = 8.0 Hz), 7.69 (2 H, d, J = 8.5 Hz), 7.64 (2 H, t, J = 7.5 Hz), 7.46 (2 H, t, J = 7.5 Hz), 7.26 (2 H, d, J = 8.0 Hz), 6.94 (2 H, s), 2.38 (3 H, s). ^{13}C NMR ($CDCl_3$): δ 183.9, 146.9, 145.6, 139.1, 135.2, 131.7, 131.1, 130.1, 127.4, 127.1, 126.9, 126.7, 125.7, 122.4, 110.8, 21.6. MS (PD): m/z = 486.6 (theory: 487.6). Anal. calcd. for $C_{26}H_{17}NO_3S_3$ (MW 487.62): C, 64.04; H, 3.51; N, 2.87. Found C, 63.80; H, 3.35; N, 2.92.

9-{*N*-Tosylpyrrolo[3,4-*d*]-1,3-dithiol-2-ylidene}-10-{4,5-bis-(methylsulfanyl)-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene (30)

To a solution of the phosphonate ester **22**[18] (0.359 g, 1.18 mmol) in dry tetrahydrofuran (50 mL) at −78 °C under argon was added lithium diisopropylamide (0.86 cm^3 of a 1.5 M solution in cyclohexane, 1.30 mmol) *via* syringe and the resultant cloudy yellow mixture was stirred for 1.5 h at −78 °C. Ketone **27** (0.500 g, 1.03 mmol) was dissolved in dry tetrahydrofuran (25 cm^3) and added to the reaction mixture *via* syringe over 30 min. The reaction mixture was stirred at −78 °C for another 2 h, whereupon it was allowed to slowly attain room temperature for 12 h. Evaporation of the solvent afforded a red residue which was dissolved in dichloromethane (100 cm^3), washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (silica gel, dichloromethane–cyclohexane, 2 : 1 v/v) afforded **30** as a yellow powder. Recrystallisation from dichloromethane–heptane gave yellow prisms suitable for X-ray crystallography (0.590 g, 86%), mp 259–260 °C. ^{1}H NMR ($CDCl_3$): δ 7.69 (2 H, d, J = 8.4 Hz), 7.66–7.64 (2 H, m), 7.56–7.54 (2 H, m), 7.33–7.30 (4 H, m), 7.25 (2 H, d, J = 8.4 Hz), 6.85 (2 H, s), 2.38 (3 H, s), 2.35 (6 H, s). ^{13}C NMR ($CDCl_3$): δ 145.3, 138.8, 135.3, 134.9, 134.8, 131.5, 130.1, 126.9, 126.7, 126.6, 126.5, 126.3, 125.9, 125.7, 125.3, 123.3, 110.5, 21.6, 19.1. UV-vis (CH_2Cl_2): λ_{max} (lg ε) 353 (4.31), 422 (4.42) nm. MS (PD): m/z = 665.0 (theory: 666.0). Anal. calcd. for $C_{31}H_{23}NO_2S_7$ (MW 665.98): C, 55.91; H, 3.48; N, 2.10. Found C, 55.93; H, 3.42; N, 2.09.

9-{*N*-Tosylpyrrolo[3,4-*d*]-1,3-dithiol-2-ylidene}-10-{4,5-bis-(butylsulfanyl)-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene (31)

This procedure is similar to the synthesis of **30** using compound **29**[18] (0.427 g, 1.10 mmol) in dry tetrahydrofuran (50 cm^3), lithium diisopropylamide (0.81 cm^3 of a 1.5 M solution in cyclohexane, 1.21 mmol) and ketone **27** (0.400 g, 0.82 mmol) in dry tetrahydrofuran (20 cm^3). Purification by column chromatography (silica gel, dichloromethane–cyclohexane, 1 : 1 v/v) afforded **31** as a yellow powder (0.560 g, 91%), mp 191–192 °C. ^{1}H NMR ($CDCl_3$): δ7.69 (2 H, d, J = 8.5 Hz), 7.66–7.64 (2 H, m), 7.60–7.58 (2H, m), 7.33–7.30 (4 H, m), 7.26 (2 H, d, J = 7.5 Hz), 6.85 (2 H, s), 2.84–2.72 (4 H, m), 2.38 (3 H, s), 1.61–1.55 (4 H, m), 1.44–1.36 (4 H, m), 0.89 (6 H, t, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 145.3, 138.6, 135.3, 135.0, 134.9, 132.0, 130.0, 126.9, 126.7, 126.62, 126.57, 126.2 (2C), 125.9, 125.2, 122.4, 110.5, 35.9, 31.7, 21.61, 21.58, 13.6. UV-vis (CH_2Cl_2): λ_{max} (lg ε) 353 (4.30), 423 (4.41) nm. MS (EI): m/z (%) 749 (100, M^+). Calcd. for $C_{37}H_{35}NO_2S_7$: 749.0713. HRMS (ES): 749.0725 (+1.6 ppm).

9-{Pyrrolo[3,4-*d*]-1,3-dithiol-2-ylidene}-10-{4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene (32)

Compound **30** (0.500 g, 0.751 mmol) was dissolved in dry degassed tetrahydrofuran–methanol, 2 : 1 v/v (50 cm^3). Sodium methoxide (2.2 cm^3 of a 30% solution in methanol, 11.3 mmol) was added to the solution and the reaction refluxed for 15 min under argon, in which time the colour changed from yellow to brown. The reaction mixture was cooled to room temperature, water was added (10 cm^3) and the mixture was concentrated to 10 cm^3 under reduced pressure. The residue was taken into dichloromethane (100 cm^3), washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (silica gel, dichloromethane–cyclohexane, 2 : 1 v/v) afforded **32** as a yellow powder which darkens upon standing (0.334 g, 87%), mp > 280 °C. ^{1}H NMR ($CDCl_3$): δ 8.17 (1 H, br s), 7.78–7.76 (2 H, m), 7.54–7.53 (2 H, m), 7.35–7.29 (4 H, m), 6.56 (2 H, d, J = 2.5 Hz), 2.36 (6 H, s). ^{13}C NMR ($CDCl_3$): δ 142.2, 135.4, 134.9, 130.6, 126.2 (2C), 126.0, 125.8, 125.3, 124.6, 124.1, 119.1, 109.0, 19.2. UV-vis (CH_2Cl_2): λ_{max} (lg ε) 362 (4.21), 428 (4.46) nm. MS (EI): m/z (%) 511 (100, M^+). Anal. calcd. for $C_{24}H_{17}NS_6$ (MW 511.79): C, 56.32; H, 3.35; N, 2.74. Found C, 56.54; H, 3.46; N, 2.76.

9-{Pyrrolo[3,4-*d*]-1,3-dithiol-2-ylidene}-10-{4,5-bis(butylsulfanyl)-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene (33)

By a procedure similar to the conversion of **30** into **32**, compound **31** (1.60 g, 2.13 mmol) in dry degassed tetrahydrofuran–methanol, 2 : 1 v/v (100 cm^3) with sodium methoxide (4.8 cm^3 of a 30% solution in methanol, 25 mmol) gave **33**. Purification by column chromatography (silica gel, dichloromethane–cyclohexane, 1 : 2 v/v) afforded **33** as a yellow solid. Recrystallisation from dichloromethane–heptane gave yellow–brown prisms, (1.05 g, 83%), mp 221–222 °C. ^{1}H NMR ($CDCl_3$): δ 8.13 (1 H, br s), 7.77–7.75 (2 H, m), 7.58–7.57 (2 H, m), 7.34–7.29 (4H, m), 6.52 (2H, d, J = 2.5 Hz), 2.84–2.79 (2H, m), 2.77–2.71 (2H, m), 1.61–1.55 (4 H, m), 1.44–1.36 (4 H, m), 0.88 (6 H, t, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 142.0, 135.4, 135.0, 131.1, 126.2 (2C), 126.1, 126.0, 125.2, 124.6, 123.0, 119.0, 109.0, 36.0, 31.7, 21.6, 13.6. UV-vis (CH_2Cl_2): λ_{max} (lg ε) 368 (4.21), 429 (4.45) nm. MS (PD): m/z = 596.7 (theory: 596.0). Anal. calcd. for $C_{30}H_{29}NS_6$ (MW 595.95): C, 60.46; H, 4.90; N, 2.35. Found C, 60.17; H, 4.87; N, 2.27.

9-{*N*-Methylpyrrolo[3,4-*d*]-1,3-dithiol-2-ylidene}-10-{4,5-bis-(butylsulfanyl)-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene (34)

To a stirred suspension of sodium hydride (0.020 g of a 60% dispersion in mineral oil, 0.50 mmol) in dry degassed *N*,*N*-dimethylformamide (20 cm^3) under nitrogen was added a degassed solution of **33** (0.100 g, 0.168 mmol) in dry *N*,*N*-dimethylformamide (10 cm^3) over 5 min, whereupon the reaction mixture turned red. The reaction was stirred for another 15 min at room temperature followed by addition of methyl iodide (0.10 cm^3, 0.227 g, 1.60 mmol): the colour turned yellow. Stirring was continued for a further 15 min after which time the reaction mixture was concentrated, taken into dichloromethane (50 cm^3), washed with water and dried ($MgSO_4$). Purification by column chromatography (silica gel, dichloromethane–cyclohexane, 1 : 1 v/v) afforded **34** as a yellow powder. Recrystallisation from dichloromethane–heptane gave yellow prisms (0.099 g, 97%), mp 214–215 °C. ^{1}H NMR ($CDCl_3$): δ 7.77–7.75 (2 H, m), 7.58–7.56 (2 H, m), 7.33–7.28 (4 H, m), 6.37 (2 H, s), 3.60 (3 H, s), 2.85–2.79 (2 H, m), 2.77–2.72 (2 H, m), 1.62–1.54 (4 H, m), 1.45–1.37 (4 H, m), 0.89 (6 H, t, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 141.9, 135.5, 135.0, 131.0, 126.2, 126.1, 126.0 (2C), 125.1, 124.4, 123.0, 118.0, 112.8, 37.1, 36.0, 31.7, 21.6, 13.6. UV-vis (CH_2Cl_2): λ_{max} (lg ε) 267 (4.32), 366 (4.19), 433 (4.46) nm. MS (PD): m/z = 611.4 (theory: 610.0). Anal. calcd. for $C_{31}H_{31}NS_6$ (MW 609.98): C, 61.04; H, 5.12; N, 2.30. Found C, 60.92; H, 5.17; N, 2.32.

9-{4-Formylpyrrolo[3,4-*d*]-1,3-dithiol-2-ylidene}-10-{4,5-bis-(methylsulfanyl)-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene (35)

Phosphorus oxychloride (0.042 cm^3, 0.069 g, 0.450 mmol) was added to dry *N*,*N*-dimethylformamide (2 cm^3) under nitrogen and stirred for 10 min at room temperature. A solution of **32** (0.150 g, 0.293 mmol) in dry *N*,*N*-dimethylformamide (2 cm^3) was added dropwise over 5 min, whereupon the resulting dark violet reaction mixture was stirred for another 20 min. A 10% aqueous solution of sodium acetate (15 cm^3) and water (10 cm^3) was added to the reaction mixture, which caused precipitation of a yellow solid. The solid was filtered and redissolved in dichloromethane (50 cm^3), washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was columned (silica gel, dichloromethane–ethyl acetate, 1 : 1 v/v) to give **35** as a yellow powder (0.145 g, 92%), mp >280 °C (yellow microcrystals from chlorobenzene–heptane, decomp.). ^{1}H NMR ($CDCl_3$): δ 9.45 (1 H, s), 9.07 (1 H, br s), 7.76–7.76 (2 H, m), 7.60–7.56 (2 H, m), 7.39–7.34 (4 H, m), 6.83 (1 H, d, J = 2.8 Hz), 2.37 (6 H, s). UV-vis (CH_2Cl_2): λ_{max} (lg ε) 306 (4.36), 358 (4.18), 425 (4.45) nm. MS (EI): m/z (%) 539 (100, M^+). Accurate mass calcd. for $C_{25}H_{17}NOS_6$: 538.96345. HRMS (EI): 538.96323 (−0.4 ppm).

9-{4-Formylpyrrolo[3,4-*d*]-1,3-dithiol-2-ylidene}-10-{4,5-bis(butylsulfanyl)-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene (36)

By analogy with the synthesis of aldehyde **35**, phosphorus oxychloride (0.036 cm^3, 0.059 g, 0.385 mmol) in dry *N*,*N*-dimethylformamide (2 cm^3) with **33** (0.153 g, 0.257 mmol) in dry *N*,*N*-dimethylformamide (2 cm^3) and column chromatography (silica gel, dichloromethane–ethyl acetate, 1 : 1 v/v) afforded **36** as a yellow powder (0.146 g, 91%), mp 169–170 °C. ^{1}H NMR ($CDCl_3$): δ 9.86 (1 H, br s), 9.32 (1 H, s), 7.73–7.59 (4 H, m), 7.36–7.31 (4 H, m), 6.74 (1 H, br s), 2.83–2.69 (4 H, m), 1.59–1.50 (4 H, m), 1.41–1.33 (4 H, m), 0.88–0.85 (6 H, m). UV-vis (CH_2Cl_2): λ_{max} (lg ε) 306 (4.37), 359 (4.20), 427 (4.46) nm. MS (PD): m/z = 622.9 (theory: 624.0). Anal. calcd. for $C_{31}H_{29}NOS_6$ (MW 623.96): C, 59.67; H, 4.68; N, 2.24. Found C, 59.82; H, 4.75; N, 2.23.

Compound 38

Compound **35** (0.038 g, 0.070 mmol) and 2,4,5,7-tetranitrofluorene **37**[24a] (0.029 g, 0.084 mmol) were dissolved in dry degassed *N*,*N*-dimethylformamide (2 cm^3) and stirred at room temperature under argon for 2.5 h. The black mixture was concentrated *in vacuo* and the residue purified by column chromatography (silica gel, dichloromethane) to give **38** as a black powder (0.049 g, 80%), mp >280 °C. ^{1}H NMR (DMSO-d_6): δ 12.32 (1 H, s), 9.57 (1 H, s), 9.16 (1 H, s), 8.77–8.66 (2 H, m), 7.74–7.65 (3 H, m), 7.58–7.55 (3 H, m), 7.48–7.41 (4 H, m), 2.36–2.33 (6 H, m). UV-vis (CH_2Cl_2): λ_{max} (lg ε) 356 (4.51), 427 (4.47), 539 (4.22) nm. MS (PD): m/z = 867.8 (theory: 868.0). Accurate mass calcd. for $C_{38}H_{21}N_5O_8S_6$: 866.97144. HRMS (EI): 866.97188 (+0.5 ppm).

Compound 39

By analogy with the synthesis of **38** compound **36** (0.025 g, 0.040 mmol) and 2,4,5,7-tetranitrofluorene **37** (0.015 g, 0.043 mmol) in dry degassed *N*,*N*-dimethylformamide (2 cm^3) and column chromatography (silica gel, dichloromethane) afforded **39** as a black powder (0.033 g, 87%), mp 192–194 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 9.05 (0.2 H, s), 8.91 (0.2 H, s), 8.83 (0.8 H, s), 8.74 (0.8 H, s), 8.70 (2 H, s), 8.52 (1 H, br s), 7.64–7.58 (4 H, m), 7.48–7.41 (3 H, m), 7.31–7.19 (2 H, m), 6.87 (1 H, s), 2.73–2.70 (4 H, m), 1.53–1.47 (4 H, m), 1.39–1.29 (4 H, m), 0.89–0.81 (6 H, m). UV-vis (CH_2Cl_2): λ_{max} (lg ε) 357 (4.50), 428 (4.48), 538 (4.23) nm. MS (PD): m/z = 951.2 (theory: 952.2). Anal. calcd. for $C_{44}H_{33}N_5O_8S_6$ (MW 952.16): C, 55.50; H, 3.49; N, 7.36. Found C, 55.51; H, 3.67; N, 7.22.

Crystallographic studies

X-Ray diffraction experiments (see Table 2) were carried out on a SMART 3-circle diffractometer with a 1K CCD area detector, with graphite-monochromated Mo–K_α radiation (λ = 0.71073 Å) and a Cryostream open-flow N_2 cryostat (Oxford Cryosystems). Full sphere of reciprocal space was covered by five sets of 0.3° ω scans, each set with different φ and/or 2θ angles. The intensities were corrected for absorption by numerical integration based on real crystal shape. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[32] Full crystallographic data, excluding structure factors, are provided in Electronic Supplementary Information and have been deposited at the Cambridge Crystallographic Data Centre. CCDC reference numbers(s) 197523–197525. See http://www.rsc.org/suppdata/ob/b2/b211153p/ for crystallographic files in .cif or other electronic format.

Table 2 Crystal data

Compound	**30**	**33**	**34**
Formula	$C_{31}H_{23}NO_2S_7$	$C_{30}H_{29}NS_6$	$C_{31}H_{31}NS_6$
Formula weight	665.92	595.90	609.93
T/K	120	120	296
Symmetry	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)
a/Å	14.013(1)	9.226(1)	12.276(3)
b/Å	14.151(1)	12.541(1)	9.688(2)
c/Å	17.216(1)	12.760(2)	25.605(5)
α/°	88.99(1)	99.64(1)	90
β/°	70.38(1)	95.44(1)	100.73(1)
γ/°	68.04(1)	108.73(1)	90
V, Å^3	2959.5(3)	1360.9(2)	2992(1)
Z	4	2	4
μ/mm^{-1}	0.56	0.52	0.48
Refls collected	33907	16873	35752
Unique refls	15459	7114	7991
R_{int}	0.025	0.033	0.053
Refls $F^2>2\sigma(F^2)$	12754	6268	5753
$R[F^2>2\sigma(F^2)]$	0.035	0.031	0.049
w$R(F^2)$, all data	0.092	0.084	0.133
$\Delta\rho$/eÅ^{-3}	0.47, −0.45	0.45, −0.30	0.40, −0.42

Acknowledgements

We thank EPSRC and the Danish Research Academy (C. A. C.) for funding, and Dr D. F. Perepichka for providing a sample of compound **37**.

References

1 N. Martín and E. Ortí, in *Handbook of Advanced Electronic and Photonic Materials and Devices*, ed. H. S. Nalwa, vol. 3, Academic Press, New York, 2001, Chapter 6, 245–265.
2 (*a*) M. R. Bryce, M. A. Coffin, M. B. Hursthouse, A. I. Karaulov, K. Müllen and H. Scheich, *Tetrahedron Lett.*, 1991, **32**, 6029; (*b*) N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela and R. Viruela, *J. Org. Chem.*, 1998, **63**, 1268; (*c*) I. Pérez, S.-G. Liu, N. Martín and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 3796; (*d*) S.-G. Liu, I. Pérez, N. Martín and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 9092.
3 (*a*) M. R. Bryce, A. J. Moore, M. Hasan, G. J. Ashwell, A. T. Fraser, W. Clegg, M. B. Hursthouse and A. I. Karaulov, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1450; (*b*) A. S. Batsanov, M. R. Bryce, M. A. Coffin, A. Green, R. E. Hester, J. A. K. Howard, I. K. Lednev, N. Martín, A. J. Moore, J. N. Moore, E. Ortí, L. Sánchez, M. Savíron, P. M. Viruela, R. Viruela and T-Q. Ye, *Chem. Eur. J.*, 1998, **4**, 2580; (*c*) A. E. Jones, C. A. Christensen, D. F. Perepichka, A. S. Batsanov, A. Beeby, P. J. Low, M. R. Bryce and A. W. Parker, *Chem. Eur. J.*, 2001, **7**, 973.
4 (*a*) N. Martín, L. Sánchez and D. M. Guldi, *Chem. Commun.*, 2000, 113; (*b*) D. Guldi, L. Sánchez and N. Martín, *J. Phys. Chem. B*, 2001, **105**, 7139.
5 (*a*) S. Triki, L. Ouahab, D. Lorcy and A. Robert, *Acta Crystallogr., Sect . C*, 1993, **49**, 1189; (*b*) M. R. Bryce, T. Finn, A. S. Batsanov, R. Kataky, J. A. K. Howard and S. B. Lyubchik, *Eur. J. Org. Chem.*, 2000, 1199; (*c*) D. F. Perepichka, M. R. Bryce, I. F. Perepichka, S. B. Lyubchik, C. A. Christensen, N. Godbert, A. S. Batsanov, E. Levillain, E. J. L. McInnes and J. P. Zhao, *J. Am. Chem. Soc.*, 2002, **124**, 14227.
6 M. A. Herranz, N. Martín, L. Sánchez, J. Garín, J. Orduna, R. Alcalá, B. Villacampa and C. Sánchez, *Tetrahedron*, 1998, **54**, 11651.
7 (*a*) G. J. Marshallsay and M. R. Bryce, *J. Org. Chem.*, 1994, **59**, 6847; (*b*) N. Martín, I. Pérez, L. Sánchez and C. Seoane, *J. Org. Chem.*, 1997, **62**, 870; (*c*) N. Martín, I. Pérez, L. Sánchez and C. Seoane, *J. Org. Chem.*, 1997, **62**, 5690.
8 (*a*) T. Finn, M. R. Bryce, A. S. Batsanov and J. A. K. Howard, *Chem. Commun.*, 1999, 1835; (*b*) N. Godbert, A. S. Batsanov, M. R. Bryce and J. A. K. Howard, *J. Org. Chem.*, 2001, **66**, 713; (*c*) C. A. Christensen, A. S. Batsanov, M. R. Bryce and J. A. K. Howard, *J. Org. Chem.*, 2001, **66**, 3313.
9 N. Godbert and M. R. Bryce, *J. Mater. Chem.*, 2002, **12**, 27.
10 (*a*) G. Kodis, P. A. Liddell, L. de la Garza, A. L. Moore, T. A. Moore and D. Gust, *J. Mater. Chem.*, 2002, **12**, 2100; (*b*) D. M. Guldi, *Chem. Soc. Rev.*, 2002, **31**, 22.
11 (*a*) Y. Yamashita, Y. Kobayashi and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1052; (*b*) A. J. Moore and M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1991, 157; (*c*) C. Boulle, O. Desmars, N. Gautier, P. Hudhomme, M. Cariou and A. Gorgues, *Chem. Commun.*, 1999, 2197.
12 M. R. Bryce, A. J. Moore, D. Lorcy, A. S. Dhindsa and A. Robert, *J. Chem. Soc., Chem. Commun.*, 1990, 471.
13 (*a*) M. R. Bryce, T. Finn and A. J. Moore, *Tetrahedron Lett.*, 1999, **40**, 3221; (*b*) M. R. Bryce, T. Finn, A. J. Moore, A. S. Batsanov and J. A. K. Howard, *Eur. J. Org. Chem.*, 2000, 51; (*c*) N. Godbert, M. R. Bryce, S. Dahaoui, A. S. Batsanov, J. A. K. Howard and P. Hazendonk, *Eur. J. Org. Chem.*, 2001, 749.
14 Preliminary communication: C. A. Christensen, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, J. O. Jeppersen and J. Becher, *Chem. Commun.*, 1999, 2433.
15 R. Gompper and E. Kutter, *Chem. Ber.*, 1965, **98**, 2825.
16 J. O. Jeppesen, K. Takimiya, N. Thorup and J. Becher, *Synthesis*, 1999, 803.
17 (*a*) J. Llacay, M. Mas, E. Molins, J. Veciana, D. Powell and C. Rovira, *Chem. Commun.*, 1997, 659; (*b*) J. Llacay, J. Veciana, J. Vidal-Gancedo, J. L. Bourdelande, R. Gonzalez-Moreno and C. Rovira, *J. Org. Chem.*, 1998, **63**, 5201; (*c*) P. Hudhomme, S. G. Liu, D. Kreher, M. Cariou and A. Gorgues, *Tetrahedron Lett.*, 1999, **40**, 2927; (*d*) P. Belik, A. Gügel, J. Spickermann and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 78.
18 A. J. Moore and M. R. Bryce, *Tetrahedron Lett.*, 1992, **33**, 1373 and references therein.
19 R. Appel, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 801.
20 N. Gautier, N. Mercier, A. Riou, A. Gorgues and P. Hudhomme, *Tetrahedron Lett.*, 1999, **40**, 5997.
21 M. A. Herranz and N. Martín, *Org. Lett.*, 1999, **1**, 2005.
22 J. O. Jeppensen, K. Takimiya, F. Jensen, T. Brimert, K. Nielsen, N. Thorup and J. Becher, *J. Org. Chem.*, 2000, **65**, 5794.
23 J. Becher, T. Brimert, J. O. Jeppersen, J. Z. Pedersen, R. Zubarev, T. Bjørnholm, N. Reitzel, T. R. Jensen, K. Kjaer and E. Levillain, *Angew. Chem., Int. Ed.*, 2001, **40**, 2497.
24 (*a*) N. M. Semenenko, V. N. Abramov, N. V. Kravchenko, V. S. Trushina, P. G. Buyanovskaya, V. L. Kashina and I. V. Mashkevich, *Zh. Obsch. Khim.*, 1985, **55**, 324; (*b*) D. F. Perepichka, I. F. Perepichka, M. R. Bryce, N. I. Sokolov and A. J. Moore, *J. Mater. Chem.*, 2001, **11**, 1772; (*c*) I. F. Perepichka, D. F. Perepichka, S. B. Lyubchik, M. R. Bryce, A. S. Batsanov and J. A. K. Howard, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1546.
25 S. Frenzel and K. Müllen, *Synth. Met.*, 1996, **80**, 175.
26 For consideration of other TTFAQ–acceptor diads see: (*a*) M. A. Herranz, S. González, I. Pérez and N. Martín, *Tetrahedron*, 2001, **57**, 725; (*b*) M. Otero, M. A. Herranz, C. Seoane, N. Martín, J. Garín, J. Orduna, R. Alcalá and B. Villacampa, *Tetrahedron*, 2002, **58**, 7463.
27 I. F. Perepichka, D. F. Perepichka, M. R. Bryce, L. M. Goldenberg, L. G. Kuz'mina, A. F. Popov, A. Chesney, A. J. Moore, J. A. K. Howard and N. I. Sokolov, *Chem. Commun.*, 1998, 819.
28 R. S. Rowland and R. J. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384.
29 (*a*) J. Lau, M. B. Nielsen, N. Thorup, M. P. Cava and J. Becher, *Eur. J. Org. Chem.*, 1999, 3335; (*b*) J. O. Jeppesen, K. Takimiya, F. Jensen and J. Becher, *Org. Lett.*, 1999, **1**, 1291; (*c*) J. G. Hansen, K. S. Bang, N. Thorup and J. Becher, *Eur. J. Org. Chem.*, 2000, 2135.
30 R. L. Beddoes, L. Dalton, J. A. Joule, O. S. Mills, J. D. Street and C. I. F. Watt, *J. Chem. Soc., Perkin Trans. 2*, 1986, 787.
31 F. Bottino, M. D. Grazia, P. Finocchiaro, F. R. Fronczek, A. Mamo and S. Pappalardo, *J. Org. Chem.*, 1988, **53**, 3521.
32 *SHELXTL*, Version 5.10, Bruker AXS, Madison, Wisconsin, USA, 1997.