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Electron Acceptors of the Fluorene Series. 9.[1] Derivatives of 9-(1,2-Dithiol-3-ylidene)-, 9-(1,3-Dithiol-2-ylidene)-, and 9-(1,3-Selenathiol-2-ylidene)fluorenes: Synthesis, Intramolecular Charge Transfer, and Redox Properties

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The synthesis and physical properties of four series of novel fluorene push−pull compounds (**4**−**7**) of the D−π−A type with intramolecular charge transfer (from 1,3- and 1,2-dithiole and 1,3-selenathiole donor (D) moieties) are described. The nature of the heteroatom (S or Se) in the donor fragment has no effect on the maxima of intramolecular absorption bands (λ_{ICT}), whereas a change of position of the heteroatoms in the dithiole moiety from 1,3 to 1,2 leads to a substantial bathochromic shift in λ_{ICT}. Solvatochromism, thermochromism, and negative halochromism in these compounds are demonstrated. Cyclic voltammograms of **4**−**7** exhibit two, separate, single-electron reversible redox waves, the potentials of which (as well as the ICT energies in the molecules) are quantitatively described by σ_p^- constants of the substituents in the fluorene ring. Compounds **4**−**7** exhibit reversible salt formation in sulfuric acid, and for compound **5g** in diluted sulfuric acid an additional absorption in the near-IR region has been observed that we attribute to radical species formation from the equilibrium [**5g**-H]$^+$ + **5g** $\rightleftarrows$ **5g**$^{\bullet+}$ + [**5g**-H]$^\bullet$.

Introduction

9-Substituted polynitrofluorenes combining high electron affinity[2] and an extended π-electron system are of considerable interest for studies on charge-transfer complexes (CTC).[3,4] Polynitro-9-fluorenones and polynitro-9-dicyanomethylenefluorenes[2c,5] whose ability to form CTC is widely used to sensitize the photoconductivity of poly-

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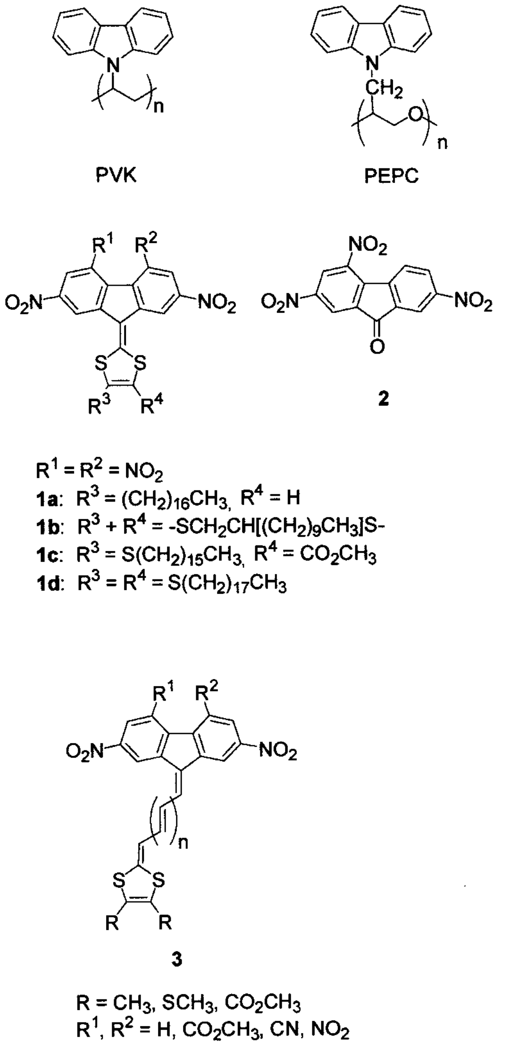
N-vinylcarbazole (PVK) and related carbazole-containing polymers[6] are the most widely known fluorene acceptors.

The attachment of electron-donating groups to electron-acceptor compounds of the fluorene series results in intramolecular charge transfer (ICT) from the donor moiety into the acceptor fluorene ring[1,7−10] that is manifested in the appearance of long-wavelength bands in the visible or even in the near-IR region of their electron absorption spectra. Recently, it has been shown that fluorene acceptors with ICT can efficiently sensitize the photoconductivity of carbazole-containing polymers in their ICT spectral region,[7−9,11−14] offering applications for photoconductive materials with selective spectral zones of photosensitivity, and control their charge (electron and hole) generation and transport properties. Especially interesting results were obtained on fluorene acceptors with ICT from a 1,3-dithiole[9,12] donor moiety. Sensitization of the photoconductivity of poly-*N*-(2,3-epoxypropyl)-carbazole (PEPC) films by acceptors **1a**−**d** ($R^1 = R^2 = NO_2$) increased the holographic sensitivity (He−Ne laser, $\lambda = 632.9$ nm) of photothermoplastic materials by 10−20 times as compared to the widely used sensitizer 2,4,7-trinitro-9-fluorenone (**2**). Redox and ICT investigations of this class of acceptors (**1d**, **3**)[9] established that they are very promising candidates for electron or hole transport materials with high photosensitivity in long-wavelength and near-IR regions of the spectrum (Chart 1).

Other promising applications of such push−pull compounds are the design of single-component organic semiconductors,[15,16] nonlinear optical materials,[10,17,18] and conductive polymers with a low band-gap.[19] Surprisingly, although 1,3-dithiole donor moieties are widely exploited as building blocks in conductive charge-transfer salts based on tetrathiafulvalenes (more than 3000 TTF derivatives, the CTCs and radical salts are known to the date), their incorporation as donor components of π-conjugated push−pull compounds is relatively limited.[1,9,12,19−25]

Chart 1


PVK

PEPC

2

$R^1 = R^2 = NO_2$

1a: $R^3 = (CH_2)_{16}CH_3$, $R^4 = H$

1b: $R^3 + R^4 = -SCH_2CH[(CH_2)_9CH_3]S-$

1c: $R^3 = S(CH_2)_{15}CH_3$, $R^4 = CO_2CH_3$

1d: $R^3 = R^4 = S(CH_2)_{17}CH_3$

3

$R = CH_3, SCH_3, CO_2CH_3$

$R^1, R^2 = H, CO_2CH_3, CN, NO_2$

In continuation of our recent report on the role of the conjugated bridge in the (1,3-dithiole)-π-fluorene systems,[9] in the present paper we study the effect of varying the heteroatoms in the heterocyclic donor unit (S or Se, compounds **4** and **5**) and their location (1,3 or 1,2, compounds **4** and **6**) on the ICT process in push−pull-type fluorene acceptors.

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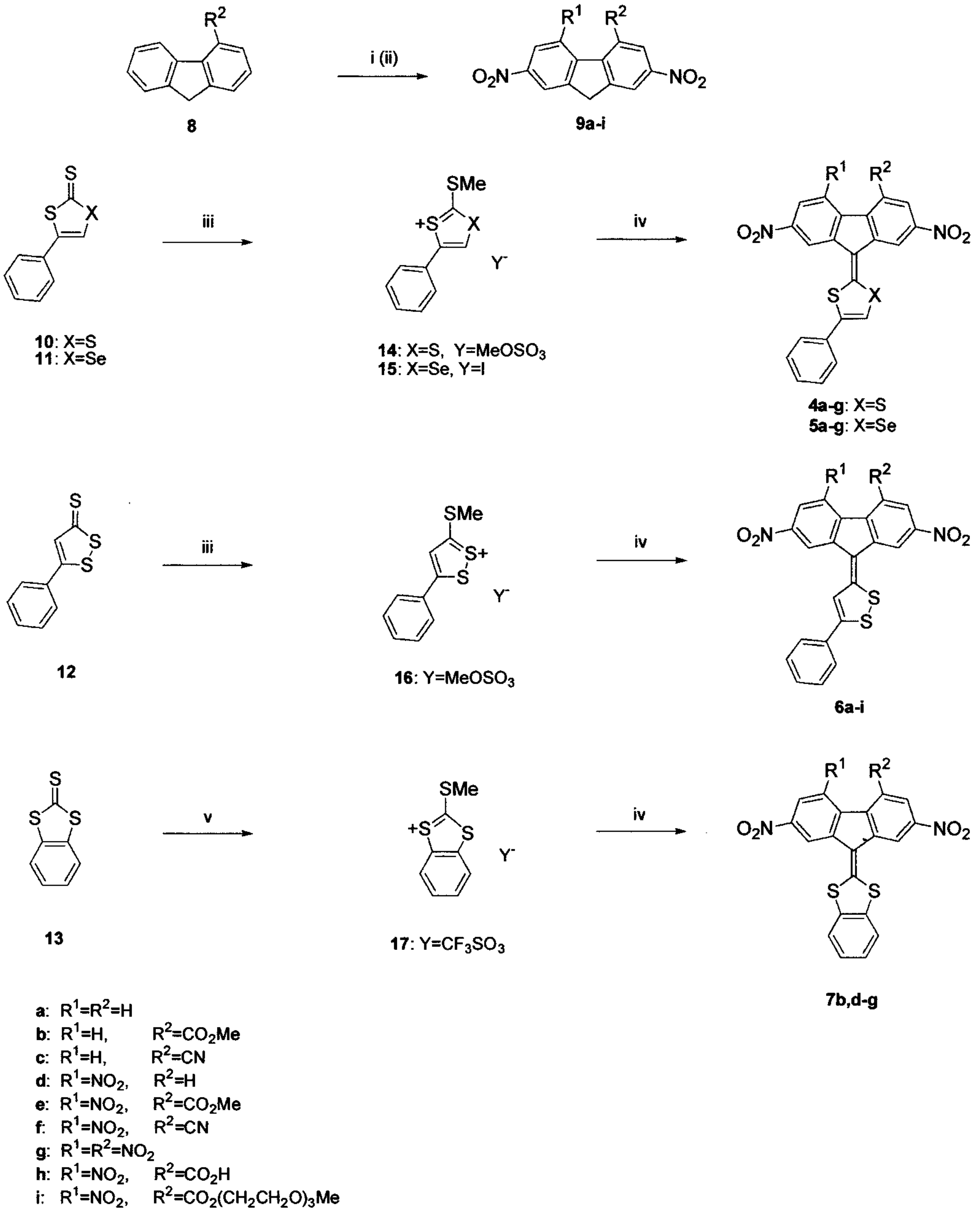
Scheme 1[a]



[a] Reagents and conditions: (i) for R^1=H: HNO_3-AcOH rt,15 h; (ii) for $R^1=NO_2$: HNO_3-H_2SO_4, rt,15 h; (iii) $(MeO)_2SO_2$ or MeI, BuOAc, reflux 5-90 min; (iv) **9a-i**, DMF, Py or DMF-Py mixture, 3 min - 25 h, 25 - 100 °C; (v) $MeOSO_2CF_3$, $CHCl_3$, 50 °C, 1 h.

To this end, we have synthesized three series of fluorene acceptors **4**−**6** (see Scheme 1) with ICT from 1,3-dithiole, 1,3-selenathiole, and 1,2-dithiole moieties, respectively, and investigated their spectral and redox properties. We also describe the synthesis and properties of the series of compounds **7** (Scheme 1) to allow a comparison of the benzo-1,3-dithiole moiety with phenyl-substituted analogue **4**. Additionally, we report quantitative effects of substitution in the fluorene ring on ICT energies and redox potentials in compounds **4**−**7**.

Results and Discussion

Synthesis. The synthesis of the novel compounds **4**−**7** is depicted in Scheme 1. Nitrosubstituted fluorenes **9** were obtained by nitration of fluorene itself or its 4-substituted derivatives (**8**) with nitric acid or its mixture with acetic or sulfuric acids, depending on the target products. Heterocyclic thiones **10**−**13** were converted into dithiolium or selenathiolium salts **14**−**17** by treatment with either methyl iodide, dimethyl sulfate, or methyl triflate. 2,7-Dinitro-4-R^1-5-R^2-fluorenes (**9**) as strong C−H acids[26] reacted readily with chalcogenathiolium salts **14**−**17** in *N*,*N*-dimethylformamide (DMF) solution yielding the corresponding substituted 9-(chalcogenathiolylidene)fluorenes (**4**−**7**). The reaction conditions depended substantially on the substituents R^1 and R^2 in fluorenes **9** and varied from 25 to 100 °C and from a few minutes to several hours. The reaction rates and

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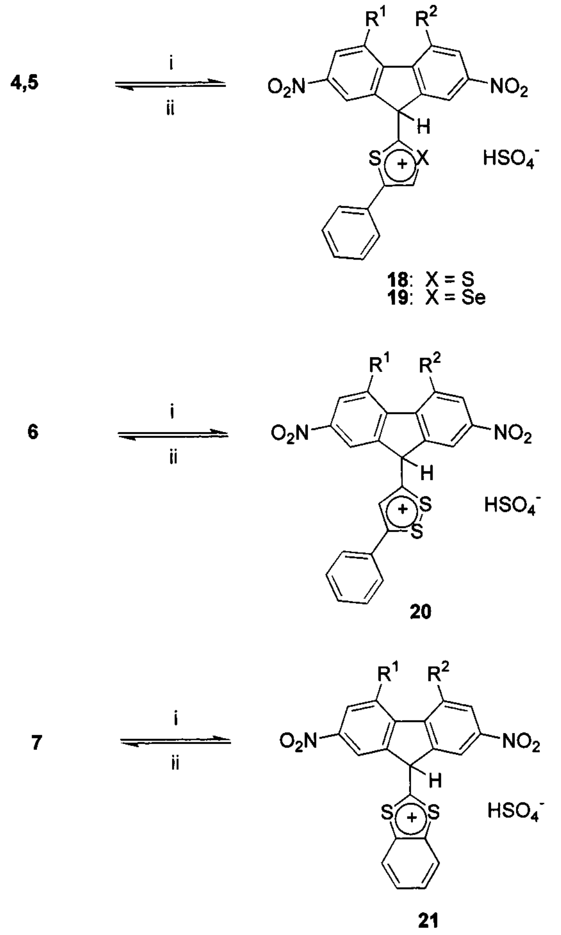
Scheme 2[a]



[a] Reagents and conditions: (i) H_2SO_4, rt; (ii) H_2O.

yields decreased with the reduction of the electron-withdrawing abilities of substituents R^1 and R^2 in the fluorene ring, and the condensation of fluorenes with poor C−H acidities (**9a**−**c**) demanded pyridine (Py) addition or even neat Py as a solvent.

Compounds **4**−**7** are air- and moisture-stable highly colored solids with high melting points and low solubility in most organic solvents. Their color depends on the substituents in the fluorene ring and varies from orange-red (for $R^1 = R^2 = H$) to black (for $R^1 = R^2 = NO_2$). Unfortunately, all our attempts to grow single crystals of compounds **4**−**6** for X-ray structure determinations were unsuccessful, yielding polycrystalline samples or twinned crystals; the X-ray crystal structure for **7g** will be reported elsewhere.

Compounds **4**−**7** dissolve in concentrated sulfuric acid [$H_0 = -9.85$ (95% H_2SO_4),[27] −8.86 (95% H_2SO_4),[28] −11.1, −11.0, −10.6 (100% H_2SO_4)[28]] to give colorless solutions due to formation of salts **18**−**21** (Scheme 2). Protonation of TTF derivatives by strong acids is known,[29,30] and the X-ray structure for $[TTF-H]^+BF_4^-$ was reported,[31] confirming covalent bonding of H with the central carbon atom of one 1,3-dithiole ring and localization of the positive charge on the other 1,3-dithiole moiety. However, one should expect a substantial decrease of both Lewis and Brønsted basicity with electron-withdrawing groups attached to the 1,3-dithiole unit, so the ability of compounds **4**−**7** to form salts is not so predictable. Indeed, in trifluoroacetic acid (H_0 = −3.1, −4.4, −5, −5.03[28]) compounds **4**−**7** do not give salts, although Gompper and Wagner reported that push−pull compounds **22** and **23** were decolored in trifluoroacetic acid due to salt formation [$CHCl_3$: λ_{max} = 645 nm (**22**), 758 nm (**23**); CF_3CO_2H: λ_{max} = 374 nm (**22**), 382 nm (**23**)].[22b] Salt formation (Scheme 2) is reversible, and on addition of water to the solution of salts **18**−**21** in H_2SO_4, starting compounds **4**−**7** were quantitatively recovered [except for derivatives where acid-sensitive substituents on the fluorene ring (CN, CO_2R) were partially hydrolyzed].

^{1}H NMR Spectra. The extremely low solubility (sometimes less than ~0.1 g L^{-1}) of the compounds under investigation in common organic solvents meant thousands of scans were needed to obtain their NMR spectra. In some cases, e.g., for the series of fluorenes **7**, insolubility prevented NMR experiments. In the case of unsymmetrical fluorene moieties ($R^1 \neq R^2$), compounds **4**−**6** can exist as *E* or *Z* isomers. Due to strong ICT in these compounds giving rise to zwitterionic resonance structures **4′**−**6′** (Chart 2), the rotation barrier around the formally double C(9)=C(2′) bond is expected to be low,[8,32] and NMR spectra show the mixture of *E*−*Z* isomers or broadened signals due to the dynamic process of *E*−*Z* isomerization. Together with the possibility of paramagnetic broadening of the NMR signals in polar/basic media due to electron transfer from a solvent, as observed previously with strong electron acceptors,[3a,33] NMR spectra were complicated in some cases, and at increased temperatures the rotation became faster leading to further broadening or disappearance of the signals precluding the use of increased temperatures (to increase the solubility) for recording NMR spectra. Data on chemical shifts of all the observed signals for compounds **4**−**6** are summarized in Table 1. Salts **18**−**21**, which were formed by dissolution of compounds **4**−**6** in concentrated sulfuric acid, are more soluble, and have no isomers to complicate their spectra, gave finely resolved spectra that confirm their structures (see the Experimental Section).

Electronic Absorption Spectra in the ICT Region. Effect of the Donor Moiety. The presence in the compounds under investigation of both electron-donor and electron-acceptor fragments leads to strong ICT that is manifested in the appearance of two long-wavelength absorption bands (ICT bands) in the visible region of their electronic spectra, which we term ICT-1 (short-wavelength ICT band) and ICT-2 (long-wavelength ICT band) (Figure 1, Table 2). Their intramolecular nature was

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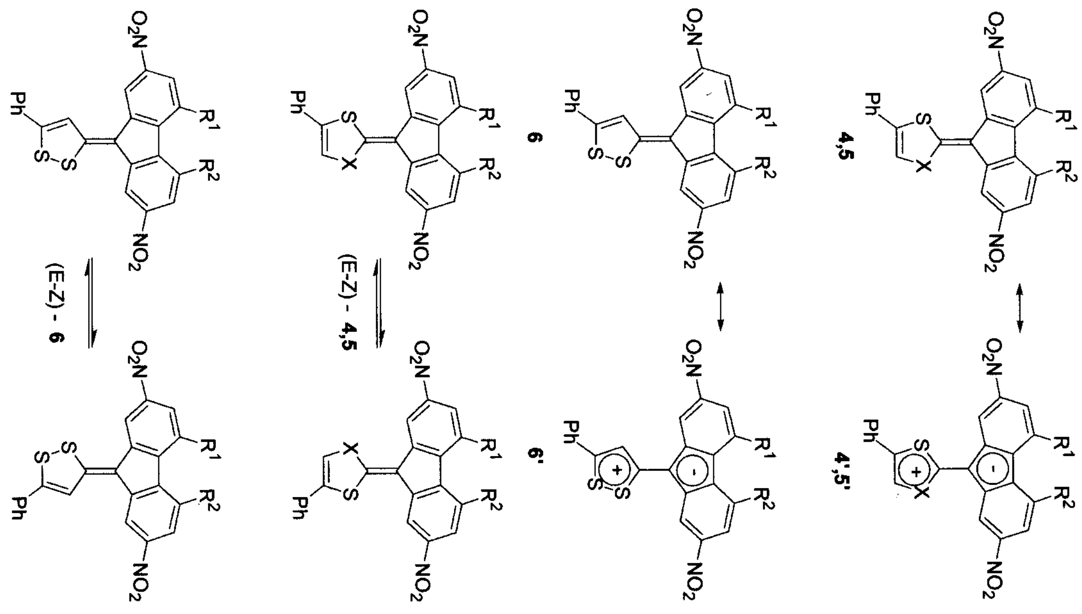
Chart 2



corroborated by the concentration dependence of their intensities showing good linear dependence (with an accuracy of ca. 3%) of an absorbance (A/l) versus concentration [e.g., for **5g**: $A_{\mathrm{ICT-1}} = 1.036$, $A_{\mathrm{ICT-2}} = 0.491$ ($C = 5.53 \times 10^{-4}$ M^{-1}, $l = 0.10$ cm cell), $A_{\mathrm{ICT-1}} = 0.994$, $A_{\mathrm{ICT-2}} = 0.472$ ($C = 2.73 \times 10^{-5}$ M^{-1}, $l = 2.00$ cm cell)]. In some solvents, the shape of both the ICT bands are unsymmetrical (nonGaussian in shape), which can be explained by overlapping of some bands with close ICT transition energies, partly arising from closely lying ICT bands for the *E* and *Z* isomers.

The absorption maxima of the ICT bands, which depend on the structure of the acceptor and the donor moieties, and the solvent properties, lie in the range of 400−510 nm for ICT-1 and 490−640 nm for ICT-2 (Table 2).

As seen from Table 2 and Figure 1, the heteroatom (S or Se, compounds **4** or **5**) in the donor moiety has no apparent influence on the location of both ICT bands ($\lambda_{\mathrm{ICT-1}}$ and $\lambda_{\mathrm{ICT-2}}$) on the difference in their energies ($h\nu_{\mathrm{ICT-1}} - h\nu_{\mathrm{ICT-2}} \approx 0.70-0.72$ eV) and on the ratio of their intensities ($A_{\mathrm{ICT-1}}/A_{\mathrm{ICT-2}} \approx 2$). However, a change in the position of sulfur atoms in the heterocycle from 1,3 to 1,2 (compounds **4** and **6**, respectively) causes a substantial bathochromic shift of both ICT bands, with the shift of a short wavelength band (ICT-1) being more

Table 1. 400 MHz ^{1}H NMR Chemical Shifts (δ_{H}) and Coupling Constants (J) for compounds 4−6 in DMSO-d_6, 25 °C

compd	heterocycl H	1-H	8-H	3-H	6-H ($J_{5,6}$)	5-H	4-H ($J_{3,4}$)	*o*-H (C_6H_5, $J_{o,m}$)	*m*,*p*-H (C_6H_5)	others
4a	8.02s	8.79s	8.77s	8.47m	8.36m	8.47m	8.53d (8.8)	7.80m	7.55m	
4b[a]	7.989, 7.981 (*E*−*Z*)	8.77s, 8.75s (*E*−*Z*)	8.64s, 8.62s (*E*−*Z*)	8.42m (2H)	8.17m			7.7m	7.56m	4.06s (CO_2CH_3)
4c	no observable signals due to low solubility									
4d	7.96	[8.30br, 8.12br][b]						7.80m	7.58m	
4e	8.07s	8.90br	8.82br	8.50br	8.30br			7.67m	7.55m	3.88s (CO_2CH_3)
4f	8.24s	9.15br (2H), 8.80br, 8.71br						7.83d (7.3)	7.60m	
4g	8.06s	8.88br (2H), 8.53br (2H)						7.62m	7.52m	
5a	8.29s	no signal due to low solubility						7.79m	7.58m	
5b	8.86s, 8.73s, 8.57s, 8.40−8.44m, 8.17−8.25m							7.68m	7.53m	4.06s (CO_2CH_3)
5c	8.37s, 8.36s (*E*−*Z*)	9.09s, 8.93s, 8.84s, 8.81s, 8.75br, 8.64br, 8.50s, 8.48br (Σ 5H)						7.79d (7.2)	7.57m	
5d	8.42s, 8.37s, 8.26s, 8.18s, 8.13s, 7.89−7.97m, 7.82d ($J_{5,6}$ 9), 7.62d ($J_{5,6}$ 9), 7.58d ($J_{5,6}$ 9)							7.30−7.50m (5H)		
5e	8.24−8.80br (3H), 8.00−8.24br (2H)							7.49br		3.85s (CO_2CH_3)
5f	8.45s	9.17br	8.90br	8.78s	8.70s			7.77m	7.57m	
5g	8.48s	broadened signals		8.68s (2H)				7.78d (7.2)	7.57m	
6a	no observable signals due to low solubility							7.97m	7.64m	
6b	no observable signals due to low solubility									4.10s (CO_2CH_3)
6c	8.60s	no observable signals due to low solubility						8.00m	7.66m	
6d	8.62s	9.40s, 9.17br, 9.00br, 8.85s, 8.65br, 8.55s, 8.21br (Σ 5H)						8.08d (7.9), 7.98d (7.9) (*E*−*Z*)	7.67m	
6e[a]	8.57s	9.36s, 9.31s, 9.24s, 8.80s, 8.69s, 8.63s, 8.57s, 8.30s (Σ 4H)						8.03d (7.3)	7.68m	4.08s, 3.86s (CO_2CH_3)
6f	8.62s	9.33s (2H)		8.77s	8.69s			8.05d (6.9)	7.68m	
6g	8.64br	9.43br (2H)		8.88br (2H)				8.08m	7.7m	
6i[c]	8.18br	9.35br 9.06br (*E*−*Z*)	9.29br 8.98br (*E*−*Z*)	8.55−8.70m				7.73−7.82m	7.56−7.66m	4.53br,m (CO_2CH_2), 3.89br,m ($CO_2CH_2CH_2$), [3.62−3.75m, 3.50−3.57m (2 −OC_2H_4O-)], 3.36s (OCH_3)

[a] Two sets of signals from both *E* and *Z* isomers are observed. [b] Not all signals are observed due to dynamic broadening. [c] Recorded in $CDCl_3$, 45 °C (200 MHz).

Table 2. $\lambda_{max}{}^{a}$ (nm) of ICT-1 and ICT-2 Bands for Compounds 4−7 in Various Solvents at 25 °C

		dioxane (2.209)[b]		chlorobenzene (5.62)[b]		$C_2H_4Cl_2$ (10.36)[b]	acetone (20.74)[b]		DMF (36.7)[b]		acetonitrile (37.5)[b]		DMSO (48.9)[b]	
compd	$\Sigma\sigma_p^-$	λ_{ICT-1}	λ_{ICT-2}	λ_{ICT-1}	λ_{ICT-2}	λ_{ICT-2}	λ_{ICT-1}	λ_{ICT-2}	λ_{ICT-1}	λ_{ICT-2}	λ_{ICT-1}	λ_{ICT-2}	λ_{ICT-1}	λ_{ICT-2}
4a	2.54						406.5	491.7						
4b	3.176						412.7	515.3						
4c	3.54	418.2	514.9	423.7	524.3		419.3	520.1			419	508	426.7	538
4d	3.81	419.6	525.3	427.2	539.4	543	420.3	530.3			421	535	426.7	545
4e	4.446	426.4	556.2	434	577.4	567	429.7	563.6			431	568	436.9	582.1
4f	4.81	426.4	552.5	435.5	580.6	569	432	563.6			432	571	439.2	580.8
4g	5.08	434.2	570.8	444.2 (22400)	596.9 (10500)	599	441.4	584.7	447.5	599	433	575	449.5	604.4
5a	2.54						403.7	489.9						
5b	3.176						410	513.8						
5c	3.54	415.8	515.9	422.3	525.8		417.9	520.2			419	521	425.6	537.1
5d	3.81	420.2	531	428.9	548		422	538.6			427	548	425.6	551
5e	4.446	424.8	555.6	433.3	573.5		429.4	564.3			430	568	436.1	583.5
5f	4.81	425.5	554.4	437	579.2		431.2	564.3			432	571	438.4	583.5
5g	5.08	433.1	571.5	443.4 (18500)	596.9 (8700)		440.6 (17500)	585.1 (8200)	446.5	602	433	575	449.5	608.5
6a	2.54						460sh	527.3						
6b	3.176						470sh	557.4						
6c	3.54	470sh	565	480sh	577.2		480sh	564.9			470sh	565	490	582.4
6d	3.81	480sh	572.2	490sh	584.7		485sh	573.1	500sh	587			490sh	590.5
6e	4.446	490.4	591.7	499.7	599.2		495sh	588.5	498	613			504.1	613.9
6f	4.81	486.1	593.1	493.8	608		490.3	601.2			492	595	501	620.4
6g	5.08	492.3	605.8	502.4 (11500)	621.1 (20000)		498.7	616.2	509	633			512.8	639.8
6h	4.538								492	604				
7b	3.176									498				
7d	3.81									513.5				
7e	4.446									542.5				
7f	4.81									549.5				
7g	5.08								425.5	569			428 (21300)	577 (10700)

[a] Molar extinction coefficients, ϵ/M^{-1} cm^{-1}, are given in parentheses. [b] Relative permittivity, ϵ_s, is given in parentheses.

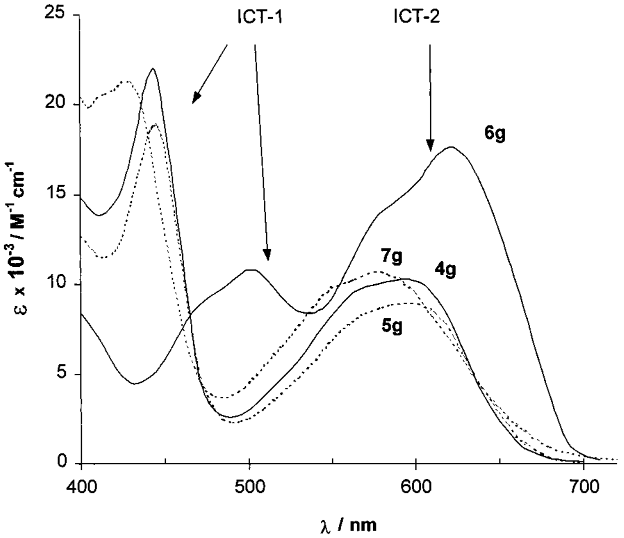


Figure 1. Intramolecular charge-transfer bands in the electronic absorption spectra of compounds **4g**−**7g** in chlorobenzene (**4g**−**6g**) and DMSO (**7g**).

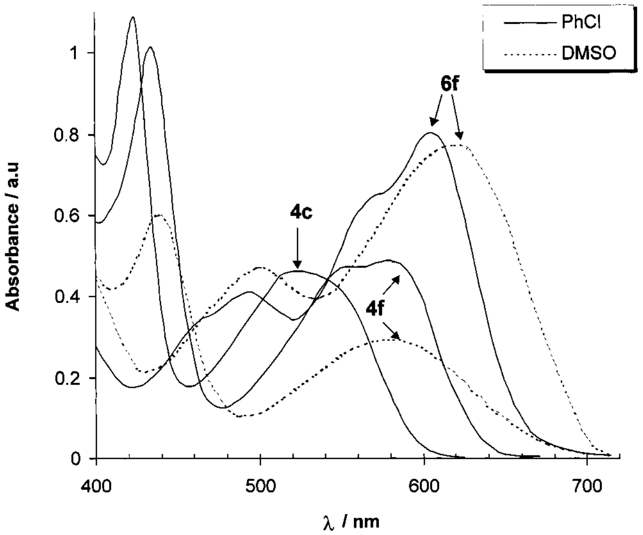


Figure 2. Electronic absorption spectra of compounds **4c**, **4f**, and **6f** in the visible region.

pronounced than that of the long wavelength band (ICT-2) (ca. 60 and 30 nm, respectively) causing a decrease in the difference in their electron transition energies: $h\nu_{ICT-1} - h\nu_{ICT-2} \approx 0.46{-}0.48$ eV. Moreover, the ratio of their intensities also changes dramatically (Figures 1 and 2). Thus, in compounds **4** and **5** it is the short wavelength absorption band, λ_{ICT-1}, which is more intense ($A_{ICT-1}/A_{ICT-2} \approx 2$), whereas in compounds **6** the situation is reversed ($A_{ICT-1}/A_{ICT-2} \approx 0.7$).

The change in the mode of benzene ring linkage to the 1,3-dithiole moiety from terminal (phenyl substituent, compounds **4**) to annelated benzene ring (compounds **7**) drastically effects the ICT energies, resulting in a hypsochromic shift of both ICT bands. However, the ratio of the intensities of ICT-1 and ICT-2 and the difference in their energies remain about the same as in compounds **4**.

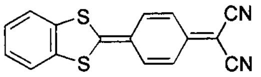
As follows from Table 3, the ICT from 1,2-dithiole moieties (compounds **23** and **25**, Chart 3) is of lower energy than from 1,3-dithiole isomers (compounds **22** and **24**): bathochromic shifts of the longest wavelength ICT absorption for a transition **22** → **25** are ~105−112 nm[22a−c]

Table 3. Electronic Absorption Maxima for Compounds 22, 23, 24, and 25 in Chloroform

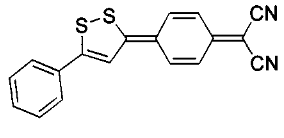
compd	λ_{max}/nm (log ϵ)	ref
22	638 (4.75), 590 (4.79), 547 (4.57)	22a
	645 (4.75)	22b
	640	22c
	641 (4.97), 589 (4.93), 548 (4.68)[a]	20b
23	700	22c
	758 (3.98), 633 (3.90), 500 (4.42)	22b
24	660, 610	22c
25	750	22c

[a] In dichloromethane.

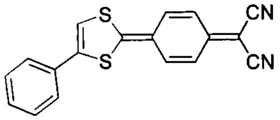
Chart 3



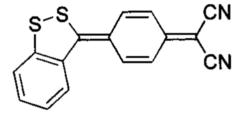
22



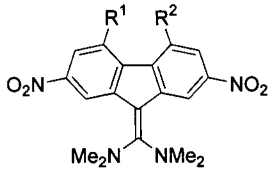
23



24



25



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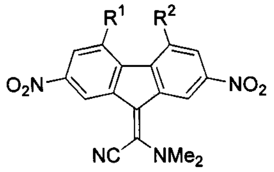

27

and for **24** → **23** are 40[22c] or 98 nm.[22b] Changing the type of link of the aromatic substituent in the 1,3-dithiole derivatives from phenyl (**24**) to annelated benzene ring (**22**) is accompanied by a hypsochromic shift of 15−22 nm. In contrast, for 1,2 dithiole derivatives such a change [**23** (λ_{max} = 700 nm) → **25** (λ_{max} = 750 nm)][22c] is accompanied by a substantial bathochromic shift of 50 nm, although in an earlier paper by the same authors a different value, λ_{max} = 758 nm, for compound **23** was reported.[22b]

Effect of the Acceptor Moiety. Increasing the acceptor character of the fluorene fragment by introduction of electron-withdrawing substituents in the fluorene ring results in a bathochromic shift of both ICT bands. To estimate quantitatively the effect of the substituents upon the energies of the ICT bands ($h\nu_{ICT}$ corresponding to λ_{ICT}) we used eq 1[8]

$$h\nu_{ICT} = h\nu^0_{ICT} + \rho_{ICT}\Sigma\sigma_p^- \tag{1}$$

where $\Sigma\sigma_p^-$ is the sum of the nucleophilic σ_p^- constants of the substituents[34] in the fluorene ring and ρ_{ICT} is a parameter of the sensitivity of ICT energies to the structure of the acceptor moiety. The parameters of correlations are collected in Table 4.

As seen from Table 4, the values of ρ_{ICT} lie in the range −0.064 to −0.096 eV for ICT-1 and −0.091 to −0.190 eV for ICT-2, which is comparable to those for other push−pull fluorene systems reported by us recently:[8] 9-[bis(dimethylamino)methylene]fluorenes (**26**), $\rho_{ICT} = -(0.050-0.086)$ eV, 9-[cyano(dimethylamino)methylene]fluorenes (**27**), and $\rho_{ICT} = -(0.13-0.18)$ eV (one ICT band only was observed for these series of compounds).

For compounds **4** and **5**, the sensitivity parameter (ρ_{ICT}) for the ICT-2 band is ca. 1.7−2.3 times higher than that for the ICT-1 band (Table 4). In the case of compounds **6** and **7**, the first ICT band maxima could not always be determined accurately, and no good correlations of $h\nu_{ICT-1}$ vs $\Sigma\sigma^-$ were observed due to overlapping of λ_{ICT-1} by other bands. Values of ρ_{ICT-2} vary only slightly within the change of the heteroatom from S to Se (from **4** to **5**) and for compounds **4**, **5**, and **7** lie in the range of −(0.14−0.19) eV, whereas the change in the location of the sulfur atom from 1,3 (**4**) to 1,2 (**6**) leads to a decrease in ρ_{ICT-2} values, which are ca. 1.5 times lower than those for compounds **4**, **5**, and **7** and lie in the range of −(0.09−0.12) eV depending on the solvent (Table 4).

It should be mentioned that regularities in changes of energies and intensities for the ICT-2 bands, and also their sensitivity to the substituents on the fluorene ring, are more important than for the ICT-1 band from the viewpoint of the design of new electronic materials based on this class of push−pull compounds (e.g., in regard to increasing the photoconductivity in the long-wavelength and near-IR region of the spectra). From this point of view, the bathochromic shift and increase in intensities of ICT-2 bands for the series of acceptors **6** provides a very promising approach for designing highly sensitive photoconductive materials for the spectral region ≥600−800 nm.

In some cases, correlation coefficients (r = 0.956−0.989 for ICT-1 and 0.968−0.994 for ICT-2) and the accuracy of ρ_{ICT} determination are lower than that observed previously for fluorene acceptors with ICT, **26**, and **27**.[8] The reason for this is the above-mentioned complication of both ICT-1 and ICT-2 bands due to overlapping ICT transitions. The observed maxima, λ_{ICT}, depend on their relative positions and intensities, which vary with a change of substituents on the fluorene ring (cf. compounds **4c** and **4f** in Figure 2) and with a change of solvent (cf. compound **6f** or **4f** in chlorobenzene and in DMSO, Figure 2).

Solvent Effects. All the compounds investigated display solvatochromic behavior (Table 2). The maximum observed shift in λ_{ICT} with a change of solvent (from dioxane to DMSO) was about 20 nm for ICT-1 and 35 nm for ICT-2. However, for these systems a single parameter, i.e., the medium polarity, is insufficient to explain the effect of solvents upon ICT energies, since most of the solvents used have pronounced electrophilic or basic properties that cannot be neglected. As mentioned above, the observed first and second ICT bands reflect different electron transitions with close energies, whose solvatochromic behavior is not the same, bringing about a change in the shape of ICT bands and complicating a quantitative evaluation of the influence of solvent properties on ICT energy.

This also explains the fact that, in contrast to the

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(34) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979; 339 p.

Table 4. Correlations[a] of ICT Energies of Compounds 4−7 by Eq 1

			4		**5**		**6**		**7**
solvent	ϵ_s		ICT-1	ICT-2	ICT-1	ICT-2	ICT-1	ICT-2	ICT-2
dioxane	2.209	$h\nu^0_{\mathrm{ICT}}$/eV	3.20 ± 0.05	2.91 ± 0.10	3.21 ± 0.05	2.88 ± 0.09	2.58 ± 0.04	2.51 ± 0.04	
		$10^2 \times \rho_{\mathrm{ICT}}$/eV	−6.4 ± 1.1	−14.5 ± 2.2	−6.5 ± 1.2	−13.8 ± 2.0	−1.1 ± 5.1	−9.1 ± 0.9	
		r	0.956	0.968	0.956	0.970	0.214[b]	0.985	
		s_0	1.5×10^{-2}	2.8×10^{-2}	1.5×10^{-2}	2.6×10^{-2}	2.3×10^{-2}	1.2×10^{-2}	
		n	5	5	5	5	3	5	
PhCl	5.62	$h\nu^0_{\mathrm{ICT}}$/eV	3.20 ± 0.05	3.00 ± 0.09	3.21 ± 0.04	2.92 ± 0.09	2.56 ± 0.32	2.48 ± 0.03	
		$10^2 \times \rho_{\mathrm{ICT}}$/eV	−7.8 ± 1.1	−18.3 ± 1.9	−7.9 ± 1.0	−16.6 ± 2.0	−1.5 ± 6.7	−9.3 ± 0.6	
		r	0.971	0.983	0.976	0.979	0.221[b]	0.994	
		s_0	1.4×10^{-2}	2.6×10^{-2}	1.3×10^{-2}	2.6×10^{-2}	3.0×10^{-2}	0.8×10^{-2}	
		n	5	5	5	5	3	5	
$C_2H_4Cl_2$	10.28	$h\nu^0_{\mathrm{ICT}}$/eV		2.86 ± 0.17					
		$10^2 \times \rho_{\mathrm{ICT}}$/eV		−15.0 ± 3.7					
		r		0.944					
		s_0		3.5×10^{-2}					
		n		4					
acetone[c]	20.74	$h\nu^0_{\mathrm{ICT}}$/eV	3.28 ± 0.02	2.91 ± 0.04	3.32 ± 0.03	2.92 ± 0.04		2.64 ± 0.03	
		$10^2 \times \rho_{\mathrm{ICT}}$/eV	−9.0 ± 0.6	−15.3 ± 1.0	−9.6 ± 0.6	−15.7 ± 1.0		−12.2 ± 0.8	
		r	0.989	0.990	0.989	0.990		0.989	
		s_0	1.3×10^{-2}	1.0×10^{-2}	1.5×10^{-2}	2.3×10^{-2}		1.9×10^{-2}	
		n	7	7	7	7		7	
DMF	36.7	$h\nu^0_{\mathrm{ICT}}$/eV						2.54 ± 0.12	3.15 ± 0.06
		$10^2 \times \rho_{\mathrm{ICT}}$/eV						−11.2 ± 2.6	−19.0 ± 1.5
		r						0.975	0.991
		s_0						2.4×10^{-2}	1.9×10^{-2}
		n						3	5
CH_3CN	37.1	$h\nu^0_{\mathrm{ICT}}$/eV	3.20 ± 0.04	3.02 ± 0.16	3.13 ± 0.06	2.80 ± 0.14			
		$10^2 \times \rho_{\mathrm{ICT}}$/eV	−6.7 ± 1.0	−17.7 ± 3.7	−5.4 ± 1.4	−13.2 ± 3.1			
		r	0.968	0.942	0.918	0.924			
		s_0	1.3×10^{-2}	4.8×10^{-2}	1.8×10^{-2}	3.1×10^{-2}			
		n	5	5	5	5			
DMSO	48.9	$h\nu^0_{\mathrm{ICT}}$/eV	3.24 ± 0.06	2.87 ± 0.09	3.27 ± 0.07	2.88 ± 0.09	2.76 ± 0.09	2.55 ± 0.04	
		$10^2 \times \rho_{\mathrm{ICT}}$/eV	−9.2 ± 1.5	−16.0 ± 2.1	−9.6 ± 1.6	−16.3 ± 2.0	−6.4 ± 1.9	−11.8 ± 0.9	
		r	0.963	0.976	0.960	0.979	0.918	0.990	
		s_0	1.9×10^{-2}	2.7×10^{-2}	2.1×10^{-2}	2.6×10^{-2}	2.3×10^{-2}	1.2×10^{-2}	
		n	5	5	5	5	4	5	

[a] Calculated by five points (**4**−**6c**−**g** and **7b,d**−**g**) of the data in Table 2. [b] No satisfactory correlations obtained due to overlapping of ICT-1 bands by other bands. [c] Calculated by seven points (**a**−**g**) of the data in Table 2.

Table 5. Effect of the Temperature on the λ_{ICT} for Compounds 4g−6g in Various Solvents and Correlations of $h\nu_{\mathrm{ICT}}$ According to Eq 2

			4g		**5g**		**6g**	
solvent	ϵ_s		ICT-1	ICT-2	ICT-1	ICT-2	ICT-1	ICT-2
PhCl	5.62	$\lambda_{\max}^{3°C}$/nm	446	601				
		$\lambda_{\max}^{25°C}$/nm	444	597	443.5	597	502.5	621
		$\lambda_{\max}^{55°C}$/nm	442	586	442	587	500	616
		$\lambda_{\max}^{92°C}$/nm	439	576	440	580	499	611
		$h\nu^{T\propto}_{\mathrm{ICT}}$/eV	2.96 ± 0.01	2.40 ± 0.02	2.92 ± 0.01	2.41 ± 0.03	2.56 ± 0.02	2.17 ± 0.00
		α/eV K	−49.32 ± 3.15	−94.39 ± 6.68	−36.1 ± 2.97	−98.81 ± 9.47	−28.08 ± 6.96	−53.05 ± 0.14
		r	0.996	0.995	0.997	0.995	0.971	1.000
		s_0	2.1×10^{-3}	4.4×10^{-3}	1.3×10^{-3}	4.1×10^{-3}	3.0×10^{-3}	6.2×10^{-5}
acetone	20.74	$\lambda_{\max}^{25°C}$/nm	441.5	585	440.5	585	499	616
		$\lambda_{\max}^{50°C}$/nm			440	582		
		α/eV K				−42[a]		
CH_3CN	37.5	$\lambda_{\max}^{25°C}$/nm		575	441	583		
		$\lambda_{\max}^{50°C}$/nm			440	582		

[a] Estimated by two points.

previous compounds **26** and **27** that showed good correlations using polarity and basicity functions of the solvents in the Koppel−Palm equation,[35] we could not obtain quantitative relationships between the ρ_{ICT} or λ_{ICT} values and any solvent parameters for compounds **4**−**7** with the series of solvents used. Correlations of ICT energies versus $E_T(30)$ or E_T^N values[36] were also unsatisfactory.

The compounds under investigation also display thermochromism, which is characteristic for solvatochromic substances due to a change in the solute/solvent interactions within the change of the temperature.[36,37] Hypsochromic shifts were observed for both the ICT-1 and ICT-2 bands with increasing the temperature (Figure 3, Table 5). In all cases, the ICT-2 band displays a much greater temperature dependence than ICT-1. Thus, the ICT-2 band of 1,3-dithiole derivative **4g** in chlorobenzene

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(35) (a) Koppel, I. A.; Palm, V. A. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London, 1972; Chapter 5, p 203. (b) Palm, V. A. *Fundamentals of Quantitative Theory of Organic Reactions*; Khimiya: Leningrad, 1977; p 109 (in Russian).

(36) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim; 1990; pp 363−371.

(37) (a) Ray, A. *J. Am. Chem. Soc.* **1971**, *93*, 7146. (b) Kiprianov, A. I.; Timoshenko, E. S. *Zh. Obsch. Khim.* **1947**, *17*, 1468.

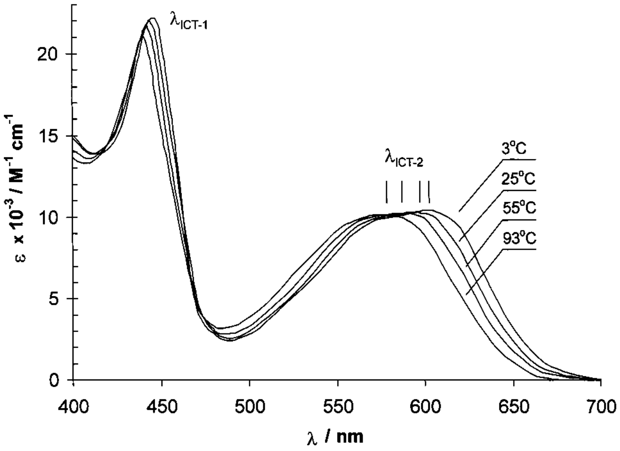

Figure 3. Effect of temperature on the position of ICT bands in compound **4g** in chlorobenzene (no correction for expansion of the solvent with temperature was made, leading to a minor decrease in observed ϵ values with increasing temperature).

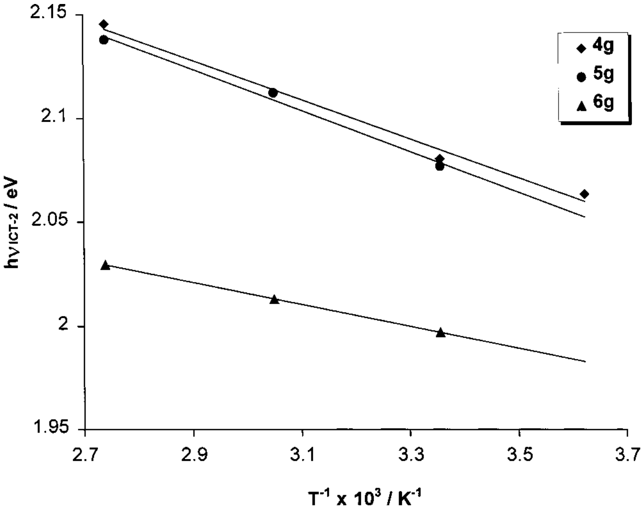

Figure 4. Plots of $h\nu_{ICT-2}$ versus $1/T$ for compounds **4g**–**6g**.

Table 6. Cyclic Voltammetry Data for Fluorene Derivatives 4–7 (vs Fc^0/Fc$^+$ Couple)[a,b]

compd	$E_{ox}^{1/2}$ (V)	$E_{1red}^{1/2}$ (V)	$E_{2red}^{1/2}$ (V)	$E_{3red}^{1/2}$ (V)	ΔE_{1-2} (V)	K_{dispr}[c] (M^{-1})
4a	+0.64[d]	−1.37	−1.54		0.17	1.3×10^{-3}
4b	+0.67[d]	−1.29	−1.49		0.20	4.1×10^{-4}
4c		−1.17	−1.35		0.18	8.9×10^{-4}
4d		−1.08	−1.27		0.19	6.0×10^{-4}
4e		−0.96	−1.19		0.23	1.3×10^{-4}
4f		−0.91	−1.12		0.21	2.8×10^{-4}
4g		−0.79	−1.01		0.22	1.9×10^{-4}
5a	+0.69[d]	−1.36	−1.54		0.18	8.9×10^{-4}
5b		−1.29	−1.49		0.20	4.1×10^{-4}
5c		−1.15	−1.33		0.18	8.9×10^{-4}
5d		−1.09	−1.30		0.21	2.8×10^{-4}
5e		−0.95	−1.17	−2.00	0.22	1.9×10^{-4}
5f		−0.91	−1.09	−1.99	0.18	8.9×10^{-4}
5g		−0.80	−1.02		0.22	1.9×10^{-4}
6a		−1.35				
6b		−1.25				
6c		−1.14				
6d		−1.09				
6e		−1.01	−1.12		0.11	1.4×10^{-2}
6f		−0.97	−1.09		0.12	9.2×10^{-3}
6g		−0.86	−1.02		0.16	1.9×10^{-3}
7e		−0.94	−1.17		0.23	1.3×10^{-4}
7g		−0.78	−1.00		0.22	1.9×10^{-4}

[a] For compounds **7b**–**d**,**f**, cyclic voltammograms were not obtained due to the very low solubility of the compounds. [b] Solvent DMA; electrolyte 0.2 M $Bu_4N^+PF_6^-$. [c] Calculated using equation $\Delta E_{1-2} = E_{1red}^{1/2} - E_{2red}^{1/2} = -0.059 \log K_{dispr}$. [d] Irreversible oxidation peak.

is blue shifted by 25 nm upon increasing the temperature from 3 to 92 °C, whereas the ICT-1 band is shifted by only 7 nm. The effect of temperture on λ_{ICT} appears to be much more pronounced in low polarity media than in high-polarity media, as follows from a comparison of λ_{ICT} shifts for **5g** in chlorobenzene (ϵ_s 5.62) with those in acetone (ϵ_s 20.74) or acetonitrile (ϵ_s 37.5) (Table 5). The $h\nu_{ICT}$ energies display good linear dependence with inverse temperature (Figure 4). To estimate quantitatively the temperature effect on the energies of ICT transitions we used eq 2:

$$h\nu_{ICT} = h\nu_{ICT}^{T_\infty} + \alpha \frac{1}{T} \qquad (2)$$

Parameters of correlations for compounds **4g**–**6g** in chlorobenzene are summarized in Table 5 confirming an excellent correlation in all the cases. The sensitivity parameters α for compounds **4g** and **5g** are very close, whereas compound **6g** shows ca. 2 times lower sensitivity of $h\nu_{ICT-2}$ to the temperature.

Compounds **4**–**7** display negative halochromism: their dissolution in concentrated sulfuric acid results in disappearance of both ICT bands due to protonation of the molecule and localization of the positive charge on the dithiole moiety, removing its donor properties. The longest wavelength absorptions in the resulting spectra are in the 350–400 nm region, similar to the corresponding polynitrofluorenes **1**.[1b] Decreasing the acidity of the solvent by gradual dilution with water resulted in reappearance of the color, followed by precipitation of the starting compounds, which were isolated in high yield. It should also be mentioned that in dilute sulfuric acid, in a certain range of concentrations, we observed in the electronic absorption spectra of **4g** and **5g** additional bands in the near-IR region that are characteristic of radical ion species. Thus, Figure 5 demonstrates that dilution with water of a colorless solution of compound **21** in H_2SO_4 leads progressively to the appearance of the absorption of starting compound **5g** at ca. 600 nm due to reverse reaction (Scheme 2) and also to the development of a new absorption band in the 800–1000 nm region with a peak at $\lambda_{max} = 940$ nm in 48% H_2SO_4. This can be explained by the electron-transfer interaction of neutral compound **5g** (formed upon dilution) with its salt **21** (i.e., $[\mathbf{5g}\text{-H}]^+HSO_4^-$) yielding radical and radical cation species:

$$\mathbf{5g} + [\mathbf{5g}\text{-H}]^+ \rightleftarrows \mathbf{5g}^{\bullet+} + [\mathbf{5g}\text{-H}]^{\bullet} \qquad (3)$$

A similar type of electron exchange interaction between TTF and $[TTF\text{-}H]^+BF_4^-$ yielding TTF$^\bullet$ and TTF$^{\bullet+}$ was proved earlier,[30] demonstrating the generation of radicals and the formation of electrically conducting materials by protic doping of TTF. More detailed electronic absorption and ESR spectral investigations of this equilibrium in **4**–**6** will be reported elsewhere.

Electrochemistry. To study the redox properties of the novel compounds **4**–**7**, we carried out cyclic voltammetry (CV) measurements in *N*,*N*-dimethylacetamide (DMA) solution at room temperature with tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

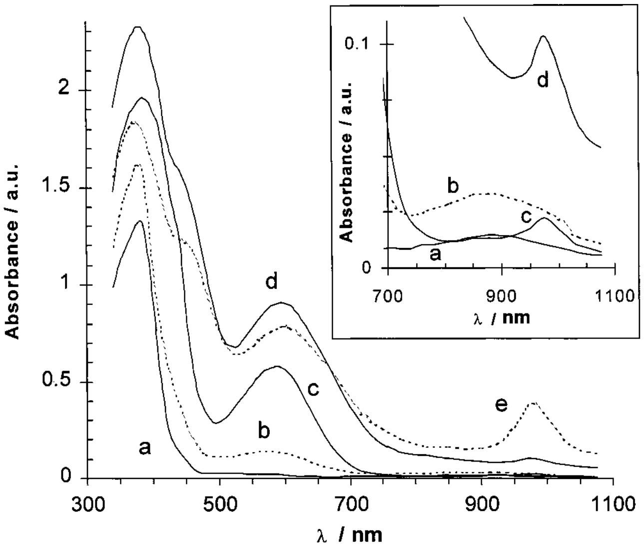

Figure 5. Electronic absorption spectra of compound **5g** in sulfuric acid of various concentrations: (a) 94% H_2SO_4 ($H_0 = -9.7$), (b) 87% H_2SO_4 ($H_0 = -8.4$), (c) 84% H_2SO_4 ($H_0 = -7.95$), (d) 73% H_2SO_4 ($H_0 = -6.25$), (e) 48% H_2SO_4 ($H_0 = -3.1$); (H_0 values were found from the plot "H_0 − %H_2SO_4" by data from ref 27).

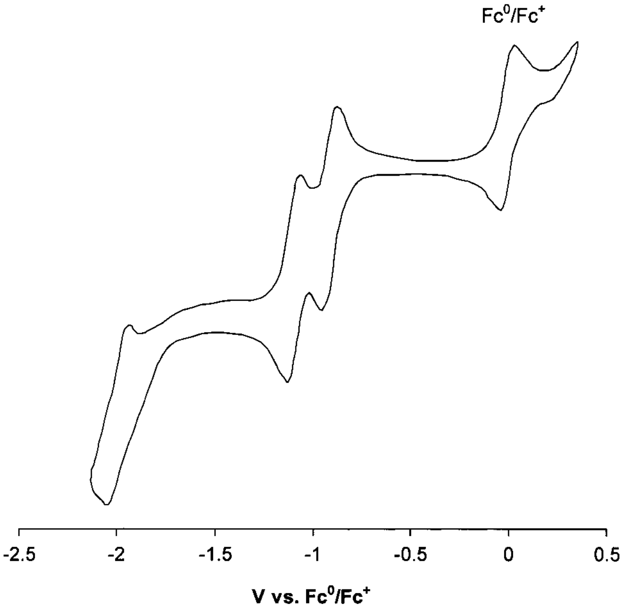

Figure 6. Cyclic voltammogram of compound **5f**: electrolyte $Bu_4N^+PF_6^-$ (0.2 M); solvent DMA; scan rate 200 mV s^{-1}; potentials are represented versus Fc^0/Fc^+.

All four series of compounds, i.e. **4**−**7**, showed similar electrochemical behavior: two closely spaced single-electron reduction waves were observed resulting in radical anion and dianion species, respectively [Figure 6, Table 6; $\Delta E_{1-2} = E_{1red}^{1/2} - E_{2red}^{1/2} = 0.17-0.23$ V (**4**), 0.18−0.22 V (**5**), ≤ 0.16 V (**6**), ≈ 0.23 V (**7**)]. The first reduction waves, $E_{1red}^{1/2}$, for compounds **4**−**7** lie in the range −(1.37−0.78) V (vs Fc^0/Fc^+) and the second reduction waves, $E_{2red}^{1/2}$, lie in the range of −(1.54−1.00) V depending on the substituents in the fluorene ring (increasing the electron affinity of the fluorene moiety leads to a positive shift in the potentials). $E_{1red}^{1/2}$ potentials of ca. −0.78−0.86 V vs Fc/Fc^+ for acceptors **4g**−**7g** characterize them as moderate electron acceptors whose electron affinities can be estimated as ca. 2.1−2.2 eV[38] [$E^{ox}_{Fc/Fc+}$ was reported to be + 0.45 V vs Ag/AgCl in CH_3CN;[8] + 0.44 V vs SCE in CH_2Cl_2[39] and DMF;[16] +0.40 V (in H_2O and MeOH), +0.34 V (CH_3CN), +0.39 V (DMF) vs SCE;[40] +0.31 V vs SCE in CH_3CN.[41]].

Table 7. Correlations of the Electrochemical Reduction Potentials for Compounds 4−7 According to Eq 4

compd	CV wave	$E_0^{1/2}$/V	$\rho^- \times 10^2$/V	r[a]	n[b]
4	$E_{1red}^{1/2}$	−1.970 ± 0.030	22.7 ± 1.4	0.991	7
4	$E_{2red}^{1/2}$	−2.094 ± 0.037	20.7 ± 1.6	0.985	7
5	$E_{1red}^{1/2}$	−1.947 ± 0.030	22.2 ± 1.3	0.991	7
5	$E_{2red}^{1/2}$	−2.106 ± 0.031	21.2 ± 1.4	0.989	7
6	$E_{1red}^{1/2}$	−1.806 ± 0.027	18.1 ± 1.2	0.989	7
6	$E_{2red}^{1/2}$	−1.810 ± 0.022	15.3 ± 5.0	0.952	3[c]
7[d]	$E_{1red}^{1/2}$	−2.06	25.2		2
7[d]	$E_{2red}^{1/2}$	−2.36	26.8		2

[a] Correlation coefficient. [b] Number of points. [c] By three points, **6e**,**f**,**g**. [d] Estimated by two points, **7e**,**g**.

For compounds **4** and **5** the number of electron-withdrawing substituents on the fluorene ring does not effect the ΔE_{1-2} value (within experimental error). Decreasing the electron-withdrawing ability of the fluorene moiety in acceptors **6** leads to a decrease in the difference between the reduction potentials $E_{1red}^{1/2}$ and $E_{2red}^{1/2}$ [ΔE_{1-2} = 0.16 eV (**6g**), 0.12 (**6f**), 0.11 (**6e**)], and for acceptors **6a**−**d** only one, two-electron reduction peak is observed (Table 6). For compounds **5**, in some cases, a third single-electron reduction wave at a considerably more negative potential (−2 V vs Fc^0/Fc^+) resulting in a radical trianion species was observed (Figure 6). All three reduction waves are reversible or quasireversible. For poor electron acceptors **4a**,**b** and **5a**, cyclic voltammetry showed an additional single-electron oxidation wave to yield the radical cation at ca. +0.64−0.69 V that was irreversible.

For a quantitative estimation of the effect of substituents in compounds **4**−**6** upon their electrochemical behavior we used eq 4

$$E^{1/2} = E_0^{1/2} + \rho_{CV}\Sigma\sigma_p^- \qquad (4)$$

where $\Sigma\sigma_p^-$ is the same as in eq 1, $E^{1/2}$ is the half-wave potential for the reduction of a compound, $E_0^{1/2}$ is $E^{1/2}$ for the reference compound (unsubstituted benzene rings in fluorenes, $\Sigma\sigma_p^- = 0$), and ρ_{CV} is a parameter showing the sensitivity of the electrochemical potential to substituents.

The results are summarized in Table 7. For the series of compounds **4** and **5**, both reduction processes, i.e., A → $A^{\bullet-}$ and $A^{\bullet-}$ → A^{2-}, are characterized by similar sensitivities: $\rho_{CV}^{1red} \approx \rho_{CV}^{2red} \approx 0.21-0.23$ V. Compounds **6** show a slightly smaller sensitivity parameter $\rho_{CV}^{1red} = 0.18 \pm 0.01$ V. For the series of compounds **26** and **27** close parameters of the sensitivity ρ_{CV} were observed [**25**: $\rho_{CV}^{1red} = 0.20$ V, $\rho_{CV}^{2red} = 0.18$ V; **27**: $\rho_{CV}^{1red} = 0.17$ V, $\rho_{CV}^{2red} = 0.14$ V].[8]

The thermodynamic stability of radical anion was estimated from the differences in the potentials of the corresponding radical anion and dianion by the equation

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$\Delta E_{1-2} = E_{1\text{red}}^{1/2} - E_{2\text{red}}^{1/2} = -0.059 \log K_{\text{dispr}}$,[42] where K_{dispr} is the disproportionation constant in the equilibrium (5):

$$2A^{\bullet+} \xrightleftharpoons{K_{\text{dispr.}}} A + A^{2-} \tag{5}$$

As seen from Table 6, compounds **4**, **5**, and **7** show similar thermodynamic stabilities of the radical anions, with K_{dispr} values in the range of $10^{-3}-10^{-4}$ L mol^{-1}, whereas the thermodynamic stabilities of the radical anions derived from compounds **6** are somewhat lower.

Conclusions

In summary, we have synthesized four series of fluorene push−pull compounds **4**−**7** that show strong ICT from the donor chalcogenathiole moiety to the acceptor fluorene ring. The influence of the nature of heteroatoms (S or Se) and their location in the donor moiety, the mode of linking the benzene ring to the 1,3-dithiole moiety, and the effects of the substituents in the fluorene ring on the energies of ICT and the redox properties in these compounds establish the following. (i) The replacement of S (1,3-dithiole) by Se (1,3-selenathiole) has no apparent effect on the maxima and the extinction coefficients of the ICT bands whereas a change in the location of S in the dithiole ring from 1,3 to 1,2 leads to a substantial bathochromic shift in the long-wavelength ICT band and an increase in its intensity. In view of the great importance of materials that possess long-wavelength ICT absorption for the design of photothermoplastic storage media, particularly in holography using He−Ne lasers ($\lambda = 632.9$ nm) or solid-state near-IR lasers, this observation is very significant as a basis for the development of new sensitizers for photoconductive materials with high holographic sensitivity in long-wavelength and near-IR regions of the spectrum. (ii) Effects of substituents in the fluorene ring on both ICT energies and reduction potentials $E^{1/2}$ in compounds **4**−**7** can be quantitatively described by Hammett-type equations. The reversible formation of salts **18**−**21** from compounds **4**−**7** by the action of sulfuric acid has been demonstrated; a new absorption band in the near-IR region (ca. 940 nm) in dilute H_2SO_4 can be attributed to the formation of radical ion species in the solution.

Experimental Section

General Methods. Dioxane, acetone, DMF, and dimethyl sulfoxide were purified as described previously.[27] Chlorobenzene and 1,2-dichloroethane were stirred with sulfuric acid, washed with water, dried over $CaCl_2$, and distilled from P_4O_{10} and then from CaO. For cyclic voltammetry experiments, platinum wire, platinum disk diameter 1.6 mm, and Ag/Ag$^+$ ($AgNO_3$ in acetonitrile) were used as counter, working, and reference electrodes, respectively. All potentials were corrected using ferrocene−ferrocenium couple (Fc^0/Fc$^+$) as internal reference. In all cases, CV experiments were performed in dry DMA (Fluka, anhydrous) with $Bu_4N^+PF_6^-$ (Fluka, puriss) as supporting electrolyte (0.2 M) under N_2 flow; concentrations of acceptors were ca. 10^{-4} M^{-1}. The scan rate was 200 mV s^{-1}.

4-Methoxycarbonylfluorene **8b** was obtained as described previously.[43]

Nitrosubstituted fluorenes **9c**,[38] **9d**,[44] **9f**,[38] and **9g**[45] were obtained as described previously (for **9g** see also ref 7 and 44).

9c: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.836 (1H, s), 8.827 (1H, s), 8.61 (1H, s), 8.47 (1H, d, $J_{5,6} = 9$ Hz), 8.44 (1H, dd), 4.29 (2H, s).

9d: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (1H, br), 8.82 (1H, d, $J_{3,1} = 1.5$ Hz), 8.62 (1H, br), 8.35 (1H, dd, $J_{6,5} = 9$ Hz, $J_{6,8} = 2$ Hz,), 8.12 (1H, d, $J_{5,6} = 9$ Hz), 4.39 (2H, s).

9f: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.98 (1H, m), 8.96 (1H, m), 8.87 (1H, d, $J_{3,1} = 1.5$ Hz), 8.79 (1H, d, $J_{6,8} = 1.5$ Hz), 4.52 (2H, s).

9g: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (2H, br), 8.79 (2H, d, $J_{3,1} = 2$ Hz), 4.60 (2H, s).

2,7-Dinitro-4-methoxycarbonylfluorene 9b. 4-Methoxycarbonylfluorene **8b** (3.60 g, 20.0 mmol) was gradually added to a well-stirred mixture of fuming nitric acid (30 mL) and glacial acetic acid (20 mL) at 10−15 °C, the resulting solution was stored for 24 h at room temperature and then diluted with acetic acid (35 mL), and after 2−3 h the resulting solid was filtered off and washed with acetic acid and then with water, yielding a pale yellow crude product **9b** (2.55 g, 47%): mp 223−228 °C. After two recrystallizations from dioxane pure **9b** (2.00 g, 37%) was obtained: mp 233−236 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 (1H, br), 8.53 (1H, br), 8.49 (1H, br), 8.42 (1H, d, $J_{5,6} = 9$ Hz), 8.24 (1H, dd), 4.21 (2H, s), 4.03 (3H, s).

2,5,7-Trinitro-4-methoxycarbonylfluorene 9e. To a well-stirred mixture containing 90% HNO_3 and 7.5% H_2SO_4 (45 mL) was added 4-methoxycarbonylfluorene **8b** (2.24 g, 10.0 mmol) in portions, keeping the temperature below −10 °C. The reaction mixture was stirred at this temperature for 1 h and stored overnight at room temperature. It was diluted with 30% aqueous acetic acid (60 mL) and cooled at 0 °C for 2−3 h, and the resulting precipitate was filtered off and washed with acetic acid (10 mL) and then with water (200−300 mL), yielding crude fluorene derivative **9e** (2.85 g, 79%), mp 195−197 °C dec. Recrystallization from a dioxane− 2-propanol mixture gave a yellow crystalline product: mp 204 °C dec: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.97 (1H, m), 8.85 (1H, m), 8.73 (1H, d, $J_{3,1} = 2$ Hz), 8.52 (1H, d, $J_{6,8} = 2$ Hz), 4.52 (2H, s), 3.84 (3H, s). Anal. Calcd for $C_{15}H_9N_3O_8$: C, 50.15; H, 2.53; N, 11.70. Found: C, 50.23; H, 2.61; N, 11.78%.

2,5,7-Trinitro-4-carboxyfluorene 9h. To a well-stirred mixture containing 90% HNO_3 and 7.5% H_2SO_4 (50 mL) was added fluorene-4-carboxylic acid **8h** (5.00 g, 23.8 mmol) in portions, keeping the temperature below −10 °C. The reaction mixture was stirred at this temperature for 1 h, and then H_2SO_4 (25 mL) was added dropwise and the mixture was stored for 1 day at room temperature. The reaction mixture was then poured into ice−water (300 mL), and the solid was filtered off, washed with water, and dried, yielding acid **9h** (7.6 g, 92.5%): mp 238 °C dec (lit.[46] mp 245 °C dec). Anal. Calcd for $C_{14}H_7N_3O_8$: C, 48.71; H, 2.04; N, 12.17. Found: C, 48.46; H, 2.12; N, 12.33. The compound was used without further purification.

2,5,7-Trinitrofluorene-4-carboxylic Acid (Triethyleneglycol Monomethyl Ether) Ester 9i. A mixture of fluorene-4-carbonyl chloride (2.44 g, 10.6 mmol), triethyleneglycol monomethyl ether (3.5 mL, 22 mmol), and DMF (one drop) was stirred at 80−85 °C for 15 h, and the resulting yellow solution was evaporated in vacuo. After cooling, the residue was dissolved in carbon tetrachloride (25 mL), thoroughly washed with dilute sodium bicarbonate solution, and dried over calcium chloride. After the solvent was removed in vacuo, the crude fluorene-4-carboxylic acid (triethyleneglycol monomethyl ether) ester **8i** (3.02 g, 80%) was obtained as a yellow oil. Without further purification, this ester (1.8 g, 3.7 mmol) was added slowly to a mixture of fuming nitric acid (25 mL, $d = 1.5$ g mL^{-1}) and concentrated sulfuric acid (2 mL) at −(6−8) °C with vigorous stirring. The resulting red solution was stirred at this temperature for 40 min and was then allowed to stand at room temperature for 6 h. The reaction mixture

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[46] Migachyov, G. I. *Zh. Vses. Khim. Ova im. D. I. Mendeleeva* **1979**, *24*, 395.

was poured onto an ice−water mixture (200 mL) and allowed to stand at 0−5 °C for 2−3 h. After the aqueous layer was decanted, a new portion of water was added to the residual oil; it was stored under the water overnight, decanted again, and dissolved in chloroform (25 mL), and the organic layer was dried over $CaCl_2$. Flash column chromatography on silica gel [eluent: chloroform containing EtOH (0.3% v/v) and acidified with concentrated aqueous HCl (0.1 g L^{-1})] gave fluorene **9i** as a yellow oil (1.59 g, 51% overall) that crystallized over several weeks: EIMS (M^+) 491; ^1H NMR (200 MHz, $CDCl_3$) δ 8.85 (1H, d, $J_{1,3} = 2$ Hz), 8.78 (1H, d, $J_{8,6} = 2$ Hz), 8.71 (1H, d, $J_{3,1} = 2$ Hz), 8.64 (1H, d, $J_{6,8} = 2$ Hz), 4.54 (2H, t, $J = 5$ Hz), 4.36 (2H, s), 3.89 (2H, t, $J = 5$ Hz), 3.77−3.53 (8H, m), 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.

4-Phenyl-1,3-dithiole-2-thione (**10**)[47] and 5-phenyl-1,2-dithiole-3-thione (**12**)[48] were obtained as described previously.

4-Phenyl-1,3-selenathiole-2-thione 11. This compound was prepared by a modified procedure.[49] 4-Phenyl-1,2,3-selenadiazole[50] (2.09 g, 10.0 mmol) was added to a stirred solution of KOH (0.80 g, 14 mmol) in 2-propanol at room temperature. The reaction mixture was stirred until nitrogen evolution ceased, and carbon disulfide (1.5 mL) was added. After 5 min, the product began to crystallize. The reaction mixture was stirred for 1 h and then left for ca. 8 h while the product crystallized. The precipitate was filtered and washed with 2-propanol (20 mL) and water yielding thione **11** (1.85 g, 72%) as a yellow powder, mp 114−117 °C. Recrystallization from ethyl acetate gave analytically pure thione **11** (1.48 g, 58%), mp 116−117 °C (lit.[49] mp 115 °C).

4-Phenyl-2-methylthio-1,3-selenathiolium iodide 15. 4-Phenyl-1,3-selenathiole-2-thione **11** (1.28 g, 4.98 mmol) and methyl iodide (5 mL) in *n*-butyl acetate (5 mL) were refluxed for 1.5 h. After cooling, the resulting solid was filtered off and washed with butyl acetate (5 mL) and dry benzene (10 mL), yielding orange plates of selenathiolium salt **15** (1.48 g, 74%), mp 111−112 °C dec.

2-Methylthio-benzo[*d*]-1,3-dithiolium triflate 17. Methyl triflate (0.40 mL, 3.5 mmol) was added to a hot solution of benzo[*d*]-1,3-dithiole-2-thione (**13)** (0.50 g, 2.7 mmol) in dry chloroform (10 mL), and the reaction mixture was kept at 50−55 °C for 1 h; a yellow-brownish oil formed and crystallized during this period. The reaction mixture was diluted with dry ether (3 mL) and kept at 0 °C for ca. 8 h, and the product was filtered off, washed with ether, and dried in vacuo, yielding salt **17** (0.88 g, 94%) as yellow crystals.

4-Phenyl-2-methylthio-1,3-dithiolium methyl Sulfate 14 and 5-Phenyl-3-methylthio-1,2-dithiolium methyl Sulfate 16. General Procedure. The corresponding thione, **10** or **12** (5 mmol), was refluxed with dimethyl sulfate (2.0 mL, 19 mmol) in *n*-butyl acetate (20 mL) for 5 min (for **10**) or 20 min (**12**) and cooled to room temperature, and the solvent was decanted from the solid. The residue of the resulting salt, **14** or **16**, in a small amount of the solvent was used for condensation with fluorenes **9** without further isolation and purification.

9-(4-Phenyl-1,3-dithiol-2-ylidene)-2,7-dinitrofluorene 4a. A solution of fluorene **9a** (0.12 g, 0.47 mmol) in pyridine (Py, 4.5 mL) was added to dithiolium salt **14,** prepared from thione **10** (0.12 g, 0.57 mmol), and the reaction mixture was heated to 100 °C for 3 min. After the mixture was cooled to room temperature during 2−3 h and diluted with acetone (10 mL), the resulting precipitate was filtered off and thoroughly washed with acetone and water, yielding compound **4a** (0.11 g, 50%). Recrystallization from DMF (25 mL) gave compound **4a** as red needles (0.10 g, 46%): mp > 360 °C; λ_{max} (acetone) 363, 383, 407, 492 nm; MS (CI) 432 (M^+); MW (calcd) 432.02385. Anal. Calcd for $C_{22}H_{12}N_2O_4S_2$: C, 61.10; H, 2.80; N, 6.48. Found: C, 61.26; H, 2.88; N, 6.33%.

9-(4-Phenyl-1,3-dithiol-2-ylidene)-2,7-dinitro-4-methoxycarbonylfluorene 4b. A solution of fluorene **9b** (0.11 g, 0.35 mmol) in Py (5 mL) was added to dithiolium salt **14**, prepared from thione **10** (0.10 g, 0.48 mmol), and the reaction mixture was heated with stirring until dissolution of the starting salt was completed. After the mixture was cooled to room temperature during 2−3 h and diluted with acetone (10 mL), the precipitate was filtered off and thoroughly washed with acetone and water, giving brick-red needles of fluorene **4b** (0.11 g, 71%). Recrystallization from DMF (25 mL) gave pure compound **4b** (0.08 g, 50%): mp 283 °C; λ_{max} (acetone) 364, 387, 413, 515 nm; MS (CI) 490 (M^+); MW (calcd) 490.02933. Anal. Calcd for $C_{24}H_{14}N_2O_6S_2$: C, 58.77; H, 2.88; N, 5.71. Found: C, 58.97; H, 2.73; N, 5.86.

9-(4-Phenyl-1,3-dithiol-2-ylidene)-2,7-dinitro-4-cyanofluorene 4c. A solution of fluorene **9c** (0.15 g, 0.53 mmol) in a mixture of DMF (5 mL) and Py (2 mL) was added to dithiolium salt **14**, prepared from thione **10** (0.10 g, 0.48 mmol) and stirred for 3−4 h. The deposition of a dark product soon began. The precipitate was filtered off and thoroughly washed with ethyl acetate, yielding **4c** (0.09 g, 55%). After recrystallization from DMF (40 mL), pure compound **4c** (0.08 g, 49%) was obtained: mp > 360 °C; λ_{max} (acetone) 359, 380sh, 419, 520 nm; HRMS 457.01800 (M^+); MW (calcd) 457.01910. Anal. Calcd for $C_{23}H_{11}N_3O_4S_2$: C, 60.38; H, 2.42; N, 9.18. Found: C, 60.22; H, 2.35; N, 9.26.

9-(4-Phenyl-1,3-dithiol-2-ylidene)-2,5,7-trinitrofluorene 4d. Fluorene **9d** (0.31 g, 1.02 mmol) and DMF (4 mL) were added to dithiolium salt **14**, prepared from thione **10** (0.21 g, 1.00 mmol), and the reaction mixture was heated to 100 °C and then stored overnight at room temperature. The precipitate was filtered off, washed with DMF (5 mL), and thoroughly with acetone, giving **4d** (0.20 g, 42%). After recrystallization from DMF (40 mL), pure compound **4d** (0.13 g, 26%) was obtained: mp 332−334 °C; λ_{max} (acetone) 360, 380sh, 420, 530 nm; HRMS 477.00899 (M^+); MW (calcd) 477.00893. Anal. Calcd for $C_{22}H_{11}N_3O_6S_2$: C, 55.34; H, 2.32; N, 8.80. Found: C, 55.30; H, 2.36; N, 8.87.

9-(4-Phenyl-1,3-dithiol-2-ylidene)-2,5,7-trinitro-4-methoxycarbonylfluorene 4e. Fluorene **9e** (0.20 g, 0.56 mmol), DMF (4 mL), and Py (5 drops) were added to dithiolium salt **14**, prepared from thione **10** (0.15 g, 0.71 mmol) and stirred for 2−3 h. The deposition of a dark product soon began. The solid was filtered off and washed with DMF (5 mL) and thoroughly with ethyl acetate, giving product **4e** (0.15 g, 67%). After recrystallization from DMF (25 mL), pure compound **4e** (0.11 g, 49%) was obtained: mp 329−333 °C; λ_{max} (acetone) 370, 390sh, 430, 564 nm; HRMS 535.01299 (M^+); MW (calcd) 535.01441. Anal. Calcd for $C_{24}H_{13}N_3O_8S_2$: C, 53.83; H, 2.45; N, 7.85. Found: C, 54.03; H, 2.51; N, 7.78.

9-(4-Phenyl-1,3-dithiol-2-ylidene)-2,5,7-trinitro-4-cyanofluorene 4f. This was obtained similarly to **4e** from fluorene **9f** and dithiolium salt **14** in 60% yield: mp 337−340 °C; λ_{max} (acetone) 361, 385sh, 432, 564 nm; HRMS 502.00301 (M^+); MW (calcd) 502.00418. Anal. Calcd for $C_{23}H_{10}N_4O_6S_2$: C, 54.98; H, 2.01; N, 11.15. Found: C, 54.80; H, 2.00; N, 11.22.

9-(4-Phenyl-1,3-dithiol-2-ylidene)-2,4,5,7-tetranitrofluorene 4g. Fluorene **9g** (0.35 g, 1.0 mmol) and DMF (4 mL) were added to dithiolium salt **14**, prepared from thione **10** (0.21 g, 1.0 mmol), and the reaction mixture was heated to 100 °C. After the mixture was cooled to room temperature, the precipitate was filtered off and washed with DMF (5 mL) and thoroughly with acetone, giving black-violet crystalline product **4g** (0.37 g, 71%). After recrystallization from DMF, pure compound **4g** (0.32 g, 62%) was obtained: mp 357−360 °C; λ_{max} (acetone) 362, 441, 585 nm; HRMS 521.99288 (M^+); MW (calcd) 521.99401. Anal. Calcd for $C_{22}H_{10}N_4O_8S_2$: C, 50.58; H, 1.93; N, 10.72. Found: C, 50.64; H, 1.91; N, 10.81.

9-(4-Phenyl-1,3-selenathiol-2-ylidene)-2,7-dinitrofluorene 5a. Salt **15** (0.120 g, 0.30 mmol) was added to a hot solution of fluorene **9a** (0.077 g, 0.30 mmol) in Py (2.5 mL) and stirred for a few minutes. The precipitation of a dark solid soon began. The reaction mixture was stored for 0.5 h and then diluted with acetone (10 mL), and dark red crystals were filtered off and washed with acetone (15 mL) and water, giving

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5a (0.08 g, 62%). After recrystallization from DMF (18 mL), pure compound **5a** (0.07 g, 54%) was obtained: mp > 360 °C; λ_{max} (acetone) 360, 380, 404, 490 nm; MS (CI) 480 (M^+); MW (calcd) 479.96830. Anal. Calcd for $C_{22}H_{12}N_2O_4SSe$: C, 55.12; H, 2.52; N, 5.84. Found: C, 54.84; H, 2.43; N, 6.07.

9-(4-Phenyl-1,3-selenathiol-2-ylidene)-2,7-dinitro-4-methoxycarbonylfluorene 5b. Salt **15** (0.120 g, 0.30 mmol) was added to a hot solution of fluorene **9b** (0.094 g, 0.30 mmol) in Py (2.5 mL) and stirred for a few minutes until the reaction mixture became a thick paste. The reaction mixture was left for 0.5 h and then diluted with acetone (10 mL), and the solid was filtered off and washed with acetone (15 mL), yielding **5b** (0.15 g, 93%). The crude compound was dissolved in hot DMF (8 mL) and diluted with acetone (10 mL). Pure compound **5b** (0.145 g, 90%) crystallized on cooling the solution: mp 280−282 °C; λ_{max} (acetone) 361, 384, 410, 514 nm; MS (CI) 538 (M^+); MW (calcd) 537.97378. Anal. Calcd for $C_{24}H_{14}N_2O_6SSe$: C, 53.64; H, 2.63; N, 5.21. Found: C, 53.52; H, 2.54; N, 5.04.

9-(4-Phenyl-1,3-selenathiol-2-ylidene)-2,7-dinitro-4-cyanofluorene 5c. Salt **15** (0.20 g, 0.50 mmol) was added to a hot solution of fluorene **9c** (0.15 g, 0.53 mmol) in a mixture of DMF (5 mL) and Py (2 mL). After the mixture was cooled to room temperature, the precipitate was filtered off and washed with DMF (10 mL) and ethyl acetate (20 mL), giving **5c** (0.22 g, 86%). After recrystallization from DMF (50 mL), pure compound **5c** (0.20 g, 78%) was obtained: mp > 360 °C; λ_{max} (acetone) 358, 375sh, 418, 520 nm; HRMS 504.96299 (M^+); MW (calcd) 504.96355. Anal. Calcd for $C_{23}H_{11}N_3O_4SSe$: C, 54.77; H, 2.20; N, 8.33. Found: C, 54.60; H, 2.12; N, 8.38.

9-(4-Phenyl-1,3-selenathiol-2-ylidene)-2,4,7-trinitrofluorene 5d. Salt **15** (0.20 g, 0.50 mmol) was added to a hot solution of fluorene **9e** (0.17 g, 0.56 mmol) in a mixture of DMF (5 mL) and Py (1 mL) followed by dilution with ethyl acetate (10 mL). After the mixture was cooled to room temperature, the precipitate was filtered off and washed with ethyl acetate, yielding **5d** (0.25 g, 94%). After recrystallization from DMF (40 mL), pure compound **5d** (0.15 g, 56%) was obtained: mp 291−293 °C; λ_{max} (acetone) 360, 380sh, 422, 539 nm; HRMS 524.95499 (M^+); MW (calcd) 524.95338. Anal. Calcd for $C_{22}H_{11}N_3O_6SSe$: C, 50.39; H, 2.11; N, 8.01. Found: C, 50.31; H, 2.07; N, 8.08.

9-(4-Phenyl-1,3-selenathiol-2-ylidene)-2,4,7-trinitro-4-methoxycarbonylfluorene 5e. Salt **15** (0.20 g, 0.5 mmol) was added to a solution of fluorene **9e** (0.17 g, 0.47 mmol) in DMF (5 mL) with Py (5 drops) and stirred for 2−3 h. The deposition of a dark product soon began. The precipitate was filtered off, washed with DMF (5 mL) and thoroughly with ethyl acetate, giving **5e** (0.25 g, 88%). For purification, crude product was dissolved in hot DMF (40 mL) and diluted with 2-propanol (50 mL), giving pure fluorene **5e** (0.18 g, 63%): mp 304−305 °C; λ_{max} (acetone) 360, 385sh, 429, 564 nm; HRMS 582.95656 (M^+); MW (calcd) 582.95886. Anal. Calcd for $C_{24}H_{13}N_3O_8SSe$: C, 49.50; H, 2.25; N, 7.21. Found: C, 49.62; H, 2.32; N, 7.25.

9-(4-Phenyl-1,3-selenathiol-2-ylidene)-2,4,7-trinitro-4-cyanofluorene 5f. Salt **15** (0.10 g, 0.25 mmol) was added to a solution of fluorene **9f** (0.09 g, 0.27 mmol) in DMF (5 mL) and stirred for 2−3 h. The precipitation of a dark product soon began. The precipitate was filtered off and washed with DMF (5 mL) and thoroughly with ethyl acetate, giving **5f** (0.16 g, 79%). After recrystallization from DMF (30 mL), pure compound (0.12 g, 59%) was obtained: mp 325−326 °C; λ_{max} (acetone) 360sh, 385sh, 431, 564 nm; HRMS 549.94582 (M^+); MW (calcd) 549.94863. Anal. Calcd for $C_{23}H_{11}N_3O_4SSe$: C, 50.28; H, 1.83; N, 10.20. Found: C, 50.12; H, 1.80; N, 10.26.

9-(4-Phenyl-1,3-selenathiol-2-ylidene)-2,4,5,7-tetranitrofluorene 5g. Salt **15** (0.40 g, 1.0 mmol) was added to a solution of fluorene **9g** (0.35 g, 1.0 mmol) in DMF (10 mL) and stirred for 2−3 h. The precipitation of dark product soon began. The reaction mixture was diluted with acetone (20 mL), and the precipitate was filtered off and thoroughly washed with acetone, giving desired **5g** (0.58 g, ~100%). After recrystallization from DMF (45 mL), pure compound (0.50 g, 88%) was obtained: mp 340−342 °C; λ_{max} (acetone) 360, 385sh, 441, 585 nm; HRMS 569.93690 (M^+). MW (calcd) 569.93846. Anal. Calcd for $C_{22}H_{10}N_4O_8SSe$: C, 46.41; H, 1.77; N, 9.84. Found: C, 46.33; H, 1.78; N, 9.93.

9-(5-Phenyl-1,2-dithiol-3-ylidene)-2,7-dinitrofluorene 6a. Fluorene **9a** (0.10 g, 0.39 mmol) and Py (4.5 mL) were added to dithiolium salt **16**, prepared from thione **12** (0.1 g, 0.48 mmol), and the reaction mixture was heated to reflux. The reaction mixture was left to cool for 30 min and diluted with acetone (10 mL), and the precipitate was filtered off, washed with acetone and then with water, giving fluorene **6a** (0.07 g, 40%). Recrystallization from DMF (25 mL) yielded dark red needles (0.06 g, 34%): mp > 360 °C; MS (CI) 432 (M^+); MW (calcd) 432.02385. Anal. Calcd for $C_{22}H_{12}N_2O_4S_2$: C, 61.10; H, 2.80; N, 6.48. Found: C, 61.10; H, 3.00; N, 6.30.

9-(5-Phenyl-1,2-dithiol-3-ylidene)-2,7-dinitro-4-methoxycarbonylfluorene 6b. Fluorene **9b** (0.15 g, 0.48 mmol) and Py (5 mL) were added to dithiolium salt **16**, prepared from thione **12** (0.12 g, 0.57 mmol), and the reaction mixture was heated until full dissolution of staring salt and deposition of product. The reaction mixture was stored for 0.5 h, diluted with acetone (5 mL), and cooled to room temperature, and the precipitate was filtered off and washed with acetone and water, giving **6b** (0.11 g, 44%). Recrystallization from DMF (15 mL) yielded dark red crystals (0.10 g, 40%): mp 326 °C; MS (CI) 490 (M^+); MW (calcd) 490.02933. Anal. Calcd for $C_{24}H_{14}N_2O_6S_2$: C, 58.77; H, 2.88; N, 5.71. Found: C, 58.50; H, 2.90; N, 5.90.

9-(5-Phenyl-1,2-dithiol-3-ylidene)-2,5,7-trinitrofluorene 6d. Fluorene **9d** (1.50 g, 5.0 mmol) and DMF (20 mL) were added to dithiolium salt **16**, prepared from thione **12** (1.05 g, 5.0 mmol), and the reaction mixture was heated to 100 °C. After the mixture was cooled to room temperature during a few hours, the precipitate was filtered off and washed with DMF (10 mL) and acetone (50 mL), giving black crystals of product **6d** (1.55 g, 65%). Recrystallization from DMF (170 mL) yielded pure **6d** (1.20 g, 50%): mp 315−317 °C; HRMS 477.00945 (M^+); MW (calcd) 477.00893. Anal. Calcd for $C_{22}H_{11}N_3O_6S_2$: C, 55.34; H, 2.32; N, 8.80; S, 13.42. Found: C, 55.36; H, 2.48; N, 9.07; S, 13.34.

9-(5-Phenyl-1,2-dithiol-3-ylidene)-2,7-dinitro-4-cyanofluorene 6c. This was prepared similarly to **6d** in 70% yield: mp 347−348 °C; HRMS 457.01898 (M^+); MW (calcd) 457.01910. Anal. Calcd for $C_{23}H_{11}N_3O_4S_2$: C, 60.38; H, 2.42; N, 9.18. Found: C, 60.16; H, 2.33; N, 9.29.

9-(5-Phenyl-1,2-dithiol-3-ylidene)-2,5,7-trinitro-4-methoxycarbonylfluorene 6e. This was prepared similarly to **6d** in 69% yield: mp 348−350 °C; HRMS 535.01439 (M^+); MW (calcd) 535.01441. Anal. Calcd for $C_{24}H_{13}N_3O_8S_2$: C, 53.83; H, 2.45; N, 7.85; S, 11.97. Found: C, 53.98; H, 2.66; N, 7.85; S, 11.59.

9-(5-Phenyl-1,2-dithiol-3-ylidene)-2,5,7-trinitro-4-cyanofluorene 6f. This was prepared similarly to **6d** in 75% yield: mp 350−353 °C; HRMS 502.00338 (M^+); MW (calcd) 502.00418. Anal. Calcd for $C_{23}H_{10}N_4O_6S_2$: C, 54.98; H, 2.01; N, 11.15. Found: C, 54.86; H, 2.04; N, 11.20.

9-(5-Phenyl-1,2-dithiol-3-ylidene)-2,4,5,7-tetranitrofluorene 6g. This was prepared similarly to **6d** in 88% yield: mp > 360 °C; HRMS 521.99444 (M^+); MW (calcd) 521.99401. Anal. Calcd for $C_{22}H_{10}N_4O_8S_2$: C, 50.58; H, 1.93; N, 10.72; S 12.27. Found: C, 50.64; H, 1.91; N, 10.81; S 12.07.

9-(5-Phenyl-1,2-dithiol-3-ylidene)-2,5,7-trinitro-4-carboxyfluorene 6h. This was prepared similarly to **6d** in 88% yield. For purification, **6e** was recrystallized from a large amount of dioxane: mp > 300 °C; IR (KBr) ν/cm^{-1} 1700 (C=O), 1570 (NO_2), 1345 (NO_2), 1320, 1240, 1160, 1100, 860. Anal. Calcd for $C_{23}H_{11}N_3O_8S_2$: C, 52.97; H, 2.13; N, 8.06; S 11.74. Found: C, 53.14; H, 2.01; N, 7.98; S 11.53.

9-(5-Phenyl-1,2-dithiol-3-ylidene)-2,5,7-trinitro-4-[(3,6,9-trioxadecyl)oxycarbonyl]fluorene 6i. To a solution of thione **12** (0.30 g, 1.4 mmol) in dry dichloromethane (2.5 mL) was added methyl triflate (0.2 mL, 1.8 mmol), resulting in an exothermic reaction. The reaction mixture was stirred at 35−40 °C for 1 h, then two-thirds of the solvent was removed in vacuo and the residue was diluted with dry ether (2 mL). The precipitated dithiolium salt was filtered off, washed with ether, and dried in vacuo, giving pure 5-phenyl-3-methylthio-1,2-dithiolium triflate **16** (Y = CF_3SO_3; Scheme 1) (0.43 g, 81%).

This dithiolium salt (93 mg, 0.249 mmol) was added to a solution of fluorene **9i** (114 mg, 0.23 mmol) in DMF (1 mL), and the resulting mixture was stirred at room temperature and left for 20 h (TLC analysis showed full conversation of the starting fluorene). The reaction mixture was diluted with acetone (2 mL) and stored for 2 h at 0−5 °C. The precipitate was filtered off, washed with acetone−2-propanol mixture (1:1 v/v), and recrystallized from toluene (3 mL), yielding pure product **6i** (100 mg, 65%): mp 210 °C. Anal. Calcd for $C_{30}H_{25}N_3O_{11}S_2$: C, 53.97; H, 3.77; N, 6.29. Found: C, 54.21; H, 3.91; N, 6.23.

9-(Benzo[*d*]-1,3-dithiol-2-ylidene)-2,7-dinitro-4-R^1-5-R^2-fluorenes 7. General Procedure. 2-Methylthio-1,3-benzodithiolium triflate **17** (164 mg, 0.47 mmol) was added to a solution of the corresponding fluorene **9** (0.40 mmol) in DMF (3 mL), and the reaction mixture was stored for several hours at 20−70 °C with monitoring of the reaction by TLC (by conversion of the starting fluorene). The reaction conditions were as follows: **7b**, 70 °C, 25 h; **7d**, 60 °C, 17 h; **7e**, 25 °C, 25 h; **7f**, 25 °C, 20 h; **7g**, 20 °C, 2 h. After the reaction was complete, the precipitate was filtered off and washed with DMF and then with acetone. The crude product was then recrystallized from DMF (yields after recrystallization are given in parentheses).

7b: 27% (25%); mp ≈ 330 °C; MS (CI) 464 (M^+); MW (calcd) 464.01368. Anal. Calcd for $C_{22}H_{12}N_2O_6S_2$: C, 56.89; H, 2.60; N, 6.03. Found: C, 56.76; H, 2.56; N, 6.10.

7d: 70% (58%); mp >360 °C; MS (CI) 451 (M^+); MW (calcd) 450.99328. Anal. Calcd for $C_{20}H_9N_3O_6S_2$: C, 53.21; H, 2.01; N, 9.31. Found: C, 53.25; H, 2.07; N, 9.30.

7e: 84% (77%); mp >360 °C; MS (CI) 527 ($M^+ + 18$), 509 (M^+); MW (calcd) 508.99876. Anal. Calcd for $C_{22}H_{11}N_3O_8S_2$: C, 51.87; H, 2.18; N, 8.25. Found: C, 51.81; H, 2.25; N, 8.29.

7f: ∼100% (89%); mp >360 °C; MS (CI) 494 ($M^+ + 18$), 476 (M^+); MW (calcd) 475.98853. Anal. Calcd for $C_{21}H_8N_4O_6S_2$: C, 52.94; H, 1.69; N, 11.76. Found: C, 53.12; H, 1.77; N, 11.70.

7g: 87% (83%); mp >360 °C; λ_{max} (DMF) 369, 426, 569 nm; MS (CI) 514 ($M^+ + 18$), 496 (M^+); MW (calcd) 495.97836. Anal. Calcd for $C_{20}H_8N_4O_8S_2$: C, 48.39; H, 1.62; N, 11.29. Found: C, 48.52; H, 1.65; N, 11.40.

Reversible Formation of Salts 18−21. The 9-chalcogenathiolylidenefluorene derivatives **4**−**7** (5−20 mg) were stirred in concentrated sulfuric acid (1−5 mL) at room temperature until complete dissolution and decoloration was observed (from 10 to 20 min to 2−4 h). The resulting solutions of salts **18**−**21** in H_2SO_4 are colorless or pale yellow and stable at ambient temperature for some days (partial hydrolysis of CN and CO_2Me groups was observed for compounds **b**,**c**,**e**,**f**). When water was added dropwise to these solutions, the initial color of **4**−**7** reappeared (from red to dark blue depending on substituents R^1 and R^2) followed by essentially quantitative precipitation of compounds **4**−**7**.

18g: δ_H [500 MHz, 98% D_2SO_4 (99.5 at. %)] 10.9s (H_2SO_4), 9.75s (1H), 9.29d (2H, $J = 2.0$ Hz), 9.07d (2H, $J = 2.0$ Hz), 7.80d (2H, $J = 7.0$ Hz), 7.75t (1H, $J = 6.5$ Hz), 7.69dd (2H, $J = 7.0, 6.5$ Hz).

19g: δ_H [500 MHz, 98% D_2SO_4 (99.5 at. %)] 10.9s (H_2SO_4), 9.28d (2H, $J = 2.0$ Hz), 9.04s (2H), 8.64s (1H), 8.05d (2H, $J = 8.0$ Hz), 7.96t (1H, $J = 7.5$ Hz), 7.80dd (2H, $J = 8.0, 7.5$ Hz).

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