Fluorene acceptors with intramolecular charge-transfer from 1,3-dithiole donor moieties: novel electron transport materials

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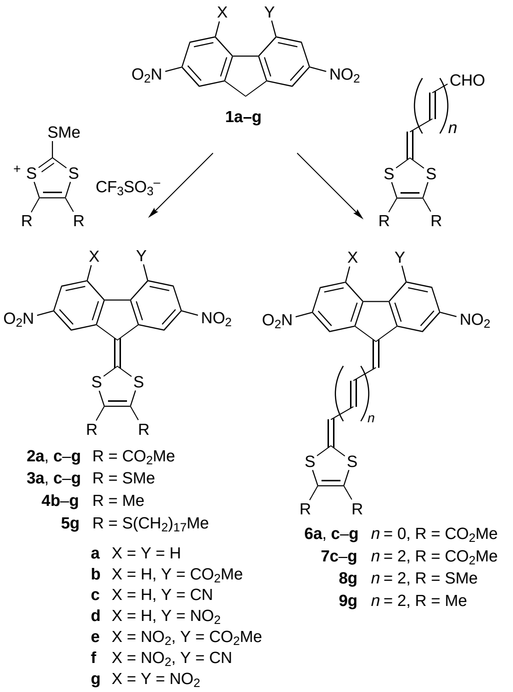
The synthesis, solution redox behaviour and intramolecular charge transfer properties of novel D(=CH–CH)$_n$=A compounds (n = 0, 1, 3; D and A are 1,3-dithiole and nitrofluorene moieties, respectively) are reported.

Organic compounds with asymmetric π-electron delocalization exhibit properties such as non-linear optical effects (NLO), photoconductivity and electron transport properties.[1] Electron acceptors of the fluorene series are widely used for optical information recording.[2] It has been shown that fluorene acceptors substituted with a donor moiety can efficiently sensitise the photoconductivity of carbazole-containing polymers in the spectral region of intramolecular charge transfer (ICT) of the acceptors.[3] Although 1,3-dithiole electron donor are well-known building blocks in conductive charge transfer salts,[4] there are few reports of 1,3-dithioles as components of π-conjugated push-pull compounds.[5] Herein we report a new series of D(=CH–CH)$_n$=A compounds containing 1,3-dithioles and nitrosubstituted fluorenes as D and A moieties, respectively.

Compounds **2**–**9** were synthesised (Scheme 1) by condensation of the substituted fluorenes **1** with the appropriate dithiolium salts (for **2**–**5**) or aldehydes (for **6**–**9**) in DMF, (20–70 °C, 0.5–50 h; 30–90%). The intramolecular charge transfer (ICT) in these compounds is manifested in the appearance of long-wavelength absorbance bands in their electronic spectra (Fig. 1, Table 1). Increasing the acceptor character of the fluorene fragment with electron withdrawing substituents results in a bathochromic shift of the ICT band that can be described quantitatively by eqn. (1), where $h\nu_{\mathrm{ICT}}$ is the

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

ICT energy defined by the maxima of the ICT band (λ_{ICT}), $h\nu^0_{\mathrm{ICT}}$ is $h\nu_{\mathrm{ICT}}$ for the reference compound (unsubstituted benzene rings in fluorenes, $\Sigma\sigma^-_{\mathrm{p}} = 0$), ρ^- is a parameter showing ICT energy sensitivity to substituents, and $\Sigma\sigma^-_{\mathrm{p}}$ is a sum of σ^-_{p} (nucleophilic constants of the substituents in the fluorene nucleus).



Scheme 1

The sensitivity parameter ρ^-_{ICT} shows only minor changes with changing the substituents in the 1,3-dithiole ring (**2** → **3** → **4**) or with lengthening the C=C chain between the D and A moieties (**2** → **6** → **7**) (Table 1). The values of $\rho^-_{\mathrm{ICT}} \approx$ 0.14–0.17 eV are higher than that reported for 9-(4-phenyl-1,2-dithiol-3-ylidene)fluorenes (0.12 ± 0.01 eV).[6]

The structure of **3g** was determined by X-ray analysis (Fig. 2).§ As a result of ICT, the exocyclic C(9)=C(14) double bond is lengthened [1.395(5) Å] and is close to that observed in another ICT compound of the fluorene series, *i.e.* 9-(α-cyano-α-dimethylaminomethylene)-2,4,5,7-tetranitrofluorene [1.388(4) Å].[3b] The distortions of the substituents in the fluorene ring are a result of the close contact between the nitro groups in positions 4 and 5. The dihedral angle between the planes of the fluorene five-membered ring and the 1,3-dithiole ring is 21.3°. Fig. 2 shows that the acceptor moieties in the molecules related by symmetry centres form stacks (interplanar distance 3.58 Å). Interstack interactions occur through weak contacts of the donor fragments; S(2b)···S(3a) and S(2a)···S(3b) distances are slightly shortened (3.543 Å) compared to double

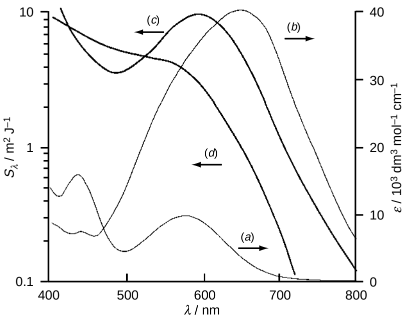


Fig. 1 Electron absorption spectra for (*a*) **3g** and (*b*) **8g** in acetone, (25 °C) and spectral distribution of $S_{\Delta V}$ for PEPC films sensitized by 5 mass% of electron acceptors (*c*) **5g** and (*d*) TNF

Table 1 Correlations[a] of ICT energies of acceptors **2**–**4**, **6** and **7** using eqn. (1), spectral data for **2g**–**4g** and **6g**–**9g** and CV data for **2g**–**4g** and **6g**

Compound	$h\nu^0_{ICT}$/eV[b]	ρ^-_{ICT}/eV[b]	$\lambda_{ICT/nm}$[b,c]	$\lambda_{ICT/nm}$[c,d]	ε_{ICT}/dm^3 mol^{-1} cm^{-1}	$E^{\frac{1}{2}}_{1red}$/V[e]	$E^{\frac{1}{2}}_{2red}$/V[e]
2	3.00 ± 0.05	−0.138 ± 0.012	544	535	9800	−0.80	−1.02
3	2.88 ± 0.02	−0.153 ± 0.008	592	578	9700	−0.81	−1.04
4	2.81 ± 0.02	−0.150 ± 0.011	611	595	8600	−0.83	−1.05
6	2.98 ± 0.02	−0.169 ± 0.006	587.5	572	21 000	−1.11	−1.32
7	2.79 ± 0.02	−0.164 ± 0.011	636	590	39 000		
8			707	650	40 000		
9			753	700			

[a] $r \geqslant 0.985$. [b] In 1,2-dichloroethane. [c] Spectral data for compounds **2g**–**4g** and **6g**–**9g**. [d] In acetone. [e] CV data for **2g**–**4g** and **6g** (see footnote ¶).

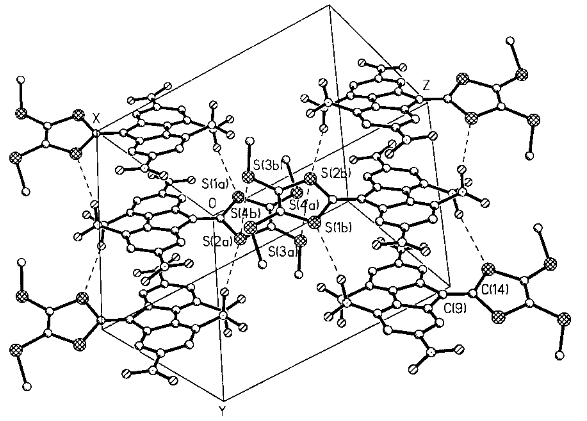


Fig. 2 Crystal packing of compound **3g**; short intermolecular S···S and S···O contacts are shown by dashed lines

the van der Waals radius of sulfur (3.6–3.7 Å).[7] There are also weak intermolecular S···O contacts (3.25–3.42 Å).

The electrochemical redox properties of the compounds **2**–**4** and **6** have been studied by cyclic voltammetry (Table 1).¶ Compounds **2**–**4** display two reversible single-electron reduction waves ($E^{\frac{1}{2}}_{1red}$ = −1.44 → −0.81 V, $E^{\frac{1}{2}}_{2red}$ = −1.60 → −1.02 V in the sequence **a** → **g**). Third quasi-reversible or irreversible single-electron reduction [$E^{\frac{1}{2}}_{3red}$ = −(1.88–2.15) V] and oxidation ($E^{\frac{1}{2}}_{ox}$ = +0.63–0.70 V) processes were observed in some, but not all, cases. Insertion of an additional double bond between the A and D moieties (**6**) leads to a shift of both $E^{\frac{1}{2}}_{1red}$ and $E^{\frac{1}{2}}_{2red}$ by *ca* . 0.3 V to more cathodic potentials. Correlation analyses of $E^{\frac{1}{2}}_{1red}$ and $E^{\frac{1}{2}}_{2red}$ for compounds **2**–**4** by eqn. (2), where $E^{\frac{1}{2}}$ is the half-wave potential of reduction or

$$E^{\frac{1}{2}} = E^{\frac{1}{2}}_0 + \rho^-_{CV}\,\Sigma\sigma^-_p \qquad (2)$$

oxidation of a compound, $E^{\frac{1}{2}}_0$ is $E^{\frac{1}{2}}$ for the reference compound (unsubstituted benzene rings in fluorenes, $\Sigma\sigma^-_p$ = 0), and ρ^- is a parameter showing electrochemical potential sensitivity to substituents, gave good linear relationships (r = 0.98–0.999); sensitivity parameters ρ^-_{CV} for the first and second reduction steps of compounds **2**–**4** were close and lay in the region of 0.20–0.24 V, which is slightly higher compared to ρ^-_{CV} for nitrosubstituted 9-aminomethylenefluorenes.[3b] The electron affinities obtained for compounds **2**–**4** from their $E^{\frac{1}{2}}_{1red}$ potentials[8] are *ca.* 0.2 eV lower than for the corresponding 4,5-X,Y-2,7-dinitrofluoren-9-ones, and for tetranitro substituted derivatives **2g**–**4g** are *ca.* 2 eV. This characterises compounds **2**–**4** as moderate acceptors.

Due to the low solubility of compound **3g** we tested the more soluble long-chain homologue **5g** as a sensitiser in photothermoplastic storage media (PTSM) based on poly[*N*-(2,3-epoxypropyl)carbazole] (PEPC).‖ Fig. 1 shows the spectral distribution of the electrophotographic sensitivity ($S_{\Delta V}$) of PTSM on the basis of PEPC films sensitized by **5g** and by 2,4,7-trinitrofluoren-9-one (TNF) which is widely used for these purposes.[2b] In contrast to TNF, for which $S_{\Delta V}$ decreases with increasing wavelength in the visible region, **5g** displays increased sensitivity in its ICT region. Excellent rheological properties of PTSM sensitised with **5g** (diffraction efficiency for plane lightwave holograms η_{max} = 25%) allowed the attainment of extremely high values of holographic sensitivity, S_η = 250–300 m^2 J^{-1} at the level of η = 1% (He-Ne laser, λ = 632.9 nm),** suggesting that this type of acceptor is extremely promising as sensitisers for hologram recording.

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Notes and References

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‡ All new compounds gave satisfactory mass spectra, ^{1}H NMR spectra and elemental analysis.

§ *Crystal data* for **3g**: $C_{18}H_{10}N_4O_8S_4$, M = 538.54, triclinic, $P\bar{1}$, a = 9.079(1), b = 10.014(1), c = 12.806(2) Å, α = 108.61(1), β = 102.30(1), γ = 103.06(1)°, V = 1022.4(4) Å^3, Z = 2, D_c = 1.749 g cm^{-3}, F(000) = 548, λ = 0.71073 Å, T = 150.0(2) K, R = 0.0580, wR = 0.1345 and goodness-of-fit 1.096, $\Delta\rho_{max}$ = 0.665 e Å^{-3}, $\Delta\rho_{min}$ = −0.588 e Å^{-3}. CCDC 182/778.

¶ *ca.* 10^{-4} mol dm^{-3} compound in dry DMA (**2**–**4**) or CH_2Cl_2 (**6**), Pt working electrode, 0.2 mol dm^{-3} $Bu_4N^+PF_6^-$; all potentials were measured *vs.* Fc^0/Fc$^+$ couple as internal reference.

‖ Details are the same as described in refs. 2(*c*) and 3(*b*).

** PTSM with 5 mass% TNF gave η_{max} = 15% and S_η = 20 m^2 J^{-1} under the same conditions [ref. 2(*b*)].

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