Electron acceptors of the fluorene series. Part 6.[1] Synthesis of 4,5-dinitro-9-X-fluorene-2,7-disulfonic acid derivatives, their charge transfer complexes with anthracene and sensitization of photoconductivity of poly-*N*-(2,3-epoxypropyl)carbazole

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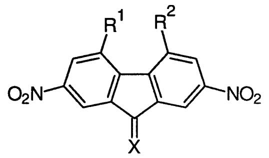
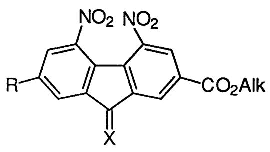
Proceeding from fluorene-2,7-disulfonyl dichloride, a number of novel fluorene electron acceptors with sulfonyl substituents have been synthesized. Formation of charge transfer complexes (CTCs) of the synthesized acceptors with anthracene in dichloroethane has been studied by appearance of long-wavelength CTC bands in the visible region of electron absorption spectra. The values of equilibrium constants determined for three acceptors (*i.e.* 18, 22a, 22b) show that the process of CTC formation is affected both by electronic and steric factors. Sensitization of poly-*N*-(2,3-epoxypropyl)carbazole (PEPC) photoconductivity with compounds 18, 21a and 22a has been studied.

Introduction

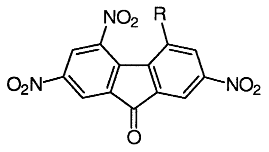
Fluorene electron acceptors are widely used in preparation and investigation of charge transfer complexes,[2–12] in activation of photoconductivity of organic semiconductors, and as electron transport materials.[13–19] Among them 9-oxo- (**a**, X = O) and 9-dicyanomethylene-substituted [**b**, $X = C(CN)_2$] polynitrofluorenes (**1**–**3**),[2,3,20] alkyl polynitrofluorene-2(4)-carboxylates (**4**–**6**),[8,21] and alkyl 4,5-dinitrofluorene-2,7-dicarboxylates (**7**)[8] have been most extensively studied. 9-Substituted polynitrofluorene acceptors containing bromine or iodine (**8, 9**)[7] and, recently, cyano groups (**10**–**12**)[22–25] in the benzene rings of fluorene nucleus have also been obtained.



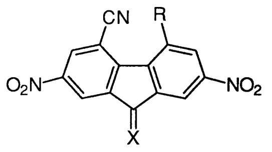
1a – c, $R^1 = R^2 = H$
2a – c, $R^1 = NO_2$; $R^2 = H$
3a – c, $R^1 = R^2 = NO_2$
4a,b, $R^1 = CO_2Alk$; $R^2 = H$
5a,b, $R^1 = CO_2Alk$; $R^2 = NO_2$
a, $X = O$; **b**, $C(CN)_2$; **c**, H_2



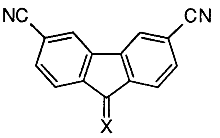
6, $R = NO_2$
7, $R = CO_2Alk$
a, $X = O$; **b**, $C(CN)_2$



8, R = Br
9, R = I

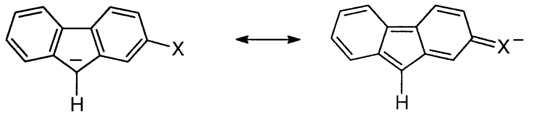


10, R = H
11, $R = NO_2$
a, $X = O$; **b**, $C(CN)_2$; **c**, H_2



12 a, $X = O$; **b**, $C(CN)_2$

We failed to find in the literature any information on fluorene acceptors containing both nitro and sulfonyl substituents in the benzene rings. However, as is seen from the substituent constants σ_I, σ_m and σ_p given in Table 1, the sulfonyl group is a rather strong electron-withdrawing substituent that can be compared to a nitro group by force. As was shown by Bowden and Cockerill[28a] and by Bordwell and McCollum[28b] in the study of ionization of 2-substituted fluorenes, position 2 (and it seems position 4 also) in the fluorene system displays considerable '*para* character' (as well as '*meta* character') due to conjugation with the reaction site (position 9 in fluorene) through the other benzene ring (**13**).



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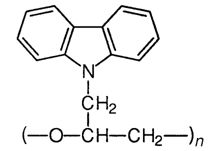
Fluorene acceptors with sulfonyl substituents having a tetrahedral configuration and high electron acceptor properties comparable to that of a flat nitro group are of interest in the investigations of electron donor–acceptor interaction in charge transfer complex (CTC) formation and as electron transport materials used for recording optical information. With this aim we synthesized 4,5-dinitro-9-X-fluorene-2,7-disulfonic acid derivatives and studied their CTC formation with anthracene and sensitization of poly-*N*-(2,3-epoxypropyl)carbazole (PEPC) photoconductivity.

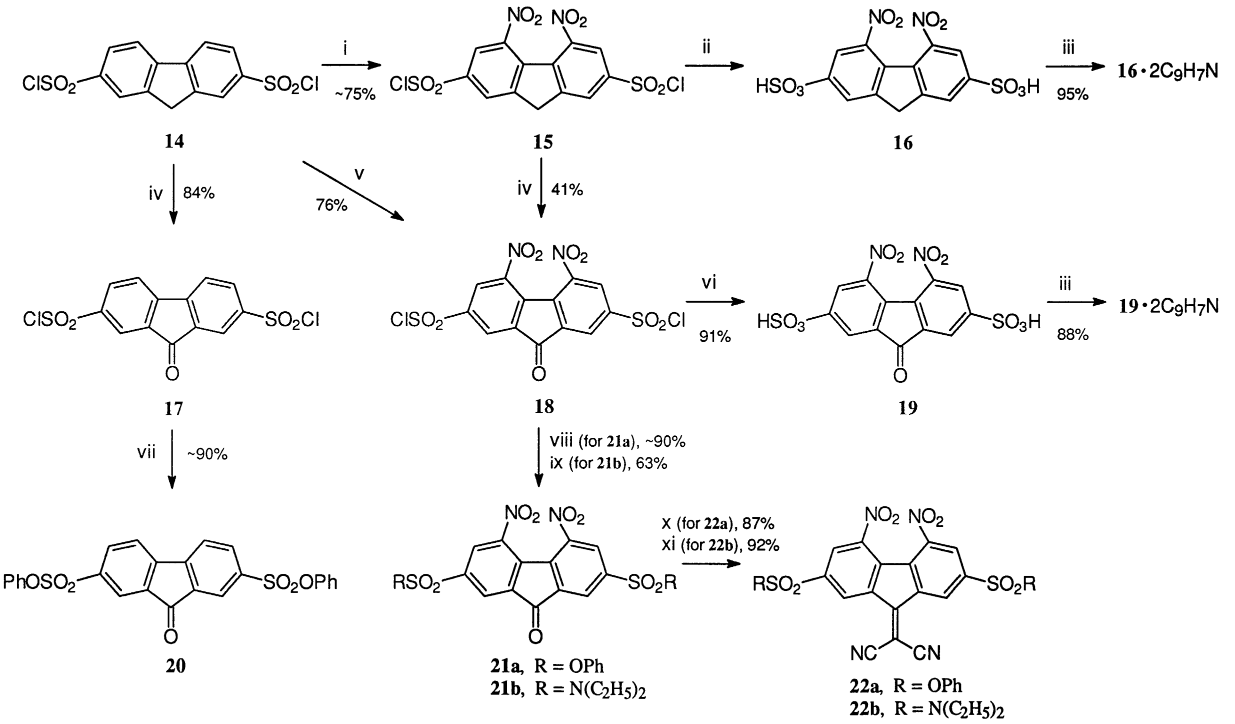


PEPC

Results and discussion

Synthesis

We have found that the readily accessible fluorene-2,7-disulf-



Scheme 1 *Reagents and conditions:* (i) HNO_3–H_2SO_4, 25 °C, 5 h; (ii) AcOH–H_2O, reflux, 4.5 h; (iii) quinoline (>2 equiv.), propan-2-ol, 25 °C, 5 min; (iv) CrO_3, Ac_2O, 25 °C, 2–3 d; (v) HNO_3–H_2SO_4, 25 °C, 8 h, then CrO_3, 15–20 °C, 12 h; (vi) AcOH–H_2O, reflux, 30 min; (vii) PhOH–Py, 100 °C, 1.5 h; (viii) PhOH–Py, 100 °C, 30 min; (ix) Et_2NH, DMF, 25 °C, 1 h; (x) $CH_2(CN)_2$, DMF, 25 °C, 30 min; (xi) $CH_2(CN)_2$, DMF, 45–50 °C, 1 h

Table 1 Comparison of the σ_I σ_m and σ_p constants for sulfonyl substituents and for nitro group[a]

Substituent	σ_I	σ_m	σ_p
SO_2CH_3	0.59	0.60	0.72
$SO_2OC_6H_5$	0.62[b]	0.36	0.33
SO_2NH_2	0.46	0.46	0.57
SO_2Cl	0.80	0.87	1.00
NO_2	0.65	0.71	0.78

[a] Most reliable values from ref. 26(*a*) are given. More complete data see in refs. 26 and 27. [b] For the substituent $SO_2OC_2H_5$ (ref. 27).

onyl dichloride (**14**)[29] can be nitrated without any noticeable hydrolysis by fuming nitric acid or by the commercially available mixture of 90% HNO_3 and 7.5% H_2SO_4 at room temperature yielding, 4,5-dinitrofluorene-2,7-disulfonyl dichloride (**15**) (Scheme 1). Compounds **14** and **15** were oxidized by chromium(VI) oxide in acetic anhydride to give corresponding fluoren-9-ones (**17**, **18**) without hydrolysis of sulfonyl chloride groups. Sulfonyl chloride **15** may also be oxidized just in the reaction mixture itself after nitration (*i.e.* with no isolation of the intermediate **15**) without hydrolysis, allowing a one-pot synthesis of **18** from **15**.

Accessibility of sulfonyl chlorides **15**, **17** and **18** permitted synthesis of other fluorene acceptors with structurally different sulfonyl substituents. In particular, diesters **20**, **21a** and bis(diethylamide) **21b** were obtained by acylation of phenol and diethylamine with sulfonyl chlorides **17** or **18**. Their condensation with malononitrile in dimethylformamide yielded stronger electron acceptors (**22a** and **22b**).

Along with the above conversions hydrolysis of sulfonyl dichlorides **15** and **18** has been studied. Due to its poor solubility sulfonyl chloride **15** was not hydrolysed in aqueous acetone at room temperature but was slowly hydrolysed in boiling aqueous acetic acid. In contrast, sulfonyl chloride **18** was rapidly hydrolysed in aqueous acetone at room temperature. The products of hydrolysis of the sulfonyl chlorides, *i.e.* sulfonic acids **16** and **19**, are hygroscopic substances and were also characterized in the form of quinolinium salts titrating as two-base acids.

^{1}H HMR spectra

The symmetric location of the sulfonyl substituents and nitro groups in compounds **15**, **16**, **18**, **19**, **21** and **22** is indicated by their ^{1}H NMR spectra in which the proton signals H-1,8 and H-3,6 are present as doublets with coupling constants $J_{1,3} = J_{6,8} = 1.4$–1.7 Hz. For compounds **17** and **20** interaction of protons H-3,4 and H-5,6 with the coupling constants 7.9–8.1 Hz, respectively, and H-1,4 and H-5,8 with the coupling constants 0.6 to 0.8 Hz, respectively, is observed. All these data are in good agreement with similar fluorene compounds made within our group.

One more peculiarity of compounds **22a** and **22b** caused by their high electron affinity should be noted. Their interaction with electron donor compounds (a polar solvent used for recording ^{1}H NMR spectra, traces of impurities in the solvent or in the compound, or specially added electron donors even in trace quantities) results in broadening of the proton signals of the fluorene system (predominantly in positions 3 and 6). Apparently, it is paramagnetic signal broadening caused by radical ion particles formed in the solution that occurs in this case. Thus, ester **22a** in [$^2H_6$]acetone shows some broadened aromatic protons [Fig. 1(*a*)]. Addition of one drop of [$^2H_7$]DMF to this solution yields the proton signals broadening for the fluorene system without changing their chemical shifts and integral intensities [Fig. 1(*b*)]. Larger broadening of the protons 3,6 indicates a greater spin density on C-3,6 atoms in radical-anion state of **22a**. Subsequent addition of trifluoroacetic acid completely restores fine resolution of the spectrum structure of compound **22a** [Fig. 1(*c*)].

Similar broadening of the signals were observed previously for ^{1}H NMR spectra of acceptors **2–5**, **10** and **11** [for $X = C(CN)_2$][30] and quite recently for polynitro-9-dicyanomethylenefluorenes containing butylsulfonyl substituents.[31] The difficulties obtaining the ^{1}H NMR spectra for another series of strong electron acceptors, namely for substituted 7,7,8,8-

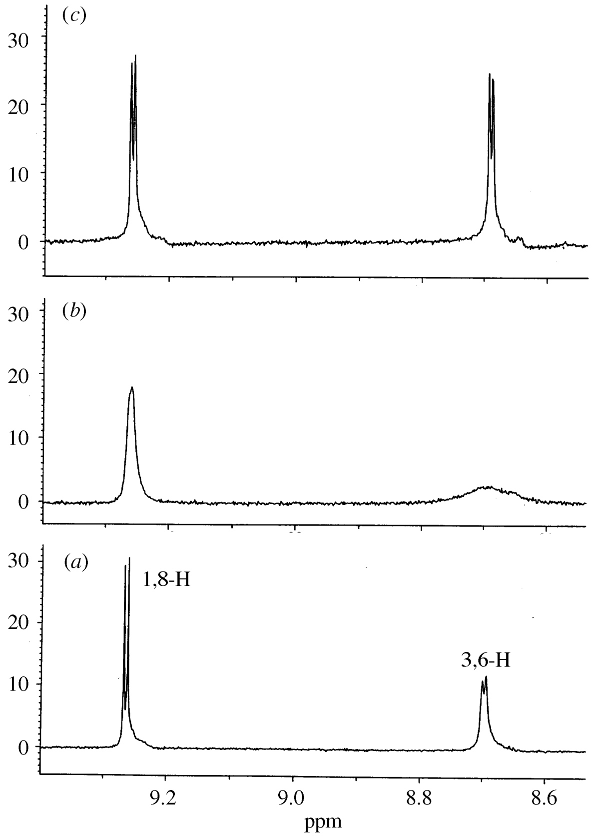


Fig. 1 200 MHz ^1H NMR spectra of acceptor **22a** in [$^2H_6$]acetone at 25 °C; (*a*) original spectrum; (*b*) one drop of [$^2H_7$]DMF was added to the solution '*a*'; (*c*) three drops of CF_3COOH were added to solution '*b*'

tetracyano-*p*-quinodimethanes for the same reasons were mentioned.[32]

Charge transfer complexes formation

The ability of fluorene acceptors to form molecular charge transfer complexes (CTCs) with electron donors like polynuclear aromatics, heteroaromatics, amines, *etc.* is well known.[2] Usually CTCs of 1 : 1 composition are formed and for a number of such CTCs X-ray diffraction structures have been determined.[33] X-Ray structures for CTCs of more complex composition (donor : acceptor, D : A = 1 : 2) were also reported[34] (although this took place for only bulky donors especially when they have two or more aromatic moieties in the molecule with a chain between them), and detailed investigations in solutions were not made.

We have found that compounds **15**, **17**, **18** and **20**–**22** form CTCs with various donors which were detected using electron absorption spectroscopy by the appearance of additional charge transfer bands in the visible region of the spectrum for the mixture of donor and acceptor which were absent in the initial components.

Fig. 2 shows CTC spectra for the synthesized acceptors with anthracene in dichloroethane. Bathochromic shifts of CT bands and their splitting are increased with an increase in the electron-withdrawing properties of substituents, *i.e.* $SO_2NEt_2 < SO_2OPh < SO_2Cl$ (at positions 2 and 7) and $H_2 < O < C(CN)_2$ (at position 9).

Using the well-known relationship in eqn. (1),[35] where E_A and

$$E_A - E_A^{\circ} = h\nu^{\circ} - h\nu \qquad (1)$$

E_A^{O} denote the electron affinity of the compound in question and the reference,† $h\nu^{\circ}$ and $h\nu$ are charge transfer energies in CTC (found from the maxima of CT bands) of the reference acceptor and acceptor under analysis in the same conditions, we estimated the values for electron affinities of the novel sulfonyl-containing acceptors by the long-wavelength maxima of their CT bands (Table 2).

Table 2 Values of maxima of charge transfer bands in CTCs of fluorene-2,7-disulfonic acid derivatives with anthracene in dichloroethane (25 °C) and electron affinities of fluorene acceptors

Compound	λ_{max}^{CT}/nm	$h\nu^{CT}$/eV	E_A/eV	$\Delta E_A = E_A - E_{Aref}$/eV[a]
15	514	2.41	2.05	−0.50
17	478	2.60	1.87	−0.68
18	532			
	611	2.03	2.43	−0.12
20	454	2.73	1.74	−0.81
21a	507			
	580sh	2.14	2.33	−0.22
21b	494			
	545sh	2.28	2.18	−0.27
22a	725	1.71	2.75	+0.20
22b	685	1.81	2.65	+0.10
2b	648	1.91	2.55	(0)

[a] E_{Aref} is electron affinity of the acceptor referred to, *i.e.* 2,4,7-trinitro-9-dicyanomethylenefluorene (**2b**).

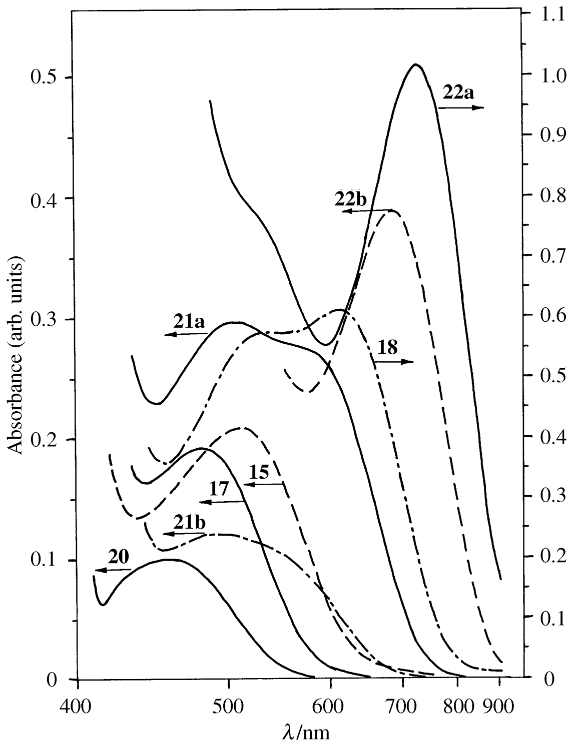


Fig. 2 Electron absorption spectra for CTCs of fluorene-2,7-disulfonic acid derivatives ($C_A = 4.0 \times 10^{-3}$ mol l^{-1}) with anthracene ($C_D = 4.0 \times 10^{-2}$ mol l^{-1}) in dichloroethane, 25 °C. Enumeration of the curves corresponds to the acceptor numbers in Scheme 1.

The influence of the substituents $ClSO_2$ and $PhOSO_2$ upon E_A values is comparable to that of the nitro group, *i.e.* 2,4,5,7-tetranitrofluoren-9-one (**3a**) has $E_A = 2.35$ eV,[25] and compounds **18** and **21a** have $E_A = 2.43$ and 2.33 eV, respectively (Table 2).

The process of complexation is affected not only by the electron-withdrawing nature of the sulfonyl substituents, but also by their size. While an increase in the electron-withdrawing properties of substituents in fluorene-2,7-disulfonic acid derivatives promotes complexation, an increase in the size of the substituents in the series $ClSO_2 < PhOSO_2 \leqslant Et_2NSO_2$ hinders it, which follows from the values of absorbances of dichloroethane solutions of CTCs prepared from those of similar anthracene concentrations (C_D) and the corresponding acceptors (C_A) (Fig. 2).

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† We took 2,4,7-trinitro-9-dicyanomethylenefluorene (**2b**) as a reference compound, $E_A = 2.55$ eV[25] (see Table 2).

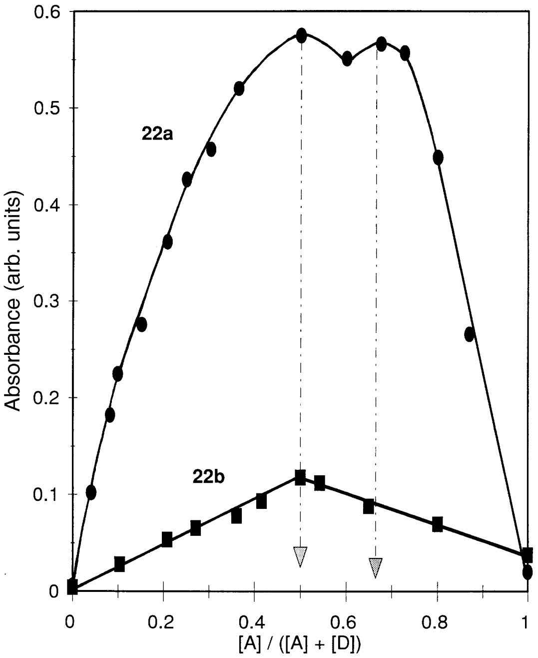

Fig. 3 Effect of donor–acceptor ratio on absorbance of solution of CTCs of anthracene with acceptors **22a** ($\lambda = 725$ nm, $C_A + C_D = 1.67 \times 10^{-2}$ mol l^{-1}) and **22b** ($\lambda = 685$ nm, $C_A + C_D = 1.06 \times 10^{-2}$ mol l^{-1}) in dichloroethane, 25 °C (method of isomolar series)

Using the method of isomolar series we investigated the stoichiometry of the complexation of synthesized fluorene acceptors with anthracene (Fig. 3). As is seen from Fig. 3, bis(diethylamide) **22b** forms only a 1 : 1 complex (or, at least, concentrations of other types of CTC are negligible for the concentrations used) whereas diphenyl ester **22a** forms two types of CTC of the composition of D : A = 1 : 1 and 1 : 2.

Methods for quantitative evaluation of equilibrium constants K for 1 : 1 CTC [eqn. (2)] are well elaborated.[36–41] However, the possibility of formation of 1 : 2 CTC in the case of acceptor **23** could give certain problems in evaluation of equilibrium constants of 1 : 1 CTC formation. Therefore we tried to make measurements at lower concentrations of acceptor **23** than those used in isomolar series experiments (concentration of [AD] complex is linear function of C_A, whereas concentration of [A$_2$D] complex depends on it quadratically).

$$\mathrm{A} + \mathrm{D} \xrightleftharpoons{K} [\mathrm{A}^{\delta-}, \mathrm{D}^{\delta+}] \qquad (2)$$

To estimate quantitatively the process of CTC formation between anthracene and acceptors **18**, **22a** and **22b** [eqn. (2)] we used the method[40,41] based on complete solution of eqn. (3)‡

$$A_{\mathrm{CTC}} = \frac{\varepsilon_{\mathrm{CTC}}}{2}\left(C_A + C_D + \frac{1}{K}\right) - \sqrt{\frac{\left(C_A + C_D + \frac{1}{K}\right)^2}{2} - C_A C_D} \qquad (3)$$

for equilibrium reaction (2) where C_A and C_D are initial concentrations of the acceptor and the donor, respectively, K is an equilibrium constant for CTC formation, $\varepsilon_{\mathrm{CTC}}$ is CTC molar coefficient of extinction on the measured wavelength, and A_{CTC} is the absorbance of the CTC solution on the measured wavelength at the given concentrations C_A and C_D.

To solve the opposite problem of eqn. (3) non-linear fitting was used (least-squares analysis with the minimization of the squares of deviations of A_{CTC} experimental values from the calculated ones). CTC formation of acceptors **18**, **22a** and **22b** with anthracene was studied in dichloroethane at 25 °C, and the values for absorbances at various donor and acceptor concentrations are summarized in Table 3. The values for equilibrium constants and CTC molar extinction coefficients calculated from the data in Table 3 are given in Table 4. As is seen from data of Table 4, the structure of acceptors **18**, **22a** and **22b** affects the complexation constants (K) more than molar extinction coefficients (ε), with both the electronic and the steric factors being significant in the acceptor. Thus, for instance, sulfonyl chloride **18**, being a weaker acceptor than amide **22b** ($E_A = 2.43$ and 2.65 eV, respectively; Table 2), has even slightly higher values for K and $\varepsilon_{\mathrm{CTC}}$ as compared to the latter (Table 4).

To compare the results which give various methods of evaluating equilibrium constants K, we have performed selective treatment of the data given in Table 3 which correspond to the restriction $C_D \gg C_A$§ (in fact, the restriction $C_D \geqslant 10\ C_A$ was used) by the Benesi–Hildebrand approximation (4),[36,37] first

$$\frac{C_A}{A_{\mathrm{CTC}}} \cong \frac{1}{\varepsilon_{\mathrm{CTC}}} + \frac{1}{K\varepsilon_{\mathrm{CTC}}}\frac{1}{C_D} \qquad (4)$$

proposed about 50 years ago and widely used,[42] and by related linear approximations, proposed by Scott[37,38] [eqn. (5)] and by Foster, Hammick and Wardley[37,39] [eqn. (6)].

$$\frac{C_A C_D}{A_{\mathrm{CTC}}} \cong \frac{1}{K\varepsilon_{\mathrm{CTC}}} + \frac{C_D}{\varepsilon_{\mathrm{CTC}}} \qquad (5)$$

$$\frac{A_{\mathrm{CTC}}}{C_D C_A} \cong K\varepsilon_{\mathrm{CTC}} + K\frac{A_{\mathrm{CTC}}}{C_A} \qquad (6)$$

The results of such treatments are summarized in Table 4. As is seen from Table 4, linear approximations (4)–(6) give close K and $\varepsilon_{\mathrm{CTC}}$ values which are in good agreement with non-linear fitting in the same conditions ($C_D \geqslant 10\ C_A$). However, these K and $\varepsilon_{\mathrm{CTC}}$ values are somewhat different from those obtained by non-linear fitting (3) of all measured data (Table 4). This demonstrates that the accuracy of the K and $\varepsilon_{\mathrm{CTC}}$ values which are obtained from the experiments with $C_D \geqslant 10\ C_A$ (or $C_D \geqslant 10\,C_D$) by linear methods needs critical judgement; at least, certain care in estimations is necessary. The drawbacks of linear models and approximations used in the Benesi–Hildebrand and related methods have been discussed in refs. 37 and 41.

Sensitization of PEPC photoconductivity by electron acceptors

The perfect photoelectric properties of thin films of the polymers of poly-N-vinylcarbazole (PVC) and PEPC type have led to their extensive application in electrophotographic and photothermoplastic systems for recording optical information. However, the intrinsic photosensitivity of such polymers is in the ultraviolet region of the spectrum. Capability of the fluorene acceptors to form CTCs with carbazole nuclei of polymers of the PVC and PEPC type is widely used for activation of photoconductivity of the latter in the visible region of the spectrum.

We have studied photophysical properties of photothermoplastic storage media (PTSM)¶ whose light-sensitive layer is a thin PEPC film containing 3–30 mass% of fluorene acceptors

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‡ Eqn. (3) and eqns. (4)–(6) have been written for the usually used pathlengths $l = 1$ cm; in general form, the term A_{CTC} should be replaced by A/l wherever it occurs.

§ A large excess of one of the components, D or A, is the necessary condition for approximations (4)–(6).

¶ For general information on photothermoplastic films on the basis of PEPC sensitized by electron acceptors of fluorene series see ref. 18(*b*).

Table 3 Absorbance (A_{CTC}) for the solutions of CTCs of fluorene acceptors **18**, **22a**, **22b** and anthracene in dichloroethane (25 °C) at various initial concentrations of both acceptor (C_{A}) and donor (C_{D})

Entry[a]	$C_{\mathrm{A}}/10^{-3}$ mol dm^{-3}	$C_{\mathrm{D}}/10^{-2}$ mol dm^{-3}	A_{CTC}	Entry[a]	$C_{\mathrm{A}}/10^{-3}$ mol dm^{-3}	$C_{\mathrm{D}}/10^{-3}$ mol dm^{-3}	A_{CTC}
4,5-Dinitro-9-oxofluorene-2,7-disulfonyl dichloride (**18**), $\lambda = 611$ nm							
1	6.16	1.28	0.337	20		3.07	0.429
2		1.03	0.272	21		2.56	0.357
3		0.769	0.205	22		2.05	0.292
4		0.512	0.139	23		1.54	0.224
5	6.00	2.85	0.691	24		1.02	0.149
6		2.45	0.599	25*	2.20	5.12	0.423
7	5.72	2.24	0.534	26*		4.48	0.374
8	5.34	1.60	0.370	27*		3.84	0.327
9	5.20	1.43	0.319	28*		3.20	0.277
10		1.22	0.275	29*		2.56	0.229
11*	4.40	5.12	0.835	30		1.92	0.175
12*		4.48	0.751	31*	2.11	2.46	0.210
13		3.84	0.660	32*		2.15	0.185
14		3.20	0.554	33		1.84	0.162
15		2.56	0.454	34*	1.10	5.76	0.236
16		1.92	0.348	35*		5.44	0.220
17		1.28	0.236	36*		5.12	0.211
18*	3.52	4.10	0.550	37*		4.80	0.192
19*		3.59	0.489				
Diphenyl 4,5-dinitro-9-dicyanomethylenefluorene-2,7-disulfonate (**22a**), $\lambda = 725$ nm							
1	7.57	1.69	0.848	18*		3.38	0.527
2		1.27	0.661	19*		3.17	0.499
3		0.950	0.511	20*		2.53	0.414
4		0.633	0.347	21		1.69	0.292
5		0.317	0.180	22		1.27	0.228
6*	3.78	5.07	1.070	23		0.950	0.178
7*		3.80	0.880	24		0.633	0.125
8		3.38	0.806	25*	1.89	2.53	0.306
9		3.17	0.761	26*		1.90	0.247
10		2.53	0.638	27		1.69	0.221
11		1.69	0.456	28		1.58	0.211
12		1.27	0.355	29		1.27	0.171
13		0.950	0.273	30*	1.26	2.53	0.208
14		0.829	0.210	31*		1.90	0.160
15		0.633	0.156	32*		1.69	0.146
16*	2.52	5.07	0.707	33*		1.58	0.137
17*		3.80	0.576				
4,5-Dinitro-9-dicyanomethylenefluorene-2,7-disulfonic acid bis(diethylamide) (**22b**), $\lambda = 685$ nm							
1*	3.95	5.12	0.533	9*		2.69	0.184
2*		4.48	0.480	10		2.31	0.163
3		3.84	0.420	11		1.92	0.131
4		3.20	0.358	12*	1.98	4.48	0.228
5		2.56	0.291	13*		3.84	0.200
6		1.92	0.224	14*		3.20	0.169
7		1.28	0.151	15*		2.56	0.131
8*	2.37	3.07	0.196				

[a] Entries, marked with an asterisk, correspond to the condition of $C_{\mathrm{D}} \geqslant 10\ C_{\mathrm{A}}$; they were used for calculations of equilibrium constants of CTC formation using linear methods (4)–(6), (see Table 4).

18, **21a** and **22a**. Fig. 4 demonstrates the curves for spectral distribution of electrophotosensitivity ($S_{\Delta V}$/m^2 J^{-1}) of the PTSM obtained for a number of acceptors at various concentrations. Spectral distributions of $S_{\Delta V}$ for sulfonyl-containing acceptors **18** and **21a** approach those for 2,4,5,7-tetranitrofluoren-9-one (**3a**) [Fig. 4(*a*), (*b*)], while the dependencies for compound **22a** are close to those for 2,4,5,7-tetranitro-9-dicyanomethylenefluorene (**3b**) [Fig. 4(*c*)].

Hypsochromic shifts of the long-wavelength photosensitivity limit on nitro group substitution in acceptors **3** by $\mathrm{ClSO_2}$ or $\mathrm{PhOSO_2}$ substituents are rather small which is in accordance with the results of CTC studies (electron affinities for acceptors **18**, **21a** and **22a** are close to that for the corresponding acceptors **3**). However, all $S_{\Delta V}$ values in the case of acceptors **18**, **21a** and **22a** are somewhat lower than those for the corresponding acceptors **3** (at identical molar concentrations) which is caused by the large bulk of the sulfonyl substituents as compared to the nitro group that hinders complexation.

In order to estimate the applicability of novel sulfonyl-containing acceptors of fluorene series in the real PTSM for recording optical holograms we have measured holographic sensitivity of the photothermoplastic films (S_η/m^2 J^{-1}) on visualized image at the wavelength of He–Ne laser irradiation (632.9 nm). The values of S_η of acceptors **18**, **21a** and **22a** are comparable to (or even greater than) those for well-known sensitizers **2** and **3** (Table 5). Charge thermo-relaxation during development of a relief image with heating is rather small which permitted us to introduce large quantities (up to 30% in the case of compound **18**) of the acceptor into the PEPC matrix to increase photosensitivity without a decrease in the diffraction efficiency (η_{max}). A substantial drawback of PTSM with acceptor **18** is its low cycling ability in information recording. After several scores of the cycles 'recording–erasure' rheological properties of a photothermoplastic film deteriorated dramatically (*i.e.* S_η and η_{max} decreased), perhaps as a result of chemical trans-

Table 4 Equilibrium constants (K/dm^3 mol^{-1}) and molar extinction coefficients (ε/mol dm^{-3} cm^{-1}) for CTC of fluorene-2,7-disulfonic acid derivatives **18**, **22a**, **22b** with anthracene in dichloroethane, 25 °C evaluated by various methods [eqns. (3)–(6)]

			Variation range of concentrations							
Compound	λ/nm[a]	Concentration conditions	$C_A/10^{-3}$ mol dm^{-3}	$C_D/10^{-2}$ mol dm^{-3}	K/dm^3 mol^{-1}	ε/mol dm^{-3} cm^{-1}	N[b]	R or r[c]	R_f or s_0[d]	Method[e]
18	611	All data	1.10–6.16	0.512–5.76	4.28 ± 0.23	1075 ± 51	37	0.9997	1.21	(3)
		$C_D < 10\,C_A$	2.11–6.16	0.512–3.84	4.22 ± 0.52	1090 ± 119	22	0.9996	1.41	(3)
		$C_D \geqslant 10\,C_A$	1.10–4.40	2.15–5.76	3.27 ± 0.26	1348 ± 94	15	0.9999	0.55	(3)
		$C_D \geqslant 10\,C_A$	1.10–4.40	2.15–5.76	3.41 ± 0.19	1285 ± 64	15	0.9998	4.7×10^{-5}	(4)
		$C_D \geqslant 10\,C_A$	1.10–4.40	2.15–5.76	3.25 ± 0.23	1340 ± 83	15	0.976	2.0×10^{-5}	(5)
		$C_D \geqslant 10\,C_A$	1.10–4.40	2.15–5.76	3.25 ± 0.22	1341 ± 105	15	−0.972	32.3	(6)
22a	725	All data	1.26–7.57	0.317–5.07	8.17 ± 0.43	989 ± 42	33	0.9994	1.90	(3)
		$C_D < 10\,C_A$	1.89–7.57	0.317–3.38	7.45 ± 0.73	1076 ± 89	18	0.9993	1.81	(3)
		$C_D \geqslant 10\,C_A$	1.26–3.78	1.58–5.07	7.89 ± 0.65	1010 ± 62	13	0.9998	1.21	(3)
		$C_D \geqslant 10\,C_A$	1.26–3.78	1.58–5.07	7.36 ± 0.47	1045 ± 57	13	0.9995	6.5×10^{-5}	(4)
		$C_D \geqslant 10\,C_A$	1.26–3.78	1.58–5.07	7.54 ± 0.39	1025 ± 43	13	0.990	1.7×10^{-6}	(5)
		$C_D \geqslant 10\,C_A$	1.26–3.78	1.58–5.07	7.45 ± 0.40	1034 ± 67	13	−0.984	82.8	(6)
22b	685	All data	1.98–3.95	1.28–5.12	3.60 ± 0.71	878 ± 150	15	0.9992	2.05	(3)
		$C_D < 10\,C_A$	2.37–3.95	1.28–3.84	5.28 ± 1.83	632 ± 184	7	0.9992	2.00	(3)
		$C_D \geqslant 10\,C_A$	1.98–3.95	2.56–5.12	2.27 ± 1.54	1303 ± 797	8	0.9989	2.31	(3)
		$C_D \geqslant 10\,C_A$	1.98–3.95	2.56–5.12	4.26 ± 1.59	731 ± 241	8	0.992	2.9×10^{-4}	(4)
		$C_D \geqslant 10\,C_A$	1.98–3.95	2.56–5.12	3.63 ± 1.49	839 ± 299	8	0.753	1.1×10^{-5}	(5)
		$C_D \geqslant 10\,C_A$	1.98–3.95	2.56–5.12	3.25 ± 1.47	925 ± 340	8	−0.669	86.9	(6)

[a] Wavelength at which measurements were made. [b] N is the number of points used in optimization procedure (3) or in correlations (4)–(6). [c] Multiple correlation coefficient (R) or correlation coefficient (r) are given for non-linear (3) and linear (4)–(6) methods, respectively. [d] The misalignment factor (R_f) between experimental data and fitting is given for non-linear method which is described as $R_f = [\Sigma(A_i^{exp} - A_i^{calc})^2/\Sigma A_i^{exp}] \times 100\%$ (where A_i^{exp} and A_i^{calc} are experimental and calculated values of a CTC absorbance for i-th point, respectively) and indicates a mean percentage deviation of experimental A_{CTC} values from the fit according to eqn. (3). Standard deviation (s_0) is given for linear methods (4)–(6). [e] Enumeration of the methods corresponds to the number of an equation in the text.

formations in the layer due to high reactivity of the $ClSO_2$ group.

At low concentrations of 9-dicyanomethylenefluorenes **22a** and **3b** the holographic sensitivities of PTSM are comparable. An increase in the concentration of acceptor **22a** yields an abrupt increase in the dark conductivity (*i.e.* $\Delta V/V$ increases) and charge thermorelaxation increases (*i.e.* η_{max} decreases) which makes recording of holograms on such photothermoplastic films unlikely (Table 5).

Although compounds **18** and **21a** as sensitizers have certain limitations and drawbacks, it should be noted that they show sensitizing properties which are comparable with those for widely used sensitizers of fluorene series **3a**,**b**, in spite of non-planar configuration of sulfonyl substituents (in contrast to planar nitro group) that should hinder CTC formation between the acceptor and carbazole nucleus of PEPC. This means that steric hindrance of these substituents has no dramatic effect on the sensitizing properties of these acceptors.

Experimental

General

Mps were recorded on a Kofler-type hot-stage microscope apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian GEMINI-200 instrument, operating at 200 MHz. Chemical shifts in [$^2H_6$]acetone, given in ppm, are relative to tetramethylsilane ($SiMe_4$) as internal standard. All J values are in Hz. Electron absorbance spectra of CTC in the visible region were recorded on a Specord M-40 spectrophotometer. Measurements of isomolar series and also absorbances of CTC for estimations of equilibrium constants were made at the maxima of CTC absorbance on a one-beam SF-26 spectrophotometer (LOMO, USSR) with the output of the signal into a 5-digital voltmeter model B7-17.

Poly-N-(2,3-epoxypropyl)carbazole (PEPC) was synthesized by anionic polymerization of N-(2,3-epoxypropyl)carbazole as described earlier,[43] M_n 800–900, T_{flow} 70–95 °C.

Dichloroethane for spectral measurements was purified as follows: it was twice treated with concentrated sulfuric acid, washed with water, dried over $CaCl_2$ and twice distilled from P_4O_{10}.

4,5-Dinitrofluorene-2,7-disulfonyl dichloride (15)

To a nitrating mixture (36 cm^3) containing 90% HNO_3 and 7.5% H_2SO_4, fluorene-2,7-disulfonyl dichloride (**14**)[29] (3.61 g, 9.9 mmol) was added over 15 min with stirring at room temp. The reaction mixture was stirred for 5 h and poured into water (300 cm^3). The solid was filtered off, washed with water, then with ethanol (300 cm^3), and dried yielding dichloride **15** (4.47 g, 99.2%). The compound was crystallized from acetic anhydride with a yield of 70–80% as colourless needles (which became light-red in air) which decomposed with heating up to 300 °C (Found: C, 34.6; H, 1.4; Cl, 15.55; N, 6.2; S, 14.1. $C_{13}H_6Cl_2N_2O_8S_2$ requires C, 34.45; H, 1.35; Cl, 15.65; N, 6.2; S, 14.15%). δ_H 8.98 (2 H, m, $J_{1,3}$ 1.8, $J_{1,9}$ 0.8, 1,8-H), 8.75 (2 H, d, $J_{1,3}$ 1.8, 3,6-H), 4.87 (2 H, m, $J_{1,9}$ 0.7, 9-H).

4,5-Dinitrofluorene-2,7-disulfonic acid (16) and its quinolinium salt (16·2C_9H_7N)

A suspension of sulfonyl chloride **15** (0.9 g, 2.0 mmol) in a mixture of acetic acid (20 cm^3) and water (5 cm^3) was refluxed to complete dissolution of the solid (about 4 h) and then for an additional 30 min. The resulting solution was diluted with water (50 cm^3) and evaporated. The solid residue was dissolved in water (25 cm^3) and evaporated again. To obtain pure acid **16** the residue was twice recrystallized from dioxane–toluene, mp >300 °C (decomp.) (Found: C, 37.35; H, 2.05; N, 6.7; S, 15.3. $C_{13}H_8N_2O_{10}S_2$ requires C, 37.5; H, 1.95; N, 6.75; S, 15.4%). δ_H 8.35 (2 H, s, 1,8-H), 8.31 (2 H, s, 3,6-H), 5.25 (2 H, br s, SO_3H), 4.41 (2 H, s, 9-H).

To obtain the quinolinium salt the residue of crude 4,5-dinitrofluorene-2,7-disulfonic acid (**16**) was dissolved in propan-2-ol (15 cm^3) and poured into a solution of quinoline (1 cm^3, 8.5 mmol) in propan-2-ol (10 cm^3). The yellow solid was filtered off, washed with propan-2-ol and dried yielding quinolinium salt **16**·2C_9H_7N (1.27 g, 95%); mp 263–264 °C (decomp.) (from propan-2-ol–water). Titrating: found equivalent 332.3; calc. 337.3 (Found: C, 55.15; H, 3.65; N,

Table 5 Results of photophysical measurements of PEPC films sensitized by fluorene acceptors **18**, **21a** and **22a**

Compound	Count of acceptor mass%	Count of acceptor mol%	V_0/V	100 $\Delta V/V_0$ (%)	$\lambda = 632.9$ nm $S_{\Delta V}$/ m^2 J^{-1}	$\lambda = 632.9$ nm S_η/ m^2 J^{-1}	η_{max} (%)
18	5	2.4	180	10–12	1.7	12–15	25
	8	3.8	180	12–15	2.6	18–20	25
	30	14.3	160	15–20	5.0	35–40	20–22
21a	5	1.9	160	5–7	2.9	30–35	>25
	15	6.0	120	15–20	4.8	35–40	20
22a	3	1.1	150	15	1.5	12–15	3–4
	6	2.1	110	20–25	3.5	—	1
	10	3.5	80	40–50	4.5	—	<0.5
2a	5	3.1	170	10–12	1.4	10–12	20
3b	3	1.6	140	17–20	3.1	12–13	5–6

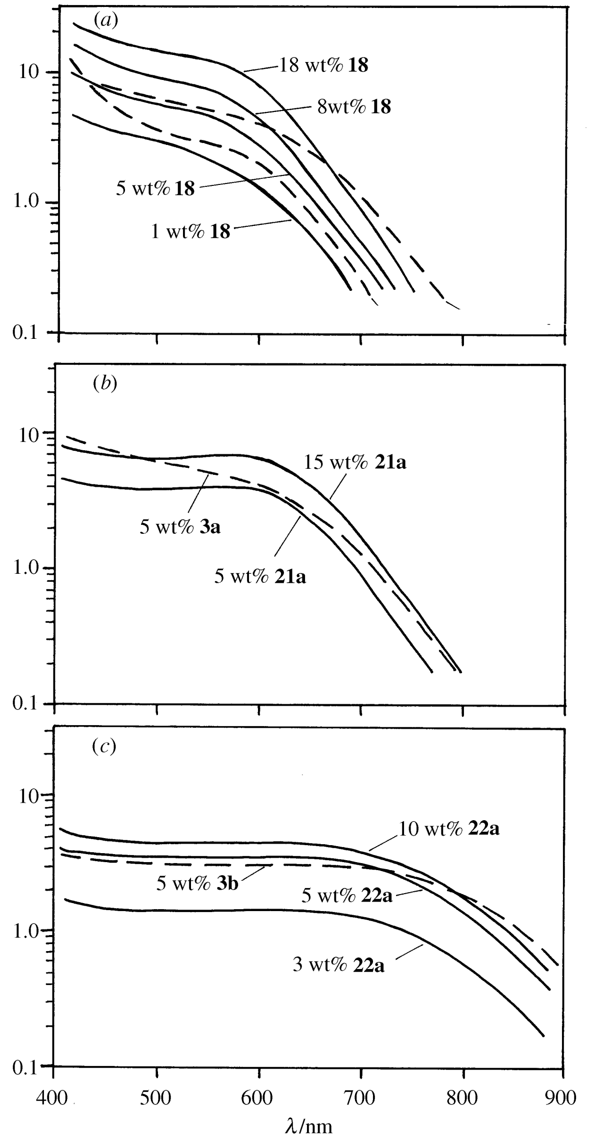

Fig. 4 Spectral distribution of electrophotographic sensitivity ($S_{\Delta V}$) of PEPC films sensitized with electron acceptors of the fluorene series (enumeration of acceptors corresponds to their numbers in Scheme 1; weight percentage of acceptors in the films is indicated)

8.35; S, 9.55. $C_{31}H_{22}N_4O_{10}S_2$ requires C, 55.2; H, 3.3; N, 8.3; S, 9.5%).

9-Oxofluorene-2,7-disulfonyl dichloride (17)

Finely powdered fluorene-2,7-disulfonyl dichloride (**14**)[29a] (21.8 g, 57.8 mmol) was suspended in acetic anhydride (220 cm^3), and CrO_3 (14.4 g, 144 mmol) was added to this suspension with stirring at room temp. for 3 h. Reaction mixture was stirred for 3 d. The solid was then filtered off, suspended in 2% HCl (100 cm^3), filtered off again and washed with water yielding dichloride **17** (19.0 g, 83.9%). Recrystallization from xylene (190 cm^3) gave light-yellow crystals (16.4 g, 72.4%) with mp 215–217 °C (lit.,[29b] 219–220.5 °C) (Found: C, 41.3; H, 1.55; Cl, 19.3; S, 16.85. $C_{13}H_6Cl_2O_5S_2$ requires C, 41.4; H, 1.6; Cl, 18.8; S, 17.0%). δ_H 8.51 (2 H, dd, $J_{3,4}$ 8.1, $J_{1,3}$ 1.7, 3,6-H), 8.48 (2 H, dd, $J_{3,4}$ 8.1 Hz, $J_{1,4}$ 0.8, 4,5-H), 8.33 (2 H, dd, $J_{1,3}$ 1.7, $J_{1,4}$ 0.8, 1,8-H).

4,5-Dinitro-9-oxofluorene-2,7-disulfonyl dichloride (18)

(*a*) CrO_3 (2.4 g, 24 mmol) was added to a suspension of 4,5-dinitrofluorene-2,7-disulfonyl dichloride (**15**) (4.47 g, 9.86 mmol) in acetic anhydride (45 cm^3) with stirring at room temp. The reaction mixture was stirred for 48 h and poured into ice (300 g). After completion of hydrolysis of acetic anhydride the solid was filtered off, washed with water and ethanol, and dried yielding sulfonyl chloride **18** (1.90 g, 41.2%), mp 244–246 °C (from toluene).

(*b*) Fluorene-2,7-disulfonyl dichloride (**14**)[29] (7.26 g, 20 mmol) was added with stirring at room temp. to a nitrating mixture (145 cm^3) containing 90% HNO_3 and 7.5% H_2SO_4. The reaction mixture was stirred for 8 h and then CrO_3 (5.5 g, 55 mmol) was slowly added at 15–20 °C. Reaction mixture was stirred at room temp. for 12 h and poured into water (at *ca.* 0 °C) (1000 cm^3). The solid was quickly filtered off, washed with water (at *ca.* 0 °C), then with propan-2-ol (50 cm^3) and dried to yield sulfonyl chloride **18** (9.1 g, 97.4%), mp 245–247 °C. Recrystallization from acetic anhydride (40 cm^3) gave light-yellow crystals of **18** (7.0 g, 76.1%) with mp 246–247 °C (Found: C, 33.5; H, 0.9; Cl, 14.95; N, 5.95; S, 13.8. $C_{13}H_4Cl_2N_2O_9S_2$ requires C, 33.4; H, 0.85; Cl, 15.2; N, 6.00; S, 13.75%). δ_H 8.95 (2 H, d, $J_{1,3}$ 1.8, 3,6-H), 8.82 (2 H, d, $J_{1,3}$ 1.8, 1,8-H).

4,5-Dinitro-9-oxofluorene-2,7-disulfonic acid (19) and its quinolinium salt (19·2C_9H_7N)

(*a*) Sulfonyl chloride **18** (0.93 g, 2.0 mmol) was hydrolysed in refluxing acetic acid (20 cm^3) with water (5 cm^3) during 30 min. Isolation of the acid **19**, its conversion to the quinolinium salt and isolation of the salt **19**·2C_9H_7N were similar to the procedure for the salt **16**·2C_9H_7N, described above. Yield of **19**·2C_9H_7N was 1.25 g (91.2%).

(*b*) 4,5-Dinitro-9-oxofluorene-2,7-disulfonyl dichloride (**18**) (0.47 g, 1.0 mmol) was dissolved in acetone (10 cm^3). Water (20 cm^3) was added during 1 h to a vigorously stirred solution. The resulting solution was diluted with water (20 cm^3) and evaporated. The residue was dissolved in water (25 cm^3) and evaporated again. Resulting 4,5-dinitro-9-oxofluorene-2,7-disulfonic acid (**19**) was dissolved in propan-2-ol (15 cm^3) and poured into a solution of quinoline (0.3 cm^3, 2.54 mmol) in propan-2-ol (5 cm^3). The solid was filtered off, washed with propan-2-ol and dried yielding quinolinium salt **19**·$2C_9H_7N$ (0.61 g, 88%); mp 198.5–200.5 °C (from propan-2-ol–water).

19, mp 140–146 °C (from dioxane–toluene) (Found: C, 54.05; H, 3.15; N, 8.25; S, 9.2. $C_{13}H_6N_2O_{11}S_2$ requires C, 36.3; H, 1.4; N, 6.5; S, 14.9%). δ_H 8.43 (2 H, d, $J_{1,3}$ 1.4, 3,6-H), 8.25 (2 H, d, $J_{1,3}$ 1.4, 1,8-H), 8.03 (2 H, br s, SO_3H).

(**19**·$2C_9H_7N$): Titrating: found 350.6; calc. 344.1 (Found: C, 54.05; H, 3.15; N, 8.25; S, 9.2. $C_{31}H_{20}N_4O_{11}S_2$ requires C, 54.05; H, 2.95; N, 8.15; S, 9.3%). δ_H 8.49 (2 H, d, $J_{1,3}$ 1.45, 3,6-H), 8.36 (2 H, d, $J_{1,3}$ 1.45, 1,8-H), quinolinium: 9.5–9.3 (4 H, m), 8.57–8.44 (4 H, m), 8.34–8.22 (4 H, m), 8.12–8.02 (2 H, m).

Diphenyl 9-oxofluorene-2,7-disulfonate (20)

A fusion cake was prepared by heating phenol (5.64 g, 60 mmol) and 9-oxofluorene-2,7-disulfonyl dichloride (**17**) (1.88 g, 5.0 mmol) at 100 °C, then dry pyridine (1.5 cm^3) was added to it and the mixture was heated at 100 °C for 1.5 h. Phenol was removed by distillation with steam and a light-yellow solid was precipitated, washed with water and dried yielding ester **20** (2.4 g, 97.8%), mp 198–199 °C (from acetic acid) (Found: C, 60.95; H, 3.5; S, 13.05. $C_{25}H_{16}O_7S_2$ requires C, 60.95; H, 3.25; S, 13.0%). δ_H 8.26 (2 H, dd, $J_{3,4}$ 7.9, $J_{1,4}$ 0.6, 4,5-H), 8.17 (2 H, dd, $J_{3,4}$ 7.9, $J_{1,3}$ 1.75, 3,6-H), 8.03 (2 H, dd, $J_{1,3}$ 1.75, $J_{1,4}$ 0.6, 1,8-H), 7.32–7.45 (6 H, m, *m,m,p*-C_6H_5), 7.10–7.18 (4 H, m, *o,o*-C_6H_5).

Diphenyl 4,5-dinitro-9-oxofluorene-2,7-disulfonate (21a)

A fusion cake was prepared by heating phenol (6.0 g, 64 mmol) and 4,5-dinitro-9-oxofluorene-2,7-disulfonyl dichloride (**18**) (1.17 g, 2.5 mmol) for 30 min at 100 °C. Dry pyridine (1.5 cm^3) was added to the cooled fusion cake and the mixture was heated at 100 °C for 30 min. Phenol was removed by distillation with steam, residual solid was precipitated, washed with water and dried yielding ester **21a** (1.4–1.45 g, 96–100%), mp 200–202 °C (from acetic acid). Additional recrystallization from benzene gave light-yellow crystals of **21a** with mp 203–204 °C (Found: C, 52.05; H, 2.8; N, 4.65; S, 11.3. $C_{25}H_{14}N_2O_{11}S_2$ requires C, 51.55; H, 2.4; N, 4.8; S, 11.0%). δ_H 8.64 (2 H, d, $J_{1,3}$ 1.7, 3,6-H), 8.44 (2 H, d, $J_{1,3}$ 1.7, 1,8-H), 7.37–7.50 (6 H, m, *m,m,p*-Ph), 7.2–7.3 (4 H, m, *o,o*-Ph).

4,5-Dinitro-9-oxofluorene-2,7-disulfonic acid bis(diethylamide) (21b)

4,5-Dinitro-9-oxofluorene-2,7-disulfonyl dichloride (**18**) (2.33 g, 5.0 mmol) was added to a stirred solution of diethylamine (5 cm^3) in *N,N*-dimethylformamide (DMF, 15 cm^3). The reaction mixture was stirred for 1 h and poured into a solution of sulfuric acid (5 cm^3) in water (50 cm^3). The solid was filtered off, washed with water and dried yielding sulfonamide **21b** (1.70 g, 63.1%), mp 291–292 °C (from dioxane–propan-2-ol) (Found: C, 46.55; H, 4.5; N, 10.4; S, 11.75. $C_{21}H_{24}N_4O_9S_2$ requires C, 46.65; H, 4.45; N, 10.35; S, 11.85%). δ_H 8.56 (2 H, d, $J_{1,3}$ 1.7, 3,6-H), 8.41 (2 H, d, $J_{1,3}$ 1.7, 1,8-H), 3.42 [8 H, q, *J* 7.15, $N(CH_2CH_3)_2$], 1.19 [12 H, t, *J* 7.15, $N(CH_2CH_3)_2$].

Diphenyl 4,5-dinitro-9-dicyanomethylenefluorene-2,7-disulfonate (22a)

Diphenyl 4,5-dinitro-9-oxofluorene-2,7-disulfonate (**21a**) (2.11 g, 3.62 mmol) and malononitrile (0.48 g, 7.27 mmol) in DMF (10 cm^3) was stirred at room temp. for 30 min. The reaction mixture was diluted with propan-2-ol (50 cm^3), the solid was filtered off and washed with propan-2-ol, yielding ester **22a** (1.98 g, 87.2%), mp 245–248 °C. The product was dissolved in hot dioxane (20 cm^3) and diluted with hot methanol (80 cm^3). After cooling yellow crystals were filtered off, washed with methanol and dried yielding ester **22a** (1.83 g, 80.1%), mp 250–251 °C (Found: C, 53.85; H, 2.4; N, 8.85; S, 9.85. $C_{28}H_{14}N_4O_{10}S_2$ requires C, 53.35; H, 2.25; N, 8.9; S, 10.15%). δ_H 9.26 (2 H, d, $J_{1,3}$ 1.5, 1.8-H), 8.70 (2 H, d, $J_{1,3}$ 1.5, 3,6-H), 7.4–7.52 (6 H, m, *m,m,p*-Ph), 7.22–7.3 (4 H, m, *o,o*-Ph).

Ester **22a** was crystallized from *o*-xylene as orange needles of the CTC with the solvent; this CTC is decomposed on heating to 120–130 °C giving initial ester **22a** (mp 248–250 °C).

4,5-Dinitro-9-dicyanomethylenefluorene-2,7-disulfonic acid bis(diethylamide) (22b)

4,5-Dinitro-9-oxofluorene-2,7-disulfonic acid bis(diethylamide) (**21b**) (1.00 g, 1.85 mol) was dissolved in DMF (7 cm^3) with heating at 50 °C. Malononitrile (0.30 g, 4.5 mol) was added with stirring to this solution and the mixture was stirred at 45–50 °C for 1 h (after some time the precipitation of dark-yellow crystals of the product were observed). The reaction mixture was diluted with propan-2-ol (25 cm^3) and was left in a fridge for 2 h. The solid was filtered off, washed with propan-2-ol, and dried yielding sulfonamide **22b** (1.00 g, 91.8%), mp >360 °C. Recrystallization from dioxane (70 cm^3) gave dark-yellow crystals of **22b** (0.75 g, 69%), mp >360 °C (Found: C, 49.15; H, 4.2; N, 14.4; S, 10.75. $C_{24}H_{24}N_6O_8S_2$ requires C, 48.95; H, 4.1; N, 14.3; S, 10.9%). δ_H 9.29 (2 H, d, $J_{1,3}$ 1.5, 1,8-H), 8.61 (2 H, d, $J_{1,3}$ 1.5, 3,6-H), 3.44 [8 H, q, *J* 7.2, $N(CH_2CH_3)_2$], 1.21 [12 H, t, *J* 7.2, $N(CH_2CH_3)_2$].

Photophysical measurements of PEPC films sensitized by fluorene acceptors 18, 21a, 22a

Photothermoplastic storage media were made in the following way: anionic PEPC (0.5 g)[43] and a corresponding amount of the acceptor were dissolved separately in methyl ethyl ketone (both 5 ml); the solutions were combined and filtered off. The resulting solution was supported on a glass base with an electroconductive SnO_2 layer. The final thickness of the photoconductive films was 1.2 ± 0.1 µm.

Measurements of photosensitivity of the photothermoplastic films were carried out at wavelengths of 400–900 nm. The charge potential of the surface of the films in the dark (V_0) made by positive corona discharge grid was measured by the dynamic sonde method. Relative dark decay of the surface potential ($\Delta V \times 100/V_0$) was estimated for 30 s ($\Delta V = V_0 - V_\tau$, where V_τ is charge potential of the surface in the dark after $\tau = 30$ s). Electrophotographic sensitivity ($S_{\Delta V}$/m^2 J^{-1}) was estimated at the 20% decay level of the initial potential under the illumination at 400–900 nm and an intensity of 0.1 µW cm^{-1}. Real holographic sensitivity (S_η/m^2 J^{-1}) was estimated at the level of 1% diffraction efficiency ($\eta = 1\%$) of the visualized image by the registration of holograms of the planar wavefront at the spatial frequency of $\nu = 450$ mm^{-1} with irradiation of He–Ne laser ($\lambda = 632.9$ nm). Maximal diffraction efficiency, achieved without amplification of the hologram recording [$\eta_{\max}$ (%)], was found as the ratio of the intensity of the first order diffracted beam to the intensity of the beam grazed on the hologram, when the ratio of the intensities of the integrating beams was 1 : 3.

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