Electron acceptors of the fluorene series. Part 8.[1] Electrochemical and intramolecular charge transfer studies of thiophene functionalised fluorenes

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The degree of intramolecular charge transfer (ICT) in 9-(1,3-dithiol-2-ylidene)fluorenes bearing fused thiophene and 2,5-dihydrothiophene units (**2** and **16**, respectively), has been investigated by UV-VIS spectroscopy. Both series of compounds show a good correlation between the ICT energies and $\Sigma\sigma_p^-$ values of the corresponding molecules. The sensitivity parameters ρ_{ICT}^- are 0.18 eV for **2** and 0.16 eV for **16**. Cyclic voltammetry of both series, **2** and **16**, reveals a single irreversible oxidation process in all compounds. However, electropolymerisation under oxidative conditions does not take place, since the radical cation intermediate is most probably derived from the electroactivity of the 1,3-dithiole–fluorene fragment. In parallel to ICT, the values of $E_{1\text{red}}^{\frac{1}{2}}$ and $E_{2\text{red}}^{\frac{1}{2}}$ in relevant compounds also show a linear relationship with σ_p^- constants in the fluorene ring. The sensitivity parameters for series **2** are 0.20 V ($\rho_{1\text{red}}^-$) and 0.17 V ($\rho_{2\text{red}}^-$), whilst those for **16** are 0.26 V ($\rho_{1\text{red}}^-$) and 0.18 V ($\rho_{2\text{red}}^-$).

Introduction

In the latter part of the 1970s, the discovery of metallic conductivity in doped polyacetylene[2] augmented interest in the highly interdisciplinary field of organic conjugated polymers. Owing to their unusual optical and electronic properties these materials, as components, have been associated with a number of applications such as sensors, plastic batteries, light emitting devices (LEDs and LECs), photovoltaics and non-linear optics. More recently, the majority of attention was focused on materials based on polythiophene, polypyrrole, poly-*p*-phenylene (PPP) and polyphenylenevinylene (PPV).[3] This trend can be attributed to the increasing synthetic efficiency in derivatisation and polymerisation methods and also to the stability, processability and high level of optical and electronic properties exhibited by these particular systems. Band structure engineering of such polymers for the development of new devices and applications remains an important goal in the field, and the design and preparation of narrow bandgap (E_g) polymers is one of the subjects of intense interest.[4]

To date, the role of fluorene in organic polymers offers a modest yet significant contribution to the field of electronic materials. Electron-deficient fluorene derivatives are well known for their photosensitising ability in carbazole-containing polymers;[5,6] indeed, the first commercial organic photoconductor was based on a charge-transfer complex of 2,4,7-trinitro-9-fluorenone with polyvinylcarbazole (PVK).[7] Fluorene systems have also been incorporated covalently into polymeric structures: oxidative electropolymerisation has been thoroughly investigated by several groups,[8] whilst blue light-emitting materials have been produced from poly(9-alkylfluorene)s prepared by chemical oxidation.[9] Electroluminescence and photoluminescence have also been observed in poly(2,7-fluorene) derivatives, obtained from nickel and palladium catalysed polymerisation of 2,7-dihalofluorenes.[10,11]

Our long-term intention is to prepare a series of polythiophene materials incorporating strong electron-withdrawing fluorene units, which are bonded covalently through conjugated spacer units to the backbone of the polymer. Due to the bulky nature of the acceptor moiety our strategy will be to prepare copolymers of our thiophene-functionalised fluorene units with unsubstituted thiophene. These materials should exhibit unusual electronic and optoelectronic properties: theoretical studies have shown that the incorporation of mixed repeating units of different bandgaps lowers the overall E_g of the polymer,[12] whilst polymers bearing strong electron-withdrawing groups or copolymers combining π-excessive and π-deficient heteroaromatic units are also known to have exceptionally low bandgap values.[13,14] Additionally, by controlling the percentage of fluorene units within the polymer, we may be able to prepare polythiophene systems with intrinsic photosensitivity.

In a previous communication[15] we have reported the preparation of polymer **1** using electrochemical polymerisation techniques. Herein, we present the synthesis, electrochemistry and UV spectroscopic studies of a series of thiophene-functionalised fluorene monomers **2**; the series represents model compounds for the investigation of intramolecular charge transfer (ICT) between the donor and acceptor moieties of the monomer systems. These studies are essential for the elucidation of structural, electronic and optoelectronic properties of polymers based on, or incorporating, the fluorene systems **2**.

Results and discussion

Synthesis

The synthesis of ester derivatives, primarily as a means of introducing solubilising substituents, was achieved using two different approaches. Neat thionyl chloride was used to convert fluorene-4-carboxylic acid **3** to the acyl chloride **4** (Scheme 1), in almost quantitative yield. Derivative **4** was then stirred at 65–110 °C in methanol, *n*-butanol or triethylene glycol monomethyl ether to give the corresponding esters **5a–c**, in good yield. The degree of nitration of **5a–c** could be controlled by varying the reaction conditions. Thus, ester **5b** was

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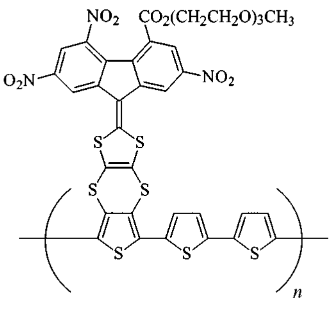

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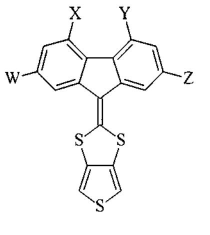


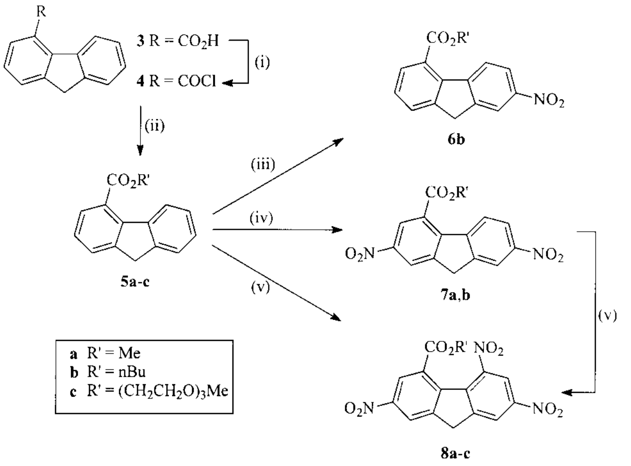
2

	W	X	Y	Z
a	H	H	H	H
b	NO_2	H	H	H
c	NO_2	H	CO_2Bu	H
d	NO_2	H	H	NO_2
e	NO_2	CO_2Me	H	NO_2
f	NO_2	CO_2Bu	H	NO_2
g	NO_2	$CO_2C_{11}H_{23}$	H	NO_2
h	NO_2	$CO_2(CH_2CH_2O)_3Et$	H	NO_2
i	NO_2	NO_2	H	NO_2
j	NO_2	CO_2Me	NO_2	NO_2
k	NO_2	CO_2Bu	NO_2	NO_2
l	NO_2	$CO_2(CH_2CH_2O)_3Me$	NO_2	NO_2
m	NO_2	NO_2	NO_2	NO_2

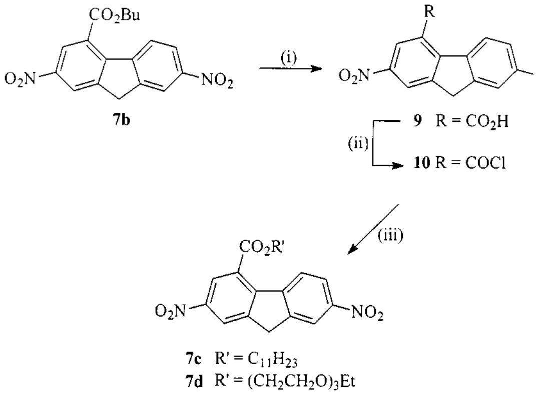
mono-substituted exclusively at the 7-position using a 3:20 mixture of nitric and acetic acids to give **6b**. 2,7-Dinitro compounds **7a** and **7b** were prepared using nitric and acetic acid (1:1, v/v), whilst 2,5,7-trinitrofluorenes **8a–c** were isolated by reacting the corresponding esters with fuming nitric acid. However, the selectivity of mono- and dinitration reactions was not particularly efficient, which led to moderate yields of target products in the case of butyl esters **6b** and **7b**. Additionally, the purification of long-chain esters **7c** and **7d** using this route proved too difficult to be employed. The nitration of all the esters with fuming nitric acid led exclusively to the trinitro derivatives. Alternatively, these compounds could be obtained by the nitration of mono- and dinitro derivatives under the same conditions; this strategy enabled us to utilise the waste products after the purification of mono- and dinitro esters. For example, the nitration of **5b** under extreme conditions gives **8b** in approximately 50% yield, whereas the strategy described above affords about 40% of **7b** and additionally *ca.* 30% of **8b** (see Experimental section). Interestingly, whereas fluorene-4-carboxylic acid (triethylene glycol monomethyl ether) ester **5c** was readily nitrated to give 2,5,7-trinitro derivative **8c**, its analogue obtained from triethylene glycol monoethyl ether under the same reaction conditions completely lost the terminal ethyl group to give, most probably, the corresponding nitrate (^1H NMR and IR evidence).

Scheme 2 represents a more efficient means for the synthesis of esters **7c** and **7d**. Acid-catalysed hydrolysis of **7b** afforded 2,7-dinitrofluorene-4-carboxylic acid **9**. Derivatives **7c** and **7d** were then prepared from the reaction of *n*-undecanol (60% yield) or triethylene glycol monoethyl ether (73% yield), respectively, with acyl chloride **10**, which was in turn prepared from **9** using thionyl chloride.

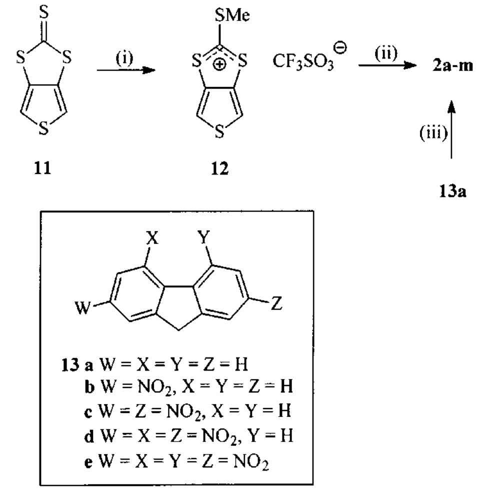
The final stage for the synthesis of thiophene-functionalised fluorenes involved the condensation of fluorene derivatives **6b**, **7a–d**, **8a–c** and **13a–e** with salt **12** (Scheme 3). Compound **12** was prepared from thieno[3,4-*d*][1,3]dithiole-2-thione[16] **11** by methylation with methyl triflate in dichloromethane (96% yield). The nitro-substituted fluorenes **13d** and **13e** were prepared using literature methods.[17,18] The conditions for the condensation step are dependent upon the nature and number of substituents on the aromatic rings of the fluorene system (see Table 1). Di-, tri- and tetranitrofluorenes were readily condensed with salt **12** in appropriate solvents (pyridine for less reactive dinitro compounds or *N*,*N*-dimethylformamide (DMF) for others); mononitro derivatives required substantially longer reaction times and afforded only low yields of target products which were difficult to purify. The upper time limit for the coupling reaction was limited by the instability of



Scheme 1 *Reagents and conditions*: (i) $SOCl_2$, reflux, 1 h; (ii) R′OH (neat), 80–100 °C, 2 h; (iii) HNO_3–AcOH, 0 °C, 2 d; (iv) HNO_3–AcOH (1:1), 10 °C, 16 h; (v) HNO_3, −10 °C, 40 min, then 20 °C, 2–6 h.



Scheme 2 *Reagents and conditions*: (i) HCl–AcOH (1:2), reflux, 16 h; (ii) $SOCl_3$, reflux, 1 h; (iii) R′OH (neat), 65–110 °C, 5 min–1 h.



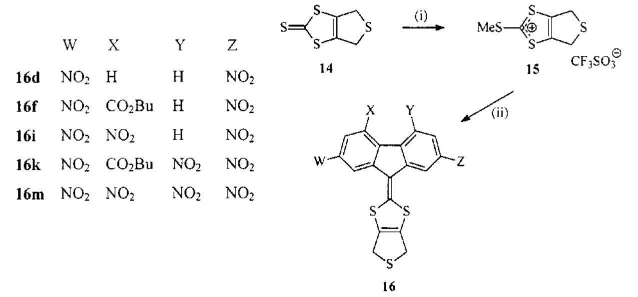
Scheme 3 *Reagents and conditions*: (i) $CH_3SO_3CF_3$, CH_2Cl_2, 25 °C, 16 h; (ii) **6b**, **7a–d**, **8a–c** or **13b–e**, pyridine or DMF, 100 °C, 3 min–2 h; (iii) THF, LDA, 0.5 h then **12**, 16 h.

Table 1 Reaction conditions and yields for the synthesis of 9-(thieno-[3,4-*d*][1,3]dithiol-2-ylidene)- and 9-(4,6-dihydrothieno[3,4-*d*][1,3]-dithiol-2-ylidene)-polynitrofluorene derivatives **2d**–**2m** and **16d,f,i,k,m**

Compound	Solvent	Reaction conditions	Yield (%)
2d	Pyridine	3 min, 100 °C	50
2e	Pyridine	10 min, 100 °C	76
2f	Pyridine	10 min, 100 °C	71
2g	Pyridine	2 h, 100 °C	59
2h	Pyridine	2 h, 100 °C	47
2i	DMF	10 min, 100 °C	41
2j	DMF	10 min, 100 °C	68
2k	DMF	10 min, 100 °C	72
2l	DMF	1.5 h, 100 °C	56
2m	DMF	10 min at 50 °C, 16 h at rt	40
16d	Pyridine	5 min, 60 °C	47
16f	Pyridine	16 h, rt	64
16i	DMF	15 min, 60 °C	48
16k	DMF	16 h, rt	50
16m	DMF	16 h, rt	63

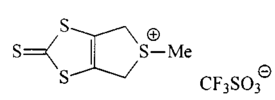
salt **12**, which decomposed within several hours under the reaction conditions to give rise to by-products. We presume, therefore, that only a small proportion of the mononitrofluorenes reacted to give the desired target compounds. Unsubstituted fluorene **13a** necessitated deprotonation with a much stronger base, such as lithium diisopropylamide (LDA).

In order to assess the electronic contribution of the thiophene ring system in compounds **2a**–**m**, we decided to synthesise and investigate the closely related dihydro analogues **16d,f,i,k,m** (lettering of the compounds corresponds to their analogues **2**, bearing the same substituents in the fluorene moiety) (Scheme 4). Compound **15** was prepared in approximately 80% yield from the reaction of methyl triflate with sulfide **14**.[16] Even in the presence of excess **14**, some by-products were formed from the alkylation of the sulfide S-5 atom in the starting compound (compounds **17a** and **17b**, by ^{1}H NMR evidence). Fortunately, these were easily removed due to their insolubility in dichloromethane in which the compound **15** is easily soluble. The condensation reactions of fluorenes **7b**, **8b** and **13c**–**e** with the dihydrothiophene salt **15** afforded compounds **16d,f,i,k,m**. The reaction times and conditions of these reactions (Table 1), indicate that salt **15** is considerably more reactive towards fluorene derivatives than its aromatic analogue **12**; this is probably due to a greater delocalisation of the positive charge in the latter.

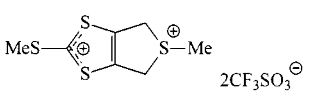


	W	X	Y	Z
16d	NO_2	H	H	NO_2
16f	NO_2	CO_2Bu	H	NO_2
16i	NO_2	NO_2	H	NO_2
16k	NO_2	CO_2Bu	NO_2	NO_2
16m	NO_2	NO_2	NO_2	NO_2

Scheme 4 *Reagents and conditions*: (i) $CH_3SO_3CF_3$, CH_2Cl_2, 25 °C, 16 h; (ii) **7b**, **8b** or **13c**–**e**, pyridine or DMF, 20–60 °C, 5 min–16 h.



17a



17b

Electron absorption studies

Intramolecular charge transfer in compounds **2** and **16** was studied by electron absorption spectroscopy, using DMF as the solvent. The absorption maxima relating to ICT are given in Table 2, together with the corresponding values in eV. The UV-VIS spectra of compounds **2m** and **16m** are shown in Fig. 1. As expected, for each of the two fluorene series, λ_{ICT} is shifted bathochromically with an increase in the number of electron-withdrawing substituents in the fluorene ring (Table 2, Fig. 2). There is also a bathochromic shift of *ca.* 30 nm in **16d,f,i,k,m** (502–596 nm) compared with the analogous compounds **2d,f,i,k,m** (474–562 nm) (Table 2, Fig. 1). The electronic behaviour of the thiophene unit in fluorenes **2a**–**m** is illustrated by this observation—the fused heterocyclopentadiene moiety behaves as an electron-withdrawing species and not as a π-resonance contributor, rendering the 1,3-dithiole system a weaker donor than the corresponding unit in **16a**–**e**. This effect has also been observed in thiophene-substituted tetrathiafulvalene (TTF) systems in which the electron-rich TTF unit experiences a decrease in donor ability.[16,19]

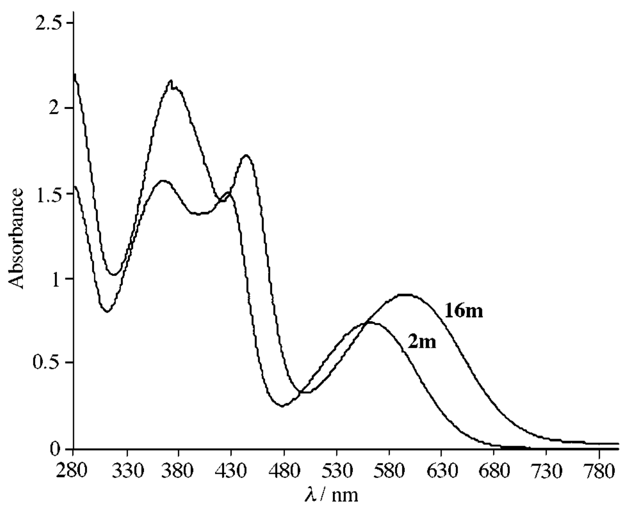


Fig. 1 Electron absorption spectra of tetranitrofluorene derivatives **2m** and **16m**, demonstrating the change in the ICT with the transition from the annelated thiophene ring to the dihydrothiophene (λ_{ICT}^{max} = 562 and 596 nm, respectively).

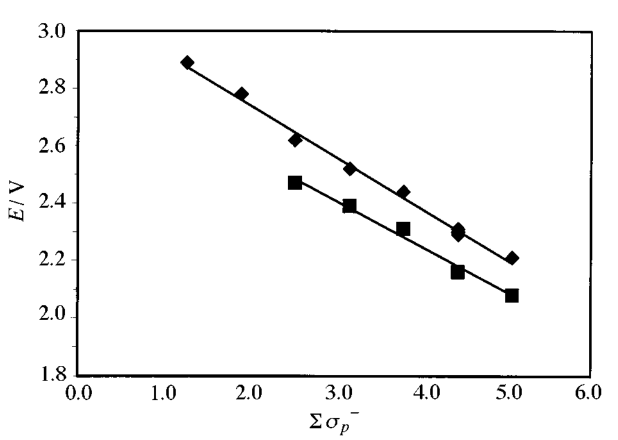


Fig. 2 Plot of absorption maxima (in eV) of compounds **2**(◆) and **16**(■) *versus* the sum of nucleophilic constants ($\Sigma\sigma_p^-$).

Eqn. (1) allows the calculation of substituent sensitivity

$$h\nu_{ICT} = h\nu^0_{ICT} + \rho^-\Sigma\sigma_p^- \qquad (1)$$

ρ^- for intramolecular charge transfer bands, where $h\nu_{ICT}$ is the ICT energy corresponding to λ_{ICT}^{max} of each derivative, $\Sigma\sigma_p^-$ is the sum of nucleophilic constants[20] of the substituents attached to the benzene rings of the fluorene system and $h\nu^0_{ICT}$ corresponds to the ICT energy in compound **2a** (or **16a**) (*i.e.* the theoretical ICT value which would be observed with

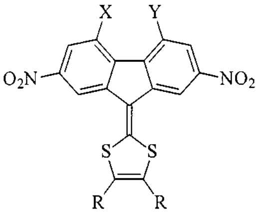
Table 2 Maxima of ICT bands (λ_{ICT}^{max}) and their energies ($h\nu_{ICT}$) in electron absorption spectra, and cyclic voltammetry data for compounds **2a**–**m** and **16d**,**f**,**i**,**k**,**m**

		Electron absorption spectroscopy[a]		Cyclic voltammetry (V *vs.* Ag/AgCl)[b]					
Compound	$\Sigma\sigma_p^-$	λ_{ICT}^{max}/nm	$h\nu_{ICT}$/eV	E_{ox}^c	$E_{1red}^{\frac{1}{2}}$	$E_{2red}^{\frac{1}{2}}$	$E_{3red}^{\frac{1}{2}}$	ΔE_{1-2}^d	$K_{dispr.}^d$/M^{-1}
								—	—
2a	0	—	—	1.08	-1.79^c			—	—
2b	1.27	429	2.89	1.37	−0.94		-1.78^c	—	—
2c	1.91	446	2.78	1.36	−0.94		-1.85^c	—	—
2d	2.54	474	2.62	1.48	−0.75	−0.89	—	0.14	4×10^{-3}
2e	3.18	492	2.52	1.50	−0.64	−0.79	—	0.15	3×10^{-3}
2f	3.18	492	2.52	1.47	−0.66	−0.80	—	0.14	4×10^{-3}
2g	3.18	492	2.52	—	—	—	—	—	—
2h	3.18	492	2.52	1.44	−0.67	−0.80	—	0.13	6×10^{-3}
2i	3.81	508	2.44	1.56	−0.51	−0.69	−1.36	0.17	1×10^{-3}
2j	4.45	538	2.31	1.59	−0.37	−0.58	−1.48	0.21	3×10^{-4}
2k	4.45	542	2.29	1.58	−0.38	−0.57	−1.48	0.19	6×10^{-4}
2l	4.45	540	2.30	1.58	−0.38	−0.58	−1.51	0.20	4×10^{-4}
2m	5.08	562	2.21	1.66	−0.21	−0.45	−1.42	0.24	9×10^{-5}
16d	2.54	502	2.47	1.44	−0.76	−0.90	—	0.14	4×10^{-3}
16f	3.18	520	2.39	1.28	−0.67	−0.80	—	0.13	6×10^{-3}
16i	3.81	537	2.31	—	—	—	—	—	—
16k	4.45	574	2.16	1.38	−0.40	−0.60	—	0.20	4×10^{-4}
16m	5.08	596	2.08	1.44	−0.24	−0.44	−1.39	0.20	4×10^{-4}

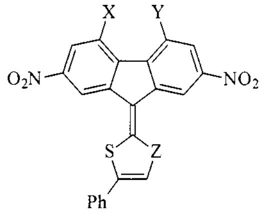
[a] DMF. [b] DMF, Bu_4NPF_6 supporting electrolyte. [c] Irreversible peaks. [d] $\Delta E_{1-2} = E_{1red}^{\frac{1}{2}} - E_{2red}^{\frac{1}{2}} = -0.059 \log K_{dispr.}$

unsubstituted benzene rings in the fluorene system, $\Sigma\sigma_p^- = 0$; however, no ICT band was observed in the electronic system of compound **2a**, since even if it existed, it would be hidden under the strong absorption of the π-system at $\lambda \leqslant 400$ nm).

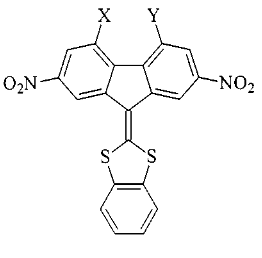
Both fluorene series **2** and **16** gave very good linear relationships with the correlation coefficients $r > 0.99$ (Table 3). The sensitivity parameter ρ^-_{ICT} for the two compounds was 0.18 eV and 0.16 eV, respectively (Table 3), which is close to those of similar ICT systems, *i.e.* 9-(1,3-chalcogenathiol-2-ylidene)fluorenes **18** (0.14–0.15 eV),[21] **19** (0.14–0.18 eV depending on the solvent used)[22] and **20** (0.19 eV),[22] and somewhat higher than that observed in isomeric dithiole–fluorene ICT compounds, *i.e.* 9-(4-phenyl-1,2-dithiol-3-ylidene)fluorenes **21** (0.09–0.12 eV depending on the solvent).[1,23]



18 R = Me, SMe, CO_2Me



19 Z = S, Se



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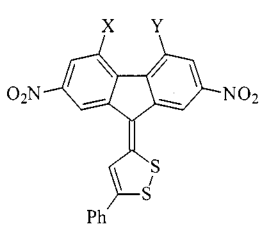

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Electrochemistry

The redox behaviour of series **2** and **16** has been studied by cyclic voltammetry (CV) in DMF solution using Bu_4NPF_6 as the supporting electrolyte (with the exceptions of compounds **2g** and **16c**, which were found to be too insoluble to give reliable data), and the results are collated in Table 2.

In most cases, both series of compounds, **2** and **16**, show similar electrochemical behaviour: (i) the oxidation process is irreversible; (ii) the reduction process shows two closely-spaced

Table 3 Correlation of ICT energies and redox potentials of compounds **2** and **16** by eqns. (1) and (2) (95% confidence level)

Compds	Eqn. (1)	$h\nu_{ICT}^0$/eV	ρ_{ICT}^-/eV	r^a	n^b
2b–**m**	$h\nu_{ICT}$	3.10 ± 0.04	0.18 ± 0.01	0.997	12
16d,**f**,**i**,**k**,**m**	$h\nu_{ICT}$	2.89 ± 0.14	0.16 ± 0.05	0.993	5
	Eqn. (2)	E_0/V	ρ^-_{CV}/V	r^a	n^b
2a–**f**,**h**–**m**	E_{OX}	1.17 ± 0.08	0.10 ± 0.02	0.957	12
2b–**f**,**h**–**m**	$E_{1red}^{\frac{1}{2}}$	−1.27 ± 0.08	0.20 ± 0.02	0.989	11
2d–**f**,**h**–**m**	$E_{2red}^{\frac{1}{2}}$	−1.34 ± 0.04	0.17 ± 0.01	0.998	9
16d,**f**,**k**,**m**	$E_{1red}^{\frac{1}{2}}$	−1.30 ± 0.22	0.21 ± 0.05	0.996	4
16d,**f**,**k**,**m**	$E_{2red}^{\frac{1}{2}}$	−1.36 ± 0.22	0.18 ± 0.06	0.994	4

[a] Correlation coefficient. [b] Number of points.

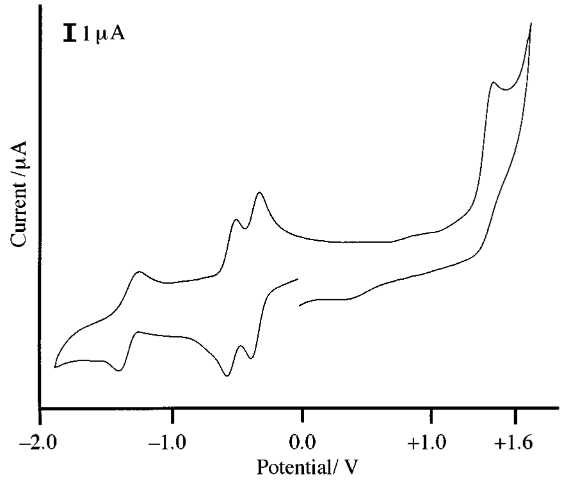

Fig. 3 Cyclic voltammogram of compound **2j** in DMF *vs.* Ag/AgCl, Pt wire counter electrode, Pt disk working electrode, at 20 °C, 0.1 M Bu_4NPF_6 supporting electrolyte, 0.001 M substrate, 200 mV s^{-1} scan rate with *iR* compensation.

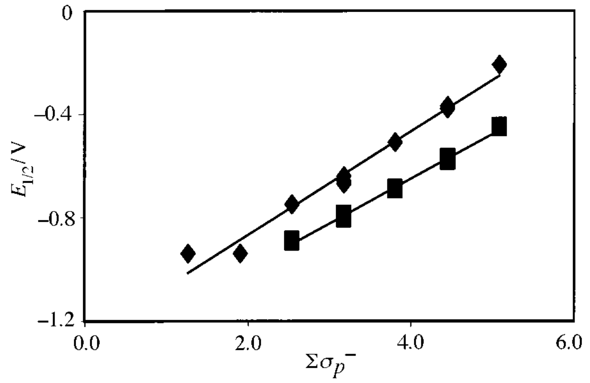

Fig. 4 Plot of $E_{1\mathrm{red}}^{\frac{1}{2}}$ potentials (◆) for series **2** (excluding **2a** and **2g**) and $E_{2\mathrm{red}}^{\frac{1}{2}}$ potentials (■) for compounds **2i**–**2m** *versus* the sum of nucleophilic constants ($\Sigma\sigma_p^-$).

single-electron reduction peaks corresponding to the reversible formation of the radical anion and dianion species, as well as a reversible (or quasi-reversible) third single-electron reduction peak at substantially more negative potentials (for compounds **2a**–**c**, the third reduction process is irreversible). A representative cyclic voltammogram is given in Fig. 3, showing the electrochemical behaviour of compound **2j**.

All nitro-substituted fluorenes, **2** and **16**, display a single-electron irreversible oxidation peak between +1.28 V and +1.66 V. From this, we can conclude that the donor units of series **2** (*i.e.* the fused, 1,3-dithiole–thiophene components), do not behave as two independent reducing species to form the corresponding dications. It is necessary, therefore, to rationalise whether the radical cation, obtained from the single-electron oxidation, is located within the thiophene or the 1,3-dithiole ring systems. In general, the 1,3-dithiol-2-ylidene unit is a more efficient donor than thiophene since, upon oxidation, the former becomes a stable aromatic 6π-electron intermediate, whereas the latter loses an electron to form a reactive radical cation. From this viewpoint, it is reasonable to speculate that the electron-donating site originates from the 1,3-dithiole fragment. In applying this hypothesis to the CV data obtained, complications arise from the oxidation potentials of series **2**, since the E_{OX} values for thiophene derivatives can fall within the limits of our results. In addition, the typical values for 1,3-dithiole substituents are usually significantly lower than those found for **2**; for instance, compounds **18** display oxidation potentials in the range (+0.63–+0.70) V.[21] However, E_{OX} for the dihydrothiophene series **16** remains quite high [+(1.28–1.44) V] and, in comparison with **2**, are not shifted by an appreciable amount, suggesting that the oxidation values for **2** could easily be due to the 1,3-dithiole species. Irrefutably, the electron-donating unit in series **16** is the 1,3-dithiole moiety, therefore, the decrease in oxidation potentials between **2** and **16** (0.04–0.22 V), is due to the absence of the electron-withdrawing thiophene ring.

The cathodic electroactivity of fluorenes **2** and **16** increases with the number of electron-withdrawing substituents on the benzene rings. Both series of compounds, **2d**–**m** and **16**, exhibit similar electrochemical behaviour: two closely-spaced ($\Delta E_{1-2}^{\frac{1}{2}} < 0.25$ V) reversible single-electron reduction waves, corresponding to the radical anion and dianion, respectively. A decrease in the difference between first and second single-electron reduction waves ($\Delta E_{1-2} = E_{1\mathrm{red}}^{\frac{1}{2}} - E_{2\mathrm{red}}^{\frac{1}{2}}$), is observed alongside a decrease in the acceptor ability of the fluorene ring (Table 2). As a result, for compounds **2b** and **2c**, ΔE_{1-2} becomes lower than the resolution of the CV experiment, to give an observed two-electron single reduction peak (at −0.94 V), corresponding to the formation of the dianion.

At substantially more negative potentials of −1.36 to −1.51 V, compounds **2i**–**m** and **16m**, which are tri- and tetranitro systems, give a third reversible (or quasi-reversible) single-electron reduction wave; however, a single third reversible wave was not observed for the trinitro derivative **16i**. Due to their low electron accepting abilities, compounds **2b** and **2c** exhibit a third irreversible reduction process at higher potentials of *ca.* −1.8 V. Finally, compound **2a** exhibits an irreversible reduction peak at a high potential of −1.79 V; as expected from its structure, this value illustrates **2a** as a poor electron acceptor.

The sensitivity parameters ρ_{CV}^- for the first and second reduction potentials of both series of compounds (Table 3) can be expressed by eqn. (2). All sets of values show linear trends

$$E^{\frac{1}{2}} = E_0^{\frac{1}{2}} + \rho_{\mathrm{CV}}^- \Sigma\sigma_p^- \qquad (2)$$

(Fig. 4), with correlation coefficients of 0.989–0.998. The sensitivity parameters ρ_{CV}^- for $E_{1\mathrm{red}}^{\frac{1}{2}}$ potentials were 0.20 V and 0.21 V for series **2** and **16**, respectively, whilst the corresponding ρ_{CV}^- values for $E_{2\mathrm{red}}^{\frac{1}{2}}$ potentials were slightly lower (0.17 V and 0.18 V, respectively). Similar minor lowering of the sensitivity from $\rho_{1\mathrm{red}}^-$ to $\rho_{2\mathrm{red}}^-$ has also been observed for related compounds **19** and **21**.[22]

The CV results showed that the reversible third reduction waves, where relevant, showed no regular dependence on the substituents in the fluorene ring. A similar independence of $E_{3\mathrm{red}}$ has also been observed in other push-pull fluorene systems.[6b]

The sensitivity parameters for the oxidation process were also calculated from eqn. (2). Although the value of ρ_{OX}^- for series **2** (0.10 V) was much lower than those calculated for $E_{1\mathrm{red}}^{\frac{1}{2}}$ and $E_{2\mathrm{red}}^{\frac{1}{2}}$, the oxidation process showed a regular dependence for the electron withdrawing nature of the fluorene moieties ($r = 0.957$). Surprisingly, the oxidation values for series **16** proved to be independent of the fluorene substituents.

The thermodynamic stability of the radical anions formed in the multi-step reversible redox process (3) can be estimated

$$\mathrm{A} \underset{-\mathrm{e}}{\overset{+\mathrm{e}}{\rightleftharpoons}} \mathrm{A}^{\bullet -} \underset{-\mathrm{e}}{\overset{+\mathrm{e}}{\rightleftharpoons}} \mathrm{A}^{2-} \qquad (3)$$

from the difference in the potentials of the corresponding radical anion and dianion, using eqn. (4),[24] where $K_{\mathrm{dispr.}}$ is the

$$\Delta E_{1-2} = E_{1\mathrm{red}}^{\frac{1}{2}} - E_{2\mathrm{red}}^{\frac{1}{2}} = -0.059 \log K_{\mathrm{dispr.}} \qquad (4)$$

disproportionation constant in the equilibrium (5). As can

$$2\mathrm{A}^{\bullet -} \overset{K_{\mathrm{dispr.}}}{\rightleftharpoons} \mathrm{A} + \mathrm{A}^{2-} \qquad (5)$$

be seen from Table 2, the donor moiety has no apparent effect on the thermodynamic stability of the radical anion, whereas increasing the number of electron-withdrawing substituents in the fluorene moiety increases the thermodynamic stability of the radical anions in both series of compounds, **2** and **16**.

During our CV experiments, we attempted the electropolymerisation of series **2**, however, we were unable to form any polymeric materials. We believe there are two main reasons for this: (i) the oxidation of the species is thought to proceed *via* the 1,3-dithiole fragment, thereby rendering the intermediate radical cation inappropriate for dimerisation; (ii) the generation of an oligomer will be impeded by steric hindrance between the fluorene monomer units.

Conclusions

We have presented the synthesis of two series of novel push-pull 9-(1,3-dithiol-2-ylidene)fluorene systems bearing fused thiophene (**2**) and 2,5-dihydrothiophene (**16**) units. Electron absorption studies reveal an intramolecular charge transfer (ICT) band corresponding to the donor–acceptor behaviour of the 1,3-dithiole and fluorene fragments. The ICT band ($\lambda_{\mathrm{ICT}}^{\mathrm{max}}$) is shifted bathochromically with an increase in the electron-withdrawing nature of the fluorene moiety, such that its energy shows a high linear correlation with the sum of the nucleophilic constants ($\Sigma\sigma_p^-$) in the fluorene ring. In the dihydrothiophene series (**16**), the ICT bands are observed at lower energies (approximately 0.13 eV), compared to analogous compounds in the aromatic series (**2**); this trend is attributed to the electron-withdrawing nature of the thiophene system.

The electrochemistry of both series has been investigated by cyclic voltammetry. All compounds exhibit amphoteric redox behaviour: a single irreversible oxidation peak is observed in all cases, whilst the reductive behaviour depends greatly upon the nature and number of substituents in the fluorene ring. For the di-, tri- and tetranitrofluorene compounds, the values of the first and second reduction potentials show a strong linear dependency to $\Sigma\sigma_p^-$.

From the CV data of **2** and **16**, we have concluded that the oxidation process is most likely to take place within the 1,3-dithiole unit. As a result, oxidative polymerisation *via* the thiophene functionality in series **2** is not realised. Consequently, we have focused our attention on the polymer **1** and are currently investigating the photoconducting properties of this material; using the results obtained from series **2** and **16**, we hope to develop a new family of electro- and photoactive polymers possessing unique conducting properties.

Experimental

General

Melting points were taken using Electrothermal Melting Point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC 250 instrument; chemical shifts, given in ppm, are relative to tetramethylsilane as internal standard; all *J* values are in Hz. Infrared spectra were recorded on a Mattson Genesis Series FTIR spectrometer and mass spectra were determined with a 7070E VG Analytical Mass Spectrometer. Elemental analyses were performed on a Carlo-Erba Strumentazione instrument. Absorption spectra were recorded on a Unicam UV2 spectrophotometer.

Electrochemical measurements

Cyclic voltammetry was performed on a BAS CV50W voltammetric analyser, with *iR* compensation, using anhydrous DMF (Aldrich) as the solvent, Ag/AgCl as the reference electrode and platinum wire and disk as the counter and working electrodes, respectively. All solutions were degassed (N_2) and contained the substrate in concentrations *ca.* 10^{-3} M, together with Bu_4NPF_6 (0.1 M) as the supporting electrolyte. The scan rate was 200 mV s^{-1}.

Fluorenes **13a–c** are available commercially (Aldrich). The synthetic procedures for 2,7-dinitrofluorene-4-carboxylic acid methyl ester **7a** and 2,5,7-trinitrofluorene-4-carboxylic acid methyl ester **8a** are described elsewhere.[22] 2,4,7-Trinitrofluorene **13d**[17] and 2,4,5,7-tetranitrofluorene **13e**[18] were prepared as described previously.

Fluorene-4-carboxylic acid *n*-butyl ester 5b

A mixture of fluorene-4-carboxylic acid **3** (0.50 g, 2.38 mmol) and thionyl chloride (2 cm^3) was refluxed for 1 h. After evaporation of excess thionyl chloride *in vacuo*, *n*-butanol (1.5 cm^3) was added and the mixture was heated at 90–100 °C for 2 h. Evaporation of the solvent under reduced pressure afforded the crude ester **5b**, which was used in subsequent steps without further purification.

2-Nitrofluorene-5-carboxylic acid *n*-butyl ester 6b

To a solution of **5b** in acetic acid (5 cm^3) was added nitric acid (0.8 cm^3, $d = 1.50$) and the reaction was stirred for 48 h at 20 °C. After the addition of cold water (50 cm^3), the mixture was allowed to stand for 2 h whence the water layer was decanted. The resulting tarry residue was washed with water and reprecipitated three times from warm acetonitrile (7 cm^3), by addition of water (3 cm^3) and subsequent cooling to 0–5 °C, to give a white solid (270 mg, 45% yield); mp 99–101 °C; EIMS (M$^+$) 311; HRMS (M$^+$) 311.11754, calculated for $C_{18}H_{17}NO_4$ 311.11575; δ_H ([$^2H_6$]DMSO) 8.46 (1H, d, *J* 1.3), 8.41 (1H, d, *J* 8.8), 8.26 (1H, dd, *J* 8.8 and 1.8), 7.90 (1H, d, *J* 7.7), 7.83 (1H d, *J* 7.6), 7.57 (1H, t, *J* 7.7), 4.43 (2H, t, *J* 6.6), 4.15 (2H, s), 1.77 (2H, m), 1.47 (2H, m) and 0.96 (3H, t, *J* 7.4); ν_{max}/cm^{-1} (KBr) 3086, 2961, 2934, 1724 (C=O), 1518 (NO_2), 1341 (NO_2), 1279, 1148 and 745.

2,7-Dinitrofluorene-4-carboxylic acid *n*-butyl ester 7b and 2,5,7-trinitrofluorene-4-carboxylic acid *n*-butyl ester 8b

To a solution of ester **5b**, obtained as above from **3** (2.00 g, 9.52 mmol), in acetic acid (20 cm^3), was added dropwise nitric acid (20 cm^3, $d = 1.50$) over 20 min with stirring and cooling using cold water; the reaction mixture was allowed to stand for 16 h at 10–15 °C. After addition of ice (30 g) and cold water (100 cm^3), the precipitate was filtered, thoroughly washed with water and reprecipitated from warm acetonitrile (50 cm^3) by adding warm water (25 cm^3) with subsequent cooling to room temperature. The crude product was dried and reprecipitated with petroleum ether (40 cm^3) from hot ethyl acetate (40 cm^3) affording **7b** (1.29 g, 38%) as a white power; mp 163–165 °C; EIMS (M$^+$) 356; HRMS (M$^+$) 356.10038, calculated for $C_{18}H_{16}N_2O_6$ 356.10083; δ_H ([$^2H_6$]DMSO) 8.72 (1H, s), 8.55 (2H, s), 8.47 (1H, d, *J* 8.8), 8.29 (1H, dd, *J* 8.8 and 2.0), 4.48 (2H, t, *J* 6.5), 4.27 (2H, s), 1.79 (2H, m), 1.46 (2H, m) and 0.97 (3H, t, *J* 7.4); ν_{max}/cm^{-1} (KBr) 3082, 2962, 2934, 1724 (C=O), 1521 (NO_2), 1345 (NO_2), 1272, 1182 and 740.

The petroleum ether–ethyl acetate filtrate obtained from the above was evaporated *in vacuo* to dryness, the flask was placed into an ice-bath, cooled to −10 °C and nitric acid (20 cm^3, $d = 1.50$) was added to the flask with vigorous stirring. The mixture was allowed to stand for 30 min at 0–5 °C and then for 2 h at 15–20 °C. After addition of ice (40 g) and cold water (50 cm^3) the precipitate was filtered, thoroughly washed with ice-cold water, dried *in vacuo* at 50–60 °C and recrystallised from cyclohexane–ethyl acetate, affording **8b** (1.18 g, 31%) as a greyish powder; mp 150–153 °C; EIMS (M$^+$) 401; HRMS (M$^+$) 401.08573, calculated for $C_{18}H_{15}N_3O_8$ 401.08591; δ_H ([$^2H_6$]-DMSO) 8.96 (1H, s), 8.85 (1H, s), 8.73 (1H, s), 8.51 (1H, s), 4.52 (2H, s), 4.28 (2H, t, *J* 6.6), 1.73 (2H, m), 1.44 (2H, m) and 0.95 (3H, t, *J* 7.3); ν_{max}/cm^{-1} (KBr) 3093, 2959, 2930, 1717 (CO), 1528 (NO_2), 1344 (NO_2), 1290 and 737.

2,7-Dinitrofluorene-4-carboxylic acid undecyl ester 7c

The product was obtained from **9** (0.17 g, 0.57 mmol) by treatment with thionyl chloride and undecyl alcohol, as described above for **5b**. The crude product was dissolved in ethyl acetate–petroleum ether (1 : 1, v/v; 25 cm^3) and filtered through a 2 cm layer of silica. After evaporation of the solvent under reduced pressure, the residue was recrystallised from hexane affording **7c** as a white powder (135 mg, 60% yield); mp 123–127 °C; EIMS (M$^+$) 454; HRMS (M$^+$) 454.21010, calculated for $C_{25}H_{30}N_2O_6$ 454.21039; δ_H ([$^2H_6$]DMSO) 8.74 (1H, d, *J* 1.7), 8.59 (2H, m), 8.51 (1H, d, *J* 8.9), 8.32 (1H, dd, *J* 8.9 and 1.7), 4.49 (2H, t, *J* 6.6), 4.33 (2H, s), 1.81 (2H, m), 1.65–1.15 (16H, m) and 0.84 (3H, t, *J* 6.8); ν_{max}/cm^{-1} (KBr) 3077, 2922, 2853, 1725 (C=O), 1517 (NO_2), 1387, 1346 (NO_2), 1270 and 740.

2,7-Dinitrofluorene-4-carboxylic acid (triethylene glycol monoethyl ether) ester 7d

A mixture of carboxylic acid **9** (0.10 g, 0.33 mmol) and thionyl chloride (2 cm^3) was refluxed for 1 h. Compound **10** was isolated after evaporation of excess thionyl chloride *in vacuo* and was used in the next step without further purification. Monoethyl ether of triethylene glycol (2 cm^3) was added to **10** and the mixture was heated at 90–100 °C for 5 min. After cooling to room temperature, the mixture was diluted with water (25 cm^3), the precipitate filtered, dried, dissolved in dichloromethane (20 cm^3), filtered through a 2 cm layer of silica and evaporated *in vacuo* to dryness, affording **7d** as a white solid (110 mg, 73% yield); mp 82–84 °C (Found C, 57.5; H, 5.3; N, 6.2. $C_{22}H_{24}N_2O_9$ requires C, 57.4; H, 5.25; N, 6.1%); δ_H (CDCl$_3$) 8.82 (1H, d, *J* 1.8), 8.73 (1H, d, *J* 8.9), 8.59 (1H, d, *J* 2.0), 8.47 (1H, d, *J*, 1.8), 8.32 (1H, dd, *J* 8.0 and 2.3), 4.67 (2H, m), 4.20 (2H, s), 3.94 (2H, m), 3.79–3.49 (10H, m) and 1.19 (3H, t, *J* 6.9); ν_{max}/cm^{-1} (KBr) 3097, 2919, 1727 (C=O), 1521 (NO$_2$), 1347 (NO$_2$), 1281, 1106 and 739.

2,5,7-Trinitrofluorene-4-carboxylic acid (triethylene glycol monomethyl ether) ester 8c

A mixture of **4** (2.44 g, 10.6 mmol), triethylene glycol monomethyl ether (3.5 cm^3, 22 mmol) and one drop of DMF was stirred at 80–85 °C for 15 h; the resulting yellow solution was evaporated *in vacuo*. After cooling, the residue was dissolved in carbon tetrachloride (25 cm^3), thoroughly washed with dilute sodium bicarbonate solution and dried over magnesium sulfate. After removing the solvent *in vacuo*, the crude ester **5c** (3.02 g, 80%) was obtained as a yellow oil. The ester (1.8 g) was added to a mixture of nitric acid (35 cm^3, $d = 1.492$) and sulfuric acid (2 cm^3, $d = 1.84$) at −8 to −10 °C with stirring, kept at this temperature for 40 min and was then allowed to stand at room temperature for 6 h. After addition of ice (50 g) and cold water (100 cm^3) the mixture was allowed to stand at 0 °C for 2 h. After this time, the aqueous layer was decanted, fresh water (200 cm^3) was added and the mixture was allowed to stand overnight. Once again, the aqueous layer was decanted and the residue was dissolved in benzene, dried over calcium chloride and the solvent removed *in vacuo*. The crude product was purified by column chromatography using chloroform containing 0.1 cm^3 dm^{-3} conc. aqueous HCl to afford 1.5 g (49% overall) of **8c** as a light yellow transparent oil (Found C, 51.6; H, 4.3; N, 8.6; $C_{21}H_{21}N_3O_{11}$ requires C, 51.3; H, 4.3; N, 8.6%); EIMS (M$^+$) 491; δ_H (CDCl$_3$) 8.85 (1H, d, *J* 2.0), 8.78 (1H, d, *J* 2.1), 8.71 (1H, d, *J* 1.7), 8.64 (1H, d, *J* 1.9), 4.54 (2H, m), 4.36 (2H, s), 3.89 (2H, m), 3.77–3.67 (6H, m), 3.55 (2H, m) and 3.37 (3H, s); ν_{max}/cm^{-1} (KBr) 3093, 2923, 2876, 1723 (C=O), 1532 (NO$_2$), 1344 (NO$_2$), 1290, 1097 and 738.

2,7-Dinitrofluorene-4-carboxylic acid 9

A solution of **7b** (0.34 g, 0.96 mmol) in a mixture of acetic acid (15 cm^3) and concentrated hydrochloric acid (7 cm^3) was allowed to reflux for 16 h. After cooling to room temperature and filtering, the product was isolated as a pale yellow crystalline solid (0.28 g, 98% yield); mp > 250 °C; EIMS (M$^+$) 300; HRMS (M$^+$) 300.03845, calculated for $C_{14}H_8N_2O_6$ 300.03824; δ_H (d$_6$-DMSO) 14.1 (1H, broad), 8.69 (1H, d, *J* 2.1), 8.66 (1H, d, *J* 8.9), 8.59 (1H, d, *J* 2.5), 8.55 (1H, d, *J* 2.4), 8.33 (1 H, dd, *J* 8.8 and 2.2) and 4.30 (2H, s); ν_{max}/cm^{-1} (KBr) 3103, 2912, 2767, 1704 (C=O), 1517 (NO$_2$), 1399, 1287 and 739.

2-(Methylthio)thieno[3,4-*d*][1,3]dithiolium triflate 12

To a suspension of **11**[16] (1.27 g, 6.68 mmol) in dry dichloromethane (10 cm^3) was added methyl triflate (0.93 cm^3, 10.6 mmol); the mixture was allowed to stir overnight at room temperature. After dilution with dry diethyl ether (15 cm^3), the suspension was cooled to 0 °C and the product was isolated by filtration as a green crystalline solid (2.27 g, 96% yield); mp > 250 °C; EIMS (M$^+$) 205; HRMS (M$^+$) 204.92905, calculated for $C_6H_5S_4$ 204.92741; δ_H ([^{2}H$_6$]acetone) 8.54 (2H, s) and 3.41 (3H, s); ν_{max}/cm^{-1} (KBr) 3123, 2927, 1276, 1251, 1161, 1025, 798, 634 and 463.

2-(Methylthio)-4,6-dihydrothieno[3,4-*d*][1,3]dithiolium triflate 15

Methyl triflate (0.114 cm^3, 1.0 mmol) was added to a suspension of **14** (0.24 g, 1.25 mmol) in dry dichloromethane (10 cm^3) and the mixture was allowed to stand overnight with stirring. The precipitate ‡ was filtered and dry toluene (15 cm^3) was added to the filtrate. The resulting mixture was evaporated *in vacuo* to a volume of *ca.* 10 cm^3; the product was filtered, washed with toluene and dried *in vacuo*, affording salt **15** (0.295 g, 83% on methyl triflate) as a pale yellow powder. Evaporation of the filtrate to dryness afforded unreacted **14** (40 mg, 17%). Since the product was found to decompose over a short period of time, salt **15** was used immediately in subsequent reactions; δ_H ([^{2}H$_6$]acetone) 4.45 (4H, s) and 3.31 (3H, s).

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)fluorene 2a

To a solution of diisopropylamine (0.1 cm^3, 0.70 mmol) in dry THF (2 cm^3), under nitrogen at −78 °C, was added *n*-butyllithium (0.44 cm^3, 1.6 M solution in hexane, 0.70 mmol) and the mixture was allowed to stir for 10 min after warming to room temperature. The solution was cooled once again to −78 °C and fluorene (0.10 g, 0.60 mmol) was added; the mixture was allowed to warm to room temperature. The reaction was then cooled again to −78 °C and the salt **12** (0.21 g, 0.60 mmol) was added. The reaction mixture was allowed to warm to room temperature and was stirred for a further 12 h. After dilution of the reaction mixture with a mixture of ethanol (20 cm^3), water (10 cm^3) and 2 drops of acetic acid, the resulting precipitate was filtered, washed with water and dried *in vacuo*. The solid was dissolved in toluene (25 cm^3) and the solution was filtered through a 3 cm layer of silica. After evaporation of the solution to dryness, the product was recrystallised from ethanol–toluene (2:1, v/v) and finally from cyclohexane. Compound **2a** was obtained as a grey powder which formed almost colourless needles after slow evaporation of its solution in dichloromethane to dryness (16 mg, 8.3%); mp 192–196 °C; EIMS (M$^+$) 322; HRMS (M$^+$) 321.99467, calculated for $C_{18}H_{10}S_3$ 321.99448; δ_H([^{2}H$_6$]DMSO) 8.00 (2H, d, *J* 7.2), 7.94 (2H, d, *J* 7.6), 7.76 (2H, d, *J* 0.7), 7.48 (2H, t, *J* 7.5) and 7.40 (2H, t, *J* 7.3); ν_{max}/cm^{-1} (KBr) 3100, 2924, 1740, 1541, 1441, 840, 767 and 716.

General procedure for 9-(thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2-nitrofluorene 2b and 9-(thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2-nitrofluorene-5-carboxylic acid *n*-butyl ester 2c

A mixture of **6b** or **13b** (0.10 mmol), salt **12** (177 mg, 0.50 mmol) and dry pyridine (0.25 cm^3) was heated in a sealed tube at 80–90 °C for 3 h. The reaction mixture was diluted with 2 ml of ethanol and the precipitate was filtered and dried. A portion (10 mg) of the crude product obtained (40 mg) was dissolved in 15 cm^3 of dichloromethane and silica was added in portions to this solution until all the liquid was absorbed. The solvent was evaporated to dryness and the silica was suspended in petroleum ether and placed into a chromatography column (id 5 × 30 cm, silica/petroleum ether). The product was eluted with petroleum ether–ethyl acetate (10:1, v/v); the solvent ratio was changed to 7:1 and 5:1 as the yellow band of the product reached a third and a half of the height of the column, respectively. Under these conditions, complete separation from the by-products was achieved. The eluate was evaporated *in vacuo* to dryness, the residue was dissolved in 5 cm^3 of dichloromethane and absorbed on silica as described above. After placing the

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‡ According to the ^{1}H NMR spectrum, the precipitate is likely to consist of **17a** and **17b** in a molar ratio approximately 5:7.

mixture onto a column (silica, id 2 × 10 cm), the residue was washed thoroughly with cyclohexane and eluted with diethyl ether; after evaporation of the solvent, the final product was washed with petroleum ether to give:

2b as an orange crystalline solid (yield 3 mg from 10 mg of crude product, 22% overall based on **13b**); mp 245 °C (decomp.); EIMS (M^+) 367; HRMS (M^+) 366.97845, calculated for $C_{18}H_9NO_2S_3$ 366.97955; δ_H ([$^2H_6$]DMSO) 8.80 (1H, s), 8.30 (2H, s), 8.22 (1H, d, *J* 7.3), 8.02 (1H, d, 7.9), 7.91 (1H, d, *J* 2.7), 7.84 (1H, d, *J* 2.8), 7.64 (1H, t, *J* 7.6) and 7.50 (1H, t, *J* 7.5); ν_{max}/cm^{-1} (KBr) 3101, 2923, 1716, 1538 (NO_2), 1335 (NO_2), 1145, 1092, 760 and 723;

2c as a red crystalline solid (yield 3 mg, 25% based on **6b**), mp 198–200 °C; EIMS (M^+) 467; HRMS (M^+) 467.03310, calculated for $C_{23}H_{17}NO_4S_3$ 467.03198; δ_H ([$^2H_6$]DMSO) 8.82 (1H, s), 8.37 (1H, d, *J* 8.8), 8.22 (2H, m), 7.90 (1H, d, *J* 2.6), 7.82 (1H, d, *J* 2.8), 7.71 (2H, m), 4.46 (2H, t, *J* 6.5), 1.78 (2H, m), 1.48 (2H, m) and 0.97 (3H, t, *J* 7.3); ν_{max}/cm^{-1} (KBr) 3102, 2957, 2925, 1716, 1514 (NO_2), 1338 (NO_2), 1276, 1121 and 759.

General procedure for 9-(thieno[3,4-*d*][1,3]dithiol-2-ylidene)- and 9-(4,6-dihydrothieno[3,4-*d*][1,3]dithiol-2-ylidene)polynitrofluorene derivatives 2d–m and 16d,f,i,k,m

To a mixture of salt **12** or **15** and fluorene derivatives **7**, **8** or **13** (in molar ratio 1.1 : 1) was added the corresponding solvent (0.25 cm³ per 100 mg of the solid mixture); the reaction was allowed to stand at the desired temperature with occasional shaking (for precise conditions see Table 1). After dilution with ethanol (2 cm³), the precipitate was filtered and recrystallised from a suitable solvent (DMF–ethanol for undecyl and triethylene glycol esters or pure DMF for other compounds).

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,7-dinitrofluorene 2d

Mp > 250 °C; EIMS (M^+) 412; HRMS (M^+) 411.96323, calculated for $C_{18}H_8O_4N_2S_3$ 411.96463; δ_H ([$^2H_6$]DMSO) 8.88 (2H, s), 8.43 (2H, d, *J* 8.4), 8.32 (2H, d, *J* 8.4) and 7.92 (2H, s); ν_{max}/cm^{-1} (KBr) 3101, 1513 (NO_2), 1461, 1332 (NO_2), 1207, 1087, 826 and 761.

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,7-dinitrofluorene-4-carboxylic acid methyl ester 2e

Mp > 250 °C; EIMS (M^+) 470; HRMS (M^+) 469.96855, calculated for $C_{20}H_{10}N_2O_6S_3$ 469.97009; δ_H ([$^2H_6$]DMSO) 9.08 (1H, s), 8.95 (1H, s), 8.52 (2H, d),§ 8.28 (1H, d, *J* 8.2), 7.95 (2H, s) and 4.15 (3H, s); ν_{max}/cm^{-1} (KBr) 3102, 1731 (C=O), 1516 (NO_2), 1327 (NO_2), 1278, 1157 and 760.

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,7-dinitrofluorene-4-carboxylic acid *n*-butyl ester 2f

Mp > 250 °C; EIMS (M^+) 512; HRMS (M^+) 512.01695, calculated for $C_{23}H_{16}N_2O_6S_3$ 512.01703; δ_H ([$^2H_6$]DMSO) 8.91 (1H, s), 8.78 (1H, s), 8.45 (2H, d),¶ 8.20 (1H, d, *J* 8.8), 7.91 (2H, s), 4.53 (2H, t, *J* 6.6), 1.81 (2H, m), 1.52 (2H, m) and 1.01 (3H, t, *J* 7.3); ν_{max}/cm^{-1} (KBr) 3101, 2959, 1725 (C=O), 1513 (NO_2), 1327 (NO_2), 1276, 1161 and 759.

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,7-dinitrofluorene-4-carboxylic acid *n*-undecyl ester 2g

Mp > 250 °C; EIMS (M^+) 610; HRMS (M^+) 610.12284, calculated for $C_{30}H_{30}N_2O_6S_3$ 610.12659; δ_H ($CDCl_3$) 9.06 (1H, s), 8.93 (1H, s), 8.62 (2H, d),|| 8.21 (1H, d, *J* 8.8), 7.36 (1H, s), 4.54 (2H, t, *J* 6.7), 1.91 (2H, m), 1.60–1.30 (16H, m), and 0.90 (3H, t, *J* 6.8); ν_{max}/cm^{-1} (KBr) 3101, 2922, 2852, 1727 (C=O), 1517 (NO_2), 1344, 1328 (NO_2), 1162 and 763.

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,7-dinitrofluorene-4-carboxylic acid (triethylene glycol monoethyl ether) ester 2h

Mp > 250 °C; EIMS (M^+) 616; HRMS (M^+) 616.06502, calculated for $C_{27}H_{24}N_2O_9S_3$ 616.06439; δ_H ([$^2H_6$]DMSO) 8.79, (1H, s), 8.63 (1H, s), 8.40 (2H, d),** 8.13 (1H, d, *J* 7.8), 7.88 (2H, s), 4.63 (2H, m), 3.88 (2H, m), 3.90–3.30 (10H, m) and 1.04 (3H, t, *J* 6.9); ν_{max}/cm^{-1} (KBr) 3100, 2919, 2861, 1727 (C=O), 1517 (NO_2), 1345, 1329 (NO_2), 1104 and 828.

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,4,7-trinitrofluorene 2i

Mp > 250 °C; EIMS (M^+) 457; HRMS (M^+) 456.94860, calculated for $C_{18}H_7N_3O_6S_3$ 456.94971; δ_H ([$^2H_6$]DMSO) 9.14 (1H, s), 8.95 (1H, s), 8.70 (1H, s), 8.28 (1H, br), 8.15 (1H, br) and 7.98 (2H, s); ν_{max}/cm^{-1} (KBr) 3087, 1574, 1516 (NO_2), 1497, 1338 (NO_2), 1224, 824 and 763.

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,5,7-trinitrofluorene-4-carboxylic acid methyl ester 2j

Mp > 250 °C; EIMS (M^+) 515; HRMS (M^+) 514.95718, calculated for $C_{20}H_9O_8N_3S_3$ 514.95520; δ_H ([$^2H_6$]DMSO) 9.20 (1H, s), 9.11 (1H, s), 8.66 (1H, s), 8.48 (1H, s), 8.02 (2H, s) and 3.90 (3H, s); ν_{max}/cm^{-1} (KBr) 3108, 2953, 1728 (C=O), 1528 (NO_2), 1504, 1341 (NO_2), 1322, 1153 and 786.

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,5,7-trinitrofluorene-4-carboxylic acid *n*-butyl ester 2k

Mp > 250 °C; EIMS (M^+) 557; HRMS (M^+) 557.00184, calculated for $C_{23}H_{15}N_3O_8S_3$ 557.00214; δ_H ([$^2H_6$]DMSO) 9.22 (1H, s), 9.14 (1H, s), 8.66 (1H, s), 8.49 (1H, s), 8.01 (2H, s), 4.34 (2H, t, *J* 6.7), 1.79 (2H, m), 1.50 (2H, m) and 0.99 (3H, t, *J* 7.3); ν_{max}/cm^{-1} (KBr) 3113, 2957, 2871, 1781 (C=O), 1525 (NO_2), 1509, 1340 (NO_2), 1321 and 786.

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,5,7-trinitrofluorene-4-carboxylic acid (triethylene glycol monomethyl ether) ester 2l

Mp > 250 °C (Found C, 48.5; H, 3.4; N, 6.4. $C_{26}H_{21}N_3O_{11}S_3$ requires C, 48.2; H, 3.3; N, 6.5%); EIMS (M^+) 647; δ_H ([$^2H_6$]DMSO) 9.14 (1H, d, *J* 1.7), 9.07 (1H, d, *J* 1.7), 8.63 (1H, d, *J* 1.7), 8.48 (1H, d, *J* 1.7), 7.97 (2H, s), 4.44 (2H, t, *J* 5.2), 3.83 (2H, t, *J* 4.7), 3.66–3.52 (6H, m), 3.43 (2H, m) and 3.25 (3H, s); ν_{max}/cm^{-1} (KBr) 3097, 2878, 1723 (C=O), 1532 (NO_2), 1503, 1341 (NO_2), 1104 and 816.

9-(Thieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,4,5,7-tetranitrofluorene 2m

Mp > 250 °C; EIMS (M^+) 502; HRMS (M^+) 501.93376, calculated for $C_{18}H_6N_4O_8S_3$ 501.93478; δ_H ([$^2H_6$]DMSO) 9.35 (2H, s), 8.74 (2H, s) and 8.11 (2H, s); ν_{max}/cm^{-1} (KBr) 3086, 1518 (NO_2), 1482, 1357, 1338 (NO_2), 1314, 1249 and 786.

9-(4,6-Dihydrothieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,7-dinitrofluorene 16d

Mp > 250 °C (Found C, 52.0; H, 2.4; N, 6.8; S, 23.2. $C_{18}H_{10}N_2O_4S_3$ requires C, 52.2; H, 2.5; N, 6.8; S, 23.2%); δ_H ([$^2H_6$]DMSO) 8.72 (2H, d, *J* 1.9), 8.39 (2H, d, *J* 8.6), 8.26 (2H, dd,

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§ This is a sum of a doublet at 8.52 ppm (*J* ≅ 9 Hz) and a singlet at 8.54 ppm.

¶ This is a sum of a doublet at 8.45 ppm (*J* ≅ 9 Hz) and a singlet at 8.43 ppm.

|| This is a sum of a doublet at 8.62 ppm (*J* ≅ 9 Hz) and a singlet at 8.64 ppm.

** This is a sum of a doublet at 8.40 ppm (*J* ≅ 9 Hz) and a singlet at 8.38 ppm.

J 8.7 and 2.0), 4.20 (4H, s); ν_{max}/cm^{-1} (KBr) 3085, 1505 (NO$_2$), 1461, 1334 (NO$_2$), 1240, 1211, 1087 and 825.

9-(4,6-Dihydrothieno[3,4-*d*][2,3]dithiol-2-ylidene)-2,7-dinitrofluorene-4-carboxylic acid *n*-butyl ester 16f

Mp > 250 °C (Found C, 53.8; H, 3.6; N, 5.5. $C_{23}H_{18}N_2O_6S_3$ requires C, 53.7; H, 3.6; N, 5.5%); EIMS (M$^+$) 514; δ_H ([^{2}H$_6$]DMSO) 8.88 (1H, s), 8.76 (1H, s), 8.55 (1H, d, J 8.0), 8.48 (1H, s), 8.23 (1H, d, J 8.0), 4.56 (2H, t, J 6.6), 4.22 (4H, s), 1.86 (2H, m), 1.54 (2H, m) and 1.01 (3H, t, J 7.4); ν_{max}/cm^{-1} (KBr) 3094, 2957, 1727 (C=O), 1509 (NO$_2$), 1330 (NO$_2$), 1276, 1241, 1164 and 826.

9-(4,6-Dihydrothieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,4,7-trinitrofluorene 16i

Mp > 250 °C (Found C, 47.3; H, 2.1; N, 9.1. $C_{18}H_9N_3O_6S_3$ requires C, 47.1; H, 2.0; N, 9.2%); δ_H ([^{2}H$_6$]DMSO) 9.04 (1H, d, J 1.9), 8.86 (d, 1H, J 2.0), 8.68 (1H, d, J 1.8), 8.28 (1H, dd, J 8.8 and 2.0), 8.21 (1H, d, J 8.9), 4.26 (4H, s); ν_{max}/cm^{-1} (KBr) 3079, 2916, 1519 (NO$_2$), 1490, 1339 (NO$_2$), 1225, 1098, 824 and 721.

9-(4,6-Dihydrothieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,5,7-trinitrofluorene-4-carboxylic acid *n*-butyl ester 16k

Mp > 250 °C (Found C, 49.5; H, 3.2; N, 7.4; S, 17.1. $C_{23}H_{17}N_3O_8S_3$ requires C, 49.4; H, 3.1; N, 7.4; S, 17.2%); δ_H (CDCl$_3$) 9.11 (1H, d, J 1.7), 9.02 (1H, d, J 2.0), 8.75 (1H, d, J 1.8), 8.65 (1H, d, J 2.0), 4.41 (2H, t, J 6.8), 4.18 (4H, s), 1.84 (2H, m), 1.54 (2H, m) and 1.03 (3H, t, J 6.4); ν_{max}/cm^{-1} (KBr) 3087, 2958, 1717 (C=O), 1539, 1525 (NO$_2$), 1494, 1323 (NO$_2$), 1160 and 816.

9-(4,6-Dihydrothieno[3,4-*d*][1,3]dithiol-2-ylidene)-2,4,5,7-tetranitrofluorene 16m

Mp > 250 °C (Found C, 42.9; H, 1.7; N, 11.1; S, 19.1. $C_{18}H_8N_4O_8S_3$ requires C, 42.9; H, 1.6; N, 11.1; S, 19.1%); δ_H ([^{2}H$_6$]DMSO) 9.22 (1H, br), 8.69 (2H, br), 4.32 (4H, s); ν_{max}/cm^{-1} (KBr) 3089, 1530 (NO$_2$), 1469, 1358, 1338 (NO$_2$), 1250, 1161 and 707.

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Paper 8/08540D