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Synthesis and intramolecular charge-transfer properties of new tetrathiafulvalene–σ-tetracyanoanthraquinodimethane diad (TTF–σ-TCNAQ) and triad (TTF–σ-TCNAQ–σ-TTF) molecules

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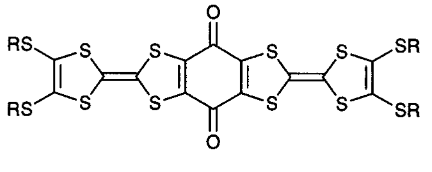
We report the use of functionalised electron acceptor tetracyanoanthraquinodimethane (TCNAQ) units in the synthesis of novel diad D–σ-A compounds **6** and **7** [D = tetrathiafulvalenyl (TTF) and ferrocenyl] and the triad TTF–σ-TCNAQ–σ-TTF assembly **8**. Compounds **6–8** display a very weak, broad, low-energy intramolecular charge-transfer band in the UV–VIS spectra. Nanosecond laser flash photolysis of compound **6** did not lead to any new transient absorptions in the 300–800 nm region, suggesting that if a charge-separated species is formed upon excitation, then back electron transfer occurs very rapidly to regenerate the ground state. Cyclic voltammetry of compounds **6–8** shows that reversible oxidation processes occur for the TTF and ferrocene moieties, and a reversible two-electron reduction occurs for the TCNAQ moiety. Spectroelectrochemical studies on compound **6** have enabled the redox processes to be assigned to the sequential formation of the TTF radical cation and dication upon oxidation, and the TCNAQ dianion upon reduction. Simultaneous electrochemistry and EPR (SEEPR) experiments provide further evidence for intramolecular interaction between the TTF and TCNAQ moieties in compound **6**. Quantum mechanical calculations on compound **6**, performed by the AM1 method, predict that in its minimum energy conformation the TTF and TCNAQ moieties are approximately orthogonal to one another, with the TCNAQ unit folded into a butterfly conformation.

Tetrathiafulvalene (TTF) and its derivatives are famous as electron donor components of charge transfer complexes and radical ion salts which are conductive in the solid state.[1] One of the many prerequisites for electronic conduction in these systems is the formation of partially-filled energy bands (mixed-valence stacks).[2] For a complex or salt of general formula $D_n:A_m$ (D = donor; A = acceptor) this is generally achieved in one of two ways: (i) $n = m$ and there is partial charge transfer from D to A, *e.g.* TTF–TCNQ,[3] for which the degree of charge transfer, $\rho = 0.59$. This situation requires a delicate balance between the ionisation potential of the donor and the electron affinity of the acceptor. (ii) Alternatively, and more commonly, $n \neq m$ and there is complete charge transfer from D to A ($\rho = 1$), *e.g.* $Et_3NH^+(TCNQ_2)^{\cdot -}$. In the crystallisation of a charge-transfer salt, it is notoriously difficult to control the stoichiometry of the D and A components. Within the TTF–TCNQ arena, one approach to this problem has been to synthesise dimeric TTFs (TTF–σ-TTF and TTF–π-TTF) of which many examples are known,[4] and dimeric TCNQs, which are rare.[5] Becker *et al.*[6] have developed the concept of D–A–D and A–D–A triads (with varied extent of conjugation between the D and A fragments) as charge transfer systems with predetermined control over the D and A stoichiometry, by virtue of the D and A fragments being integral parts of a single molecule. Other workers have extended these ideas to include a range of new systems.[7] For example, several D–TCNQ–D systems (D = electron rich benzene derivative)[6] and A–TTF–A systems (A = electron deficient benzene derivative[7a,b] or bipyridinium dication[8]) have been studied.

In this context, the covalent attachment of TTF to TCNQ has obvious appeal, but it has proved to be a great challenge.[9] One example of a TTF–σ-TCNQ molecule has been prepared by a low-yielding and very lengthy synthesis, using 5-bromo-2-(2-hydroxyethoxy)-TCNQ as the acceptor component.[10] Very recently, Frenzel and Müllen studied the solution electrochemistry and charge-transfer properties of the interesting bis-carbonyl bridged bis-TTF system **1** as a conjugated TTF–A–TTF molecule, and they identified the derived TCNQ system as a target for future studies.[11] We now present the synthesis, electrochemistry and intramolecular charge-transfer properties of new TTF–σ-TCNAQ and TTF–σ-TCNAQ–σ-TTF systems and a related ferrocene–σ-TCNAQ molecule (TCNAQ = 11,11,12,12-tetracyanoanthraquinodimethane). Our approach is based upon the use of the readily-accessible TCNAQ derivatives **4** and **5**[12] as the functionalised TCNQ component (Scheme 1).



1 R = n-C_4H_9, n-C_6H_{13}

Results and Discussion

For the present work the key features of TCNAQ[12] are: (i) although it is a weaker acceptor than TCNQ, it still has a reasonably high electron affinity [$E_{1/2}$ – 0.285 V (a two-electron wave) in MeCN *vs.* SCE];[12a,b] (ii) in contrast to TCNQ (which is essentially planar) TCNAQ adopts a 'butterfly' conformation,[13] and we reasoned that this non-planarity should suppress the rapid formation of insoluble intermolecular charge-transfer complexes with functionalised TTF derivatives, thereby allowing covalent linkage of the acceptor to TTF. Indeed, unsubstituted TCNAQ was reported to interact with π-electron donors (including TTF) to form weak intermolecular

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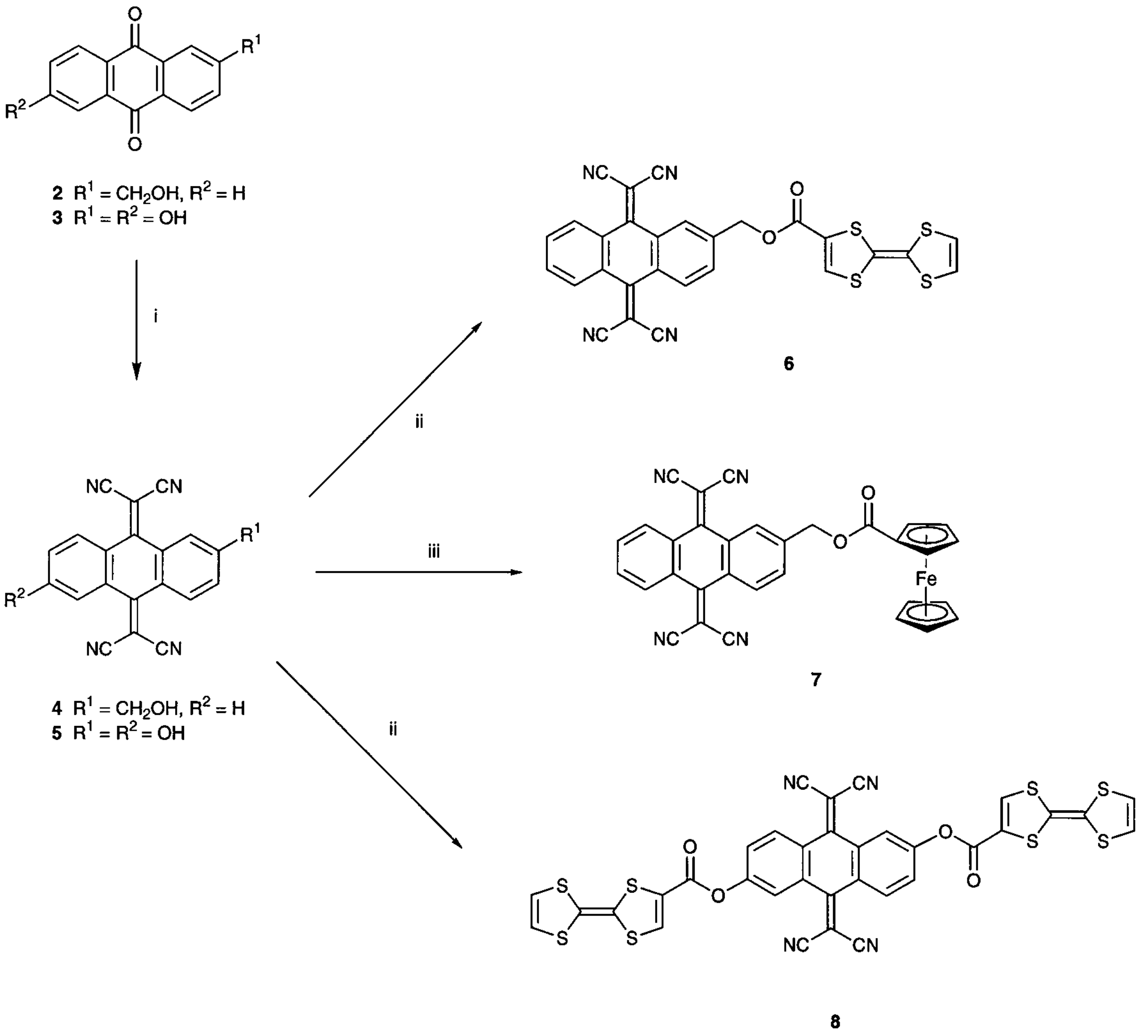


Scheme 1 *Reagents and conditions*: i, malononitrile, $TiCl_4$, pyridine, β-alanine, CH_2Cl_2, reflux; ii, tetrathiafulvalenecarbonyl chloride, Et_3N, CH_2Cl_2, 20 °C; iii, ferrocenecarbonyl chloride, Et_3N, CH_2Cl_2, 20 °C

complexes which were unstable and readily dissociated in solution.[12c]

Synthesis

The preparation of the compounds **4** and **5** from anthraquinone derivatives **2** and **3**, respectively, followed the literature procedure (titanium tetrachloride-mediated Knoevenagel condensation of malononitrile in pyridine in the presence of β-alanine).[12d] We note that the presence of β-alanine, as a weakly basic catalyst, was essential for the formation of **4** and **5**, although it is not needed for the synthesis of unsubstituted TCNAQ[12a–c] and several other derivatives which do not contain alcohol substituents.[14] (β-Alanine has been used previously as the base for condensation of cyclohexane-1,4-dione with malononitrile.[15]) Alcohol **4** reacted with tetrathiafulvalenecarbonyl chloride and ferrocenecarbonyl chloride to form the TCNAQ–σ-TTF and TCNAQ–σ-Fc systems **6** and **7**, respectively (30–40% yield) and diol **5** reacted similarly with two equivalents of TTF-carbonyl chloride to furnish the TTF–σ-TCNAQ–σ-TTF assembly **8** (30% yield). Compounds **6–8** were isolated as very dark coloured, air-stable solids. Their structures were unambiguously assigned as covalent D–σ–A molecules, and not intermolecular $D^{\cdot +}$ $A^{\cdot -}$ charge-transfer complexes, on the basis of elemental analysis, mass spectrometric, IR and ^1H NMR spectroscopic data.

Electrochemical and spectroscopic studies

The solution electrochemistry of compounds **6–8** has been studied by cyclic voltammetry (CV) and the data are collated in Table 1. Scanning anodically, compound **6** exhibits two reversible one-electron oxidation waves to form, sequentially, the radical cation and dication of the TTF moiety and one reversible two-electron wave is observed on the cathodic scan, corresponding to the reduction of the TCNAQ system to the dianion.[12a,b] Consequently, for compound **8** all three redox waves correspond to two-electron transfer processes, demonstrating that the two TTF rings of **8** act as independent redox units. There is no evidence for interaction of the donor and acceptor moieties in the CV of compounds **6–8**. We also note that the CV of model TTF compound **9** was unchanged by

Table 1 Cyclic voltammetric data, *vs.* Ag/AgCl, for compounds **6–8**, together with data for TTF and TCNAQ presented for comparison

compound	$E_1^{1/2}$ (ox)/V	$E_2^{1/2}$ (ox)/V	$E^{1/2}$ (red)/V
6[a]	+0.52 (1e)	+0.94 (1e)	−0.31 (2e)
7[a]	+0.71 (1e)		−0.31 (2e)
8[b]	+0.53 (2e)	+0.90 (2e)	−0.20 (2e)
TTF[a]	+0.34 (1e)	+0.74 (1e)	
TCNAQ[c]			−0.28 (2e)

[a] Solvent MeCN, electrolyte Bu_4NClO_4. [b] Solvent MeCN–CH_2Cl_2, electrolyte Bu_4NClO_4. [c] Solvent MeCN, electrolyte Et_4NBF_4.

the addition of an equimolar amount of model TCNAQ derivative **10**. The CV of compound **8** is shown in Fig. 1. These data are notable as they demonstrate remarkably clean amphoteric redox behaviour for TTF-based donor–acceptor derivatives.[16] In this respect the CV of **8** is qualitatively similar to that of system **1** which undergoes a single-electron reduction to the quinone anion radical, and two-stage oxidation of the TTF units to reach the tetracation.[11] For compound **7** the expected one-electron ferrocene/ferrocenium redox couple, and the two-electron reduction of TCNAQ were observed. We note that the redox potential of the TTF and ferrocene moieties are raised slightly by the ester substituent, in agreement with previous studies on TTF esters[17] and ferrocene esters.[18]

The absorption spectra of the radical cation, dication and dianion of **6** were obtained by spectroelectrochemistry within a potential range of -0.7 to $+1.5$ V (Fig. 2). At a potential of -0.6 V, a peak with a large extinction coefficient is visible at 520 nm which is assigned to the dianion $\mathbf{6}^{2-}$ and/or the radical anion $\mathbf{6}^{\cdot -}$.[12a] On oxidation of the system at a potential of $+0.8$ V the spectrum displays a sharp band at 430 nm and two weak shoulders at 500 and 580 nm which can be assigned to the TTF radical cation.[19] On increasing the potential, the absorption of the radical cation steadily decreased and in the spectrum obtained at $+1.2$ V a new band appeared at 500 nm, assigned to the formation of TTF dication $\mathbf{6}^{2+}$. These assignments were supported by complementary spectroelectrochemical studies on unsubstituted TTF and compound **4**, which gave absorption bands at similar wavelengths.

The frequency of the nitrile stretching band of TCNQ is known to be sensitive to the charge distribution which is localised on the $C(CN)_2$ groups of the acceptor molecule (ν_{max} 2180 and 2225 cm^{-1} are characteristic of $TCNQ^{\cdot -}$ and $TCNQ^0$, respectively).[15a,20] The corresponding data for TCNAQ anions are not available as stable salts have not been isolated.[12] For compounds **6–8** the CN absorption was at essentially the same frequency (ν_{max} 2222–2225 cm^{-1}) as in the starting materials **4** and **5** (ν_{max} 2221 cm^{-1}) which could imply that there is very little charge transfer in compounds **6–8**. However, we must be very tentative about this conclusion, especially in the light of Yamashita's observation that the nitrile stretching frequency of heterocyclic analogues of TCNAQ (with the outer benzene rings replaced by 1,2,5-thiadiazole rings) cannot be correlated with the degree of charge transfer.[21]

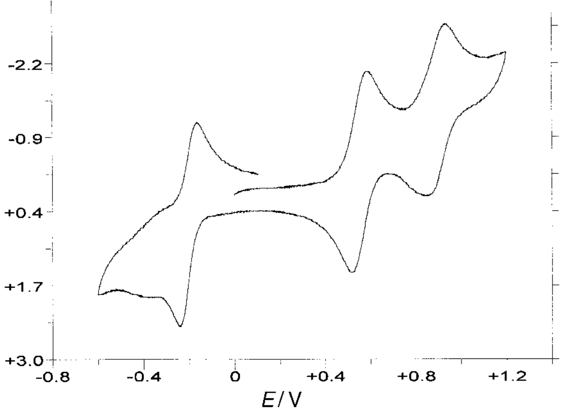


Fig. 1 Cyclic voltammogram of compound **8** *vs.* Ag/AgCl

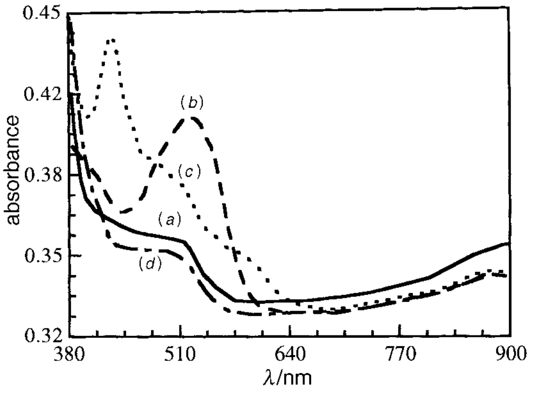
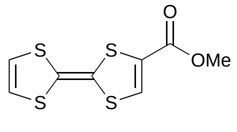


Fig. 2 Visible spectra of compound **6** measured at different potentials *vs.* Ag wire; (*a*) open circuit, (*b*) -0.6, (*c*) $+0.8$ and (*d*) $+1.2$ V

The UV–VIS spectrum of compounds **6** and **8** in acetonitrile showed, in addition to the usual TCNAQ[12a] and TTF[19] absorption bands, a very weak ($\varepsilon < 300$) broad absorption band in the λ 420–680 nm region which points to a weak charge transfer interaction, responsible for the dark colour of these compounds. Fig. 3 shows the UV–VIS spectrum of compound **6**. Compound **7** similarly showed a very weak band in the λ 420–660 nm region from the ferrocene fragment to the acceptor moiety. The spectra were recorded at various concentrations of compounds **6–8**, and the extinction coefficient of this low energy band varied in accordance with the Beer–Lambert law. We, therefore, assign this band to an intramolecular (rather than an intermolecular) charge-transfer band.



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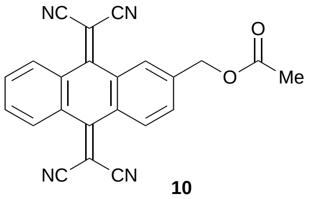

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As a model TTF derivative for comparison, we synthesised 4-methoxycarbonyltetrathiafulvalene **9**, which displayed a quite different UV–VIS spectrum: the lowest energy band was at λ_{max} 420 nm, with a higher extinction coefficient than that of the lowest energy band for **6** and **8**. The UV–VIS spectrum of an equimolar mixture of **9** and **10** in acetonitrile was a superimposition of the spectra of the two components, with no evidence for intermolecular interactions between the two molecules. Taken together these data strongly suggest that there is very weak intramolecular charge-transfer from the TTF unit(s) to the TCNAQ acceptor in compounds **6** and **8**. Consistent with the very weak charge-transfer properties, electrical conductivity was not observed for compounds **6–8** ($\sigma_{rt} = < 10^{-8}$ S cm^{-1}, two-probe, compressed pellet measurement.)

To provide further qualitative evidence for intramolecular interaction of the TTF and TCNAQ moieties in compound **6** we performed simultaneous electrochemistry and EPR

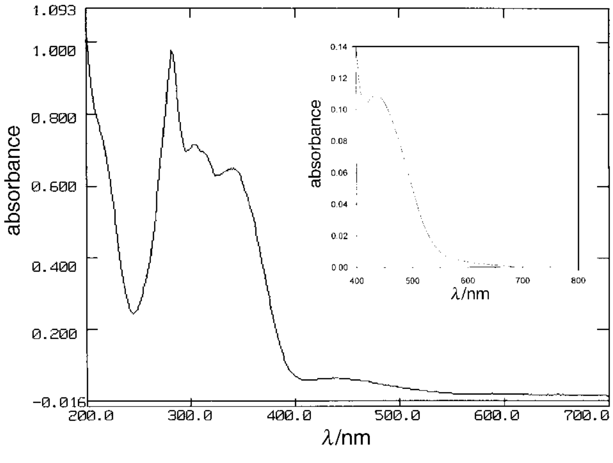

Fig. 3 UV–VIS spectrum of compound **6** in acetonitrile. The inset shows an expansion of the intramolecular charge transfer band observed in the 420–680 nm region.

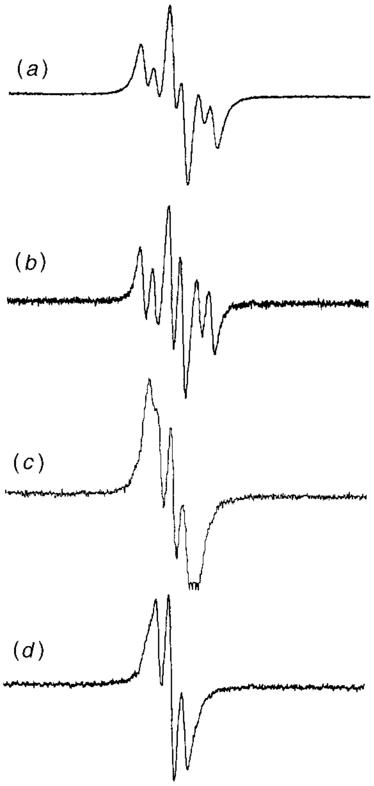

Fig. 4 SEEPR in CH_2Cl_2, tetrabutylammonium perchlorate carrier (0.1 M); (*a*) compound **9**, 10^{-3} M, +700 mV (*vs.* AgCl), (*b*) compound **9** and compound **10**, both 10^{-3} M, +700 mV, (c) compound **6**, 10^{-3} M, +568 mV and (*d*) compound **6**, 8×10^{-5} M, +677 mV

(SEEPR) experiments. Oxidation of a dichloromethane solution of model TTF compound **9** gave the EPR spectrum shown in Fig. 4(*a*), arising from the cation radical species. Performing the same experiment in the presence of an equimolar amount of model TCNAQ derivative **10** gave rise to a very similar EPR spectrum [Fig. 4(*b*)] suggesting there is no significant intermolecular interaction between the two species. However, upon oxidation of a solution of the conjugate species **6** to generate the cation radical [at the same concentration as used in Fig. 4(*a*) and (*b*)] a very different EPR spectrum was obtained [Fig. 4(*c*)]. We also obtained the spectrum of compound **6** at considerably lower concentration to remove any possible aggregation effects: a sharper spectrum was observed [Fig. 4(*d*)] which is still decisively different from that of compound **9**. These SEEPR data demonstrate that the spin density distribution in the cation radical of **6** is modulated intramolecularly by the adjacent TCNAQ moiety.

We have considered the possibility that charge transfer could be enhanced in the excited state, and to this end we studied the fluorescence of diad **6**. However, no fluorescence ($\Phi_f = < 10^{-4}$) was observed in acetonitrile solution. Similarly, no fluorescence was observed from either alcohol **4** or TTF-carboxylic acid under the same conditions. The possibility that compound **6** could form long-lived ($T > 100$ ns) excited states was investigated by nanosecond laser flash photolysis in degassed acetonitrile solution. Samples were excited at 355 nm, but no bleaching of the ground state could be detected, nor were any new transient absorption bands detected in the range 300–800 nm. These data suggest that if a charge-separated species is formed upon excitation, then back electron transfer occurs very rapidly to regenerate the ground state.

Quantum mechanical calculations

To gain an insight into the conformation of compound **6**, quantum mechanical calculations were performed by the AM1 method. Using different starting geometries, with geometry optimisation until the root mean square gradient limit of 0.01 kcal mol^{-1} Å^{-1} (1 cal = 4.184 J) was reached, several local minima were found with energies varying within *ca.* 7 kcal mol^{-1} (total energy −220.1457 to −220.1339 au). It is noteworthy that the energy and oscillator strength of the calculated electronic absorption involving the HOMO–LUMO charge transfer transition strongly depend upon the conformation, which explains the appearance of a broad long wavelength band in the spectra. Molecular dynamics simulations were performed in order to reach the conformation with the minimal energy. Using the previously found optimised geometries, several runs involving 2 ps heating to 300 K, 5 ps simulation and 2 ps cooling and subsequent optimisation to a root mean square gradient of 0.01 kcal mol^{-1} Å^{-1} afford a conformation with the total energy of −220.1465 au, which is shown in Fig. 5. In this conformation, the donor and acceptor moieties are approximately orthogonal to one another, with the TCNAQ system folded into a butterfly conformation, similar to that observed previously in X-ray crystal structures and in theoretical calculations of TCNAQ and its derivatives.[13]

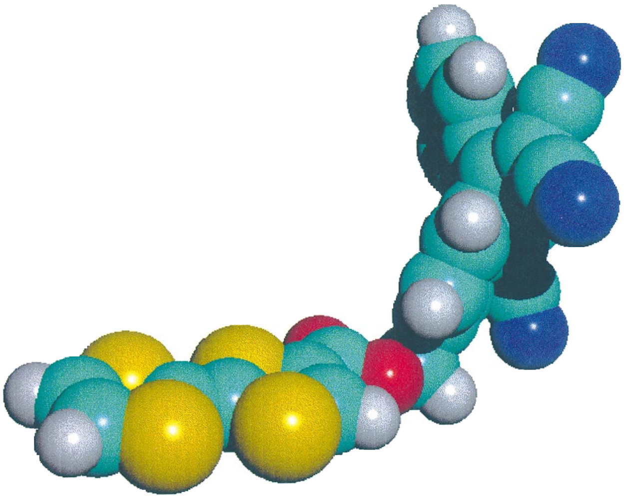

Fig. 5 Minimum energy conformation calculated for compound **6** using HYPERCHEM® (green = carbon, yellow = sulfur, grey = hydrogen, red = oxygen, blue = nitrogen)

Conclusions

Novel donor–σ-acceptor compounds **6** and **7**, and donor–σ-acceptor–σ-donor compound **8**, have been synthesised by attaching TTF (compounds **6** and **8**) and ferrocene (compound **7**) as donor substituents to the TCNAQ acceptor unit. These compounds present a very weak, low-energy absorption in the UV–VIS spectra which is assigned to an intramolecular charge transfer band. SEEPR experiments provide further evidence for intramolecular interaction between the TTF and TCNAQ moieties in compound **6**. Cyclic voltammetry measurements reveal that clean oxidation (of the TTF and ferrocene) and reduction (of the TCNAQ) processes occur in solution, giving rise to stable cations and anions, respectively. Quantum mechanical calculations performed on compound **6** predict that in its minimum energy conformation the TTF and TCNAQ moieties are approximately orthogonal to one another, with the TCNAQ unit folded into a butterfly conformation. Further studies on intramolecular charge-transfer interactions in functionalised TTF and TCNAQ systems will be reported in due course: one aim of our work in this area is to synthesise systems with increased intramolecular donor–acceptor interactions, and to study these interactions both in solution and in the solid state.

Experimental

Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1720 FTIR spectrophotometer and UV–VIS spectra on a Kontron Uvikon 930 instrument. ^{1}H NMR spectra were recorded on a Varian 200 instrument; chemical shifts, given in ppm, are relative to Me_4Si as the internal standard, and J values are given in Hz. Mass spectra were obtained on a VG 7070E instrument operating at 70 eV; ammonia was used as the impingent gas for chemical ionisation mode. Elemental analyses were performed on a Carlo-Erba Strumentazione. TLC analyses were performed using Merck pre-coated silica (0.2 mm) aluminium backed sheets. Column chromatography was carried out using Merck silica gel (70–230 mesh). Solvents were distilled prior to use in chromatography. Cyclic voltammetry experiments were performed in MeCN in a one-compartment cell with platinum working and counter electrodes and a silver/silver chloride reference electrode and using tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte (unless otherwise stated in Table 1). Measurements were made with a BAS CV 50 electrochemical analyser using *iR* compensation. Spectroelectrochemical measurements were made on a Perkin-Elmer Lambda 19 spectrophotometer using a Pyrex cell, with an indium–tin oxide thin layer working electrode, silver wire reference electrode and a platinum wire counter electrode in MeCN/0.1 M $Bu_4N^+ClO_4^-$. All solutions were purged with argon and retained under an inert atmosphere while the data were recorded. Solutions were prepared using reagent grade CH_2Cl_2 dried *via* distillation over CaH_2.

For SEEPR experiments tetrabutylammonium perchlorate (TBAP, obtained from SACHEM, electrometric grade) was recrystallised twice from water and dried for several days under high vacuum. Due to the lossy nature of the samples and to minimize perturbation of the microwave field by the working electrode, SEEPR experiments were carried out in a quartz flat cell.[22] A second glass part containing three ACE #7 threaded joints sealed *via* Teflon ferrules to hold the electrodes and a septum capped ground glass joint for degassing and sample injection was connected to the top of the cell. The working electrode, a platinum gauze electrode, was inserted into the flat part of the cell. The Ag wire pseudoreference electrode was positioned directly above the working electrode in order to minimize the *iR*-drop and the auxiliary electrode, a platium wire spiral of large surface area, occupied the solvent reservoir above the flat section. The electrode leads were insulated *via* Teflon heat shrink tubing. After each experiment the working electrode was cleaned in conc. HNO_3. EPR spectra were recorded on an IBM ESP 300 X-band spectrometer equipped with a TE_{104} dual cavity. Solutions (CH_2Cl_2, 0.1 M TBAP) were degassed by bubbling argon through them for 5 min and then injected into the cell, which was previously flushed with argon. The cell was mounted within the spectrometer using custom manufactured cell holders, which allow for precise alignment of the cell within the cavity in order to maximize the Q-factor. Bulk electrolysis was carried out simultaneous to signal acquisition (25 kHz field modulation, modulation amplitude 0.0475 G).

Computations were performed on Pentium 166 PC, 64 Mb RAM, using HYPERCHEM® version 5.01 software.

General procedure for the condensation of anthraquinone systems 2 and 3 with malononitrile

To a well-stirred mixture of the corresponding anthraquinone derivative **2** or **3** (4 mmol), malononitrile (121 mmol) and β-alanine (24.6 mmol) in dry CH_2Cl_2 (70 cm^3) under an Ar atmosphere was added dropwise $TiCl_4$ (22 mmol, 1.0 M in CH_2Cl_2). A yellow slurry formed, to which was added a solution of pyridine (3.75 cm^3) in dry CH_2Cl_2 (30 cm^3). The resultant dark mixture was heated at reflux temperature for 4 h under Ar. After this period, the reaction mixture was poured into iced water. The aqueous phase was extracted with CH_2Cl_2 and then with EtOAc. The organic layers were combined, dried (anhydrous $MgSO_4$), and evaporated under reduced pressure to yield an oily product, which contained unreacted malononitrile. Silica gel column chromatography separated the products **4** and **5**.

2-Hydroxymethyl-11,11,12,12-tetracyanoanthraquinodimethane 4. This compound was purified on silica gel, eluent acetone–hexane (20:80 v/v) followed by recrystallization from EtOAc–hexane, and isolated as a pale orange solid, 42% yield, mp 256–258 °C (lit. 256–257 °C).[12d]

2,6-Dihydroxy-11,11,12,12-tetracyanoanthraquinodimethane 5. Chromatography of the crude reaction mixture on silica gel, eluent acetone–dichloromethane (10:90 v/v), afforded compound **3b** (40%) as an orange solid: mp > 250 °C (Calc. for $C_{20}H_8N_4O_2$: C, 71.42; H, 2.38; N, 16.60. Found; C, 71.74; H, 2.77; N, 17.00%); m/z (DCI) 337 ($M^+ + 1$); δ_H ([$^2H_6$] acetone) 10.10 (2H, br s), 8.16 (2H, d, J 8.7), 7.69 (2H, d, J 2.4), 7.20 (2H, dd, $J_{1,2}$ 2.4 and $J_{1,3}$ 8.7); ν_{max} (KBr)/cm^{-1} 3311, 2221, 1608, 1563, 1528, 1480, 1458, 1338, 1311, 1237, 1186, 1116, 827.

2-(Tetrathiafulvalenylcarbonyloxymethyl)-11,11,12,12-tetracyanoanthraquinodimethane 6

To a solution of compound **4** (257 mg, 0.77 mmol) in dry CH_2Cl_2 (30 cm^3) at 20 °C under Ar, was added tetrathiafulvalenecarbonyl chloride[10,23] (246 mg, 0.92 mmol) in dry CH_2Cl_2 (30 cm^3) followed by dry triethylamine (0.128 cm^3, 0.92 mmol). Stirring was continued for 2 h after which time chromatography of the crude reaction mixture on a silica gel column, eluent acetone–hexane (10:90 v/v), afforded compound **6** (130 mg, 30%) as a dark brown solid: mp > 250 °C (Calc. for $C_{28}H_{12}N_4O_2S_4$: C, 59.51; H, 2.12; N, 9.92. Found; C, 59.11; H, 2.12; N, 9.97%); m/z (DCI) (relative intensity) 565 ($M^+ + 1$), 248 (38), 204 (100), 180 (7), 148 (59), 134 (64); δ_H ($CDCl_3$) 5.37 (2H, s), 6.33 (2H, s), 7.50 (1H, s), 7.75 (3H, m), 8.25 (4H, m); ν_{max} (KBr)/cm^{-1} 2223, 1709, 1555, 1539, 1277, 1195, 1065; λ_{max} (MeCN)/nm (ε) 435 (2300), 339 (31 000), 306 (34 700), 282 (47 000).

2-(Ferrocenylcarbonyloxymethyl)-11,11,12,12-tetracyanoanthraquinodimethane 7

To a solution of compound **4** (257 mg, 0.77 mmol) in dry CH_2Cl_2 (30 cm^3) at 20 °C under Ar, was added ferrocenecarbonyl chloride[24] (228 mg, 0.92 mmol) in dry CH_2Cl_2 (30 cm^3) followed by dry triethylamine (0.128 cm^3, 0.92 mmol). Stirring was continued for 2 h, after which time chromatography of the crude reaction mixture on a silica gel column, eluent acetone–hexane (20:80 v/v), followed by recrystallization from acetonitrile, afforded compound **7** (168 mg, 40%) as a green dark solid: mp > 250 °C (Calc. for $C_{32}H_{18}N_4O_2Fe$: C, 70.35; H, 3.32; N, 10.25. Found; C, 70.04; H, 3.30; N, 10.21%); m/z (DCI) (relative intensity) 547 ($M^+ + 1$, 7), 318 (3), 269 (4), 247 (59), 229 (100), 212 (100); δ_H ($CDCl_3$) 4.17 (5H, s), 4.46 (2H, t, J 2.1), 4.89 (2H, t, J 2.1), 5.39 (2H, s), 7.74 (3H, m), 8.25 (4H, m); ν_{max} (KBr)/cm^{-1} 2222, 1711, 1556, 1537, 1459, 1274, 1136; λ_{max} (MeCN)/nm (ε) 440 (370), 344 (19 700), 304 (15 000), 282 (25 200).

2,6-Bis(tetrathiafulvalenylcarbonyloxy)-11,11,12,12-tetracyanoanthraquinodimethane 8

To a solution of compound **5** (259 mg, 0.77 mmol) in dry CH_2Cl_2 (30 cm^3) at 20 °C under Ar, was added tetrathiafulvalenecarbonyl chloride (513 mg, 1.92 mmol) in dry CH_2Cl_2 (50 cm^3) followed by dry triethylamine (0.27 cm^3, 1.94 mmol).

Stirring was continued for 2 h and then column chromatography of the crude reaction mixture on silica gel, eluent acetone–dichloromethane (20:80 v/v), afforded compound **8** (130 mg, 30%) as a black solid, which had low solubility in common organic solvents, mp >250 °C (Calc. for $C_{34}H_{12}N_4O_4S_8$: C, 51.24; H, 1.52; N, 7.03. Found; C, 51.00; H, 1.32; N, 7.21%); *m/z* (DCI) 798 ($M^+ + 1$); δ_H ([$^2H_6$]DMSO) 6.78 (4H, s), 7.81 (2H, dd, $J_{1,2}$ 2.0 and $J_{1,3}$ 8.2), 8.16 (2H, d, *J* 2.0), 8.24 (2H, s), 8.33 (2H, d, *J* 8.2); ν_{max} (KBr)/cm^{-1} 2225, 1716, 1593, 1559, 1531, 1468, 1257, 1188, 1111, 1021, 954; λ_{max} (MeCN)/nm (ε) 437 (2 700), 298 (32 040).

4-Methoxycarbonyltetrathiafulvalene 9

A suspension of TTF–carboxylic acid[23] (500 mg, 2.01 mmol), methanol (0.4 cm^3, 9.8 mmol), dimethylaminopyridine (246 mg, 2.01 mmol) and dicyclohexylcarbodiimide (415 mg, 2.01 mmol) in dry Cl_2CH_2 (50 cm^3) was stirred for 2 h at room temp. After cooling, chromatography of the crude reaction mixture on a silica gel column, eluent dichloromethane–hexane (1:1 v:v), afforded compound **9** (350, 66%) as a red solid, mp 88–89 °C (Calc. for $C_8H_6O_2S_4$: C, 36.62; H, 2.30. Found: C, 36.55 H, 2.52%); *m/z* (EI) 262 (M^+); ν_{max} (Nujol)/cm^{-1} 3035, 1708, 1566, 1537, 1442, 1248, 1060; δ_H ($CDCl_3$), 7.35 (s, 1H), 6.33 (s, 2H), 3.81 (s, 3H).

2-Acetoxymethyl-11,11,12,12-tetracyanoanthraquinodimethane 10

To a solution of compound **2** (200 mg, 0.56 mmol) and dry triethylamine (0.12 cm^3, 0.53 mmol) in dry dichloromethane (40 cm^3) at 20 °C under argon was added freshly distilled acetyl chloride (0.1 cm^3, 1.4 mmol). Stirring was continued for 2 h after which time chromatography of the crude reaction mixture on a silica gel column, eluent dichloromethane, afforded compound **10** (130 mg, 58%) as a yellow solid: mp 287–289 °C (Calc. for $C_{23}H_{12}N_4O_2$: C, 73.40; H, 3.21; N, 14.88. Found: C, 73.00; H, 2.92; N, 14.59%); *m/z* (CI) 376 (M^+); ν_{max} (Nujol)/cm^{-1} 2227, 1743, 1559, 1225; δ_H ($CDCl_3$) 8.24 (m, 4H), 7.76 (m, 3H), 5.24 (s, 2H), 2.16 (s, 3H).

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