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Electron Acceptors of the Fluorene Series. 10.[1] Novel Acceptors Containing Butylsulfanyl, Butylsulfinyl, and Butylsulfonyl Substituents: Synthesis, Cyclic Voltammetry, Charge-Transfer Complexation with Anthracene in Solution, and X-ray Crystal Structures of Two Tetrathiafulvalene Complexes

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2,4,5,7-Tetranitro-9-fluorenone (**1b**) reacts readily with *n*-butanethiol in dipolar aprotic solvents with selective substitution of nitro groups by butylsulfanyl groups in positions 2 and 7 (**2**, **3**); the 2,5-isomer **4** was formed only as a minor product (<1%). Condensation of fluorenones **2**−**4** with malononitrile yielded 9-dicyanomethylene derivatives **5**−**7**, which showed strong intramolecular charge transfer ($\lambda \approx 510-560$ nm) and were found to sensitize the photoconductivity of carbazole-containing polymer films. Oxidation of sulfides **2**−**4** gave sulfoxide **8** or sulfones **9**−**11**, which then were converted into their corresponding dicyanomethylene derivatives **12**−**15**. All these novel acceptors showed three reversible single-electron reduction waves (cyclic voltammetry) yielding radical anion, dianion, and radical trianion; moreover, acceptors **13**−**15** showed also a fourth reduction wave, representing reversible tetraanion formation. Substitution of the oxygen of the carbonyl group in the fluorenones by a dicyanomethylene group increased the thermodynamic stability (K_{SEM} growth) of the radical anion; K_{SEM} ranged from 3×10^5 to 3×10^9 M^{-1}. CV measurements characterize compounds **3**, **4** (EA = 1.86−1.89 eV) as poor acceptors, **2**, **6**−**11** (EA = 2.13−2.31 eV) as moderate acceptors, and **5**, **12**−**15** (EA = 2.53−2.66 eV) as strong electron acceptors. Charge-transfer complex (CTC) formation between acceptors **9**, **10**, **13**, **14**, and anthracene as a donor was monitored by the appearance of additional low-energy bands in the visible region (CTC bands) of their electron absorption spectra. Increasing the EA of the acceptors from 9-fluorenones to the corresponding 9-dicyanomethylenefluorenes increases the complexation constants K_{CTC} by 2.5−3 times, while sulfonyl substituents present substantial steric hindrance for complexation (as compared to the nitro group), decreasing K_{CTC} values. Two CTCs for acceptors **14** and **17** with tetrathiafulvalene (TTF) were obtained, and their structures were solved by single-crystal X-ray diffractometry, giving the stoichometries **14**:TTF, 2:3, and **17**:TTF:PhCl, 1:1:0.5. In the former complex the packing motif is a mixed ...DDAD′A... stack; in the latter complex the D and A moieties form unusually close CT pairs, which pack in a herringbone motif.

Introduction

Electron acceptors of the fluorene series are of considerable interest in the study of charge-transfer complexes (CTC) with semiconducting and photoconducting properties and as electron transport materials.[2,3] An extended π-system structurally similar to that in carbazole determines the fact that among different classes of electron acceptors fluorene derivatives are the most effective photoconductivity sensitizers for poly-*N*-vinylcarbazole (PVK), poly-*N*-(2,3-epoxypropyl)carbazole (PEPC), and related carbazole-containing polymers.[4,5] Recently, other applications of this class of electron acceptors in advanced materials have been demonstrated: (i) polynitro-9-dicyanomethylenefluorenes were found to form 1:2 CTCs with bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) with metallic-type electrical conductivity;[6] (ii) the polynitro-

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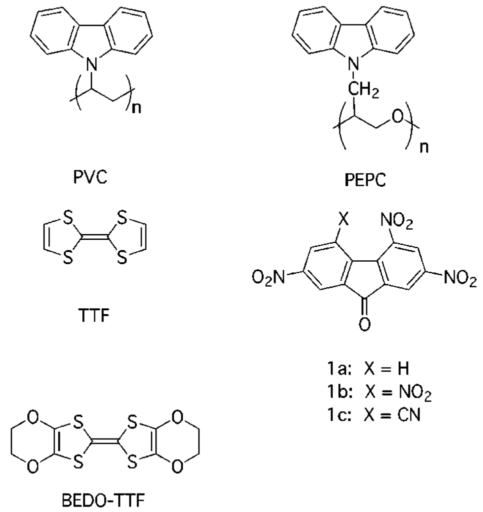
fluoren-9-ylidene fragment was used as a terminal acceptor unit in push−pull D−π−A chromophores with high second-order nonlinear optical (NLO) susceptibility[7] and as a side group in an electroactive polythiophene system.[8] Our recent X-ray crystallographic investigations of CTC of fluorene acceptors with TTF donors have demonstrated the possibility of various stoichometries (D:A = 1:1 and 2:1), different motifs of crystal packing within the stacks (DADA, DDADDA), and supramolecular architectures for the CTC depending on the structures of the components, offering an approach to crystal engineering and the design of CTC with predictable electronic properties.[9−12] These studies are motivating increased interest in fluorene acceptors within the field of materials chemistry.

Nitro derivatives of 9-fluorenone and 9-dicyanomethylenefluorene are the best known in this series of electron acceptors. Among other electron-withdrawing substituents on the benzene rings, derivatives containing CO_2H, CO_2R, $CONH_2$, CONHR, $CONR_2$, CN, Cl, Br, and I have been synthesized.[2,13−15]

Recently, proceeding from the readily accessible fluorene-2,7-disulfonyl chloride, we synthesized a series of derivatives containing sulfonyl groups, i.e., 4,5-dinitro-9-X-fluorene-2,7-disulfonic acids derivatives, and demonstrated their ability to form CTC and to sensitize PEPC photoconductivity.[16] In the framework of our interest in nucleophilic substitution reactions in fluorene acceptors[17] we have now synthesized new polynitro fluorene derivatives with substituents BuS, BuSO, and $BuSO_2$ and studied their electrochemical behavior, *intra*molecular charge transfer (ICT) for derivatives with donor butylsulfanyl substituents, and the formation of *inter*molecular charge-transfer complexes (CTC) with anthracene in solution and with tetrathiafulvalene (TTF) in the solid state. We have also evaluated two derivatives as sensitizers of photoconductivity in hole transport materials.

Chart 1



Results and Discussion

Synthesis. Polynitro-9-fluorenones are known to react with various proton-containing nucleophiles with substitution of the nitro group by a nucleophile.[18−20] Thus, 2,4,5,7-tetranitro-9-fluorenone (**1b**) reacts with secondary aliphatic amines with the selective substitution of the nitro group at position 2 by the amino group.[17,18] Reaction of **1b** with water in hexamethylphosphoric triamide (HMPA) yields a mixture of products from substitution of the nitro groups by OH at positions 2 and 4, the ratio of which depends on the reaction conditions.[19] Nitro group substitution by the hydroxy group in 2,4,7-trinitro-9-fluorenone (**1a**)[19] and 2,5,7-trinitro-4-cyano-9-fluorenone (**1c**)[20] occurs selectively at position 4 under the action of water in HMPA. On the other hand, Ong showed[21] that polynitro-9-fluorenones react with 1-butanethiol in the presence of equimolar quantities of $AlCl_3$ to yield the corresponding polynitrofluorene-9-thioacetals. We now report that in bipolar aprotic solvents, i.e. dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and HMPA, the reaction occurs by another route, namely, with the substitution of nitro groups similarly to other nucleophiles considered above. Depending on the reaction conditions, substitution of one or two nitro groups by butylsulfanyl groups was observed. The reaction proceeded selectively in positions 2 and 7 of the fluorene nucleus, and 4(5)-isomers were formed only in trace amounts (Scheme 1). Thus, when the reaction was carried out in HMPA, in addition to the 2,7-isomer **3** as the major product, the 2,5-isomer **4** was isolated as a minor product in ca. 1% yield.

Acceptors **2**−**4** are orange crystalline compounds, their color being due to intramolecular charge transfer (ICT)

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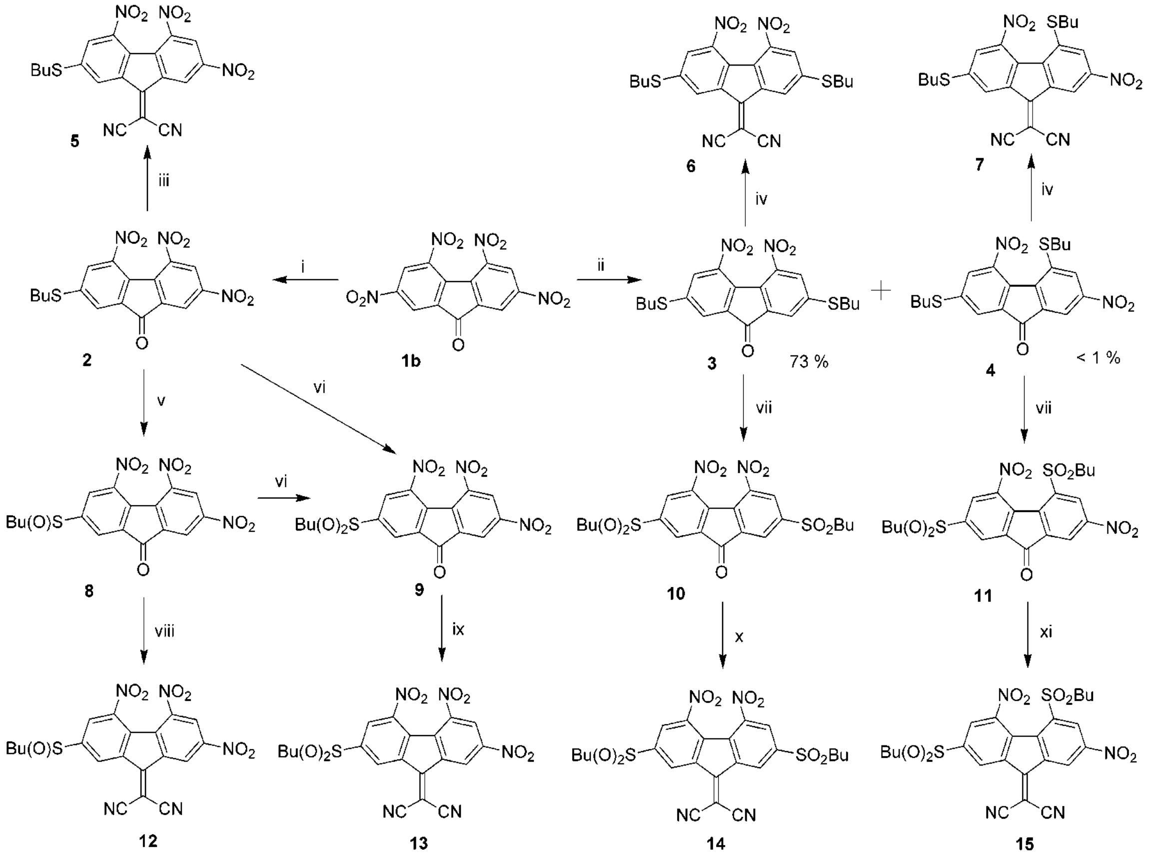
Scheme 1[a]



[a] (i) 4.4 equiv BuSH, HMPA, rt, 2 days; or 2.8 equiv BuSH, DMSO, 80 °C, 30−60 min; (ii) 4.4 equiv BuSH, DMSO, 80 °C, 1 h; or 3.4 equiv BuSH, HMPA, rt, 4 days; (iii) $CH_2(CN)_2$, DMF, rt, 2 h; (iv) $CH_2(CN)_2$, DMF, 60-65 °C, 2 h; (v) 27% H_2O_2, AcOH, 65 °C, 2.5 h; (vi) 27% H_2O_2, AcOH, 60−65 °C, 24 h; (vii) 27% H_2O_2, AcOH, 100−108 °C, 6 h; (viii) $CH_2(CN)_2$, DMF, rt, 4 h; (ix) $CH_2(CN)_2$, DMF, rt, 1 h; (x) $CH_2(CN)_2$, DMF, 40-45 °C, 4 h; (xi) $CH_2(CN)_2$, DMF, 50 °C, 25 h.

from the donor sulfur atom to the acceptor fluorene moiety. Still more intensive ICT (dark-violet color) is observed in their 9-dicyanomethylene derivatives **5**−**7** obtained by condensation of fluorenones **2**−**4** with malononitrile in DMF. Oxidation of the sulfides **2**−**4** with 27% aqueous hydrogen peroxide in acetic acid gave the corresponding sulfoxide (**8**) and sulfones (**9**−**11**). Their condensation with malononitrile in DMF yielded 9-dicyanomethylenefluorenes **12**−**15**, respectively (Scheme 1).

^{1}H NMR Spectra. Chemical shifts and coupling constants in the ^{1}H NMR spectra confirm their structures. The aromatic proton signals were assigned in the light of previous chemical shift data.[1,9,16,17,22] The C_4H_9S and $C_4H_9SO_2$ fragments in compounds **2**−**7** and **9**−**11**, **13**−**15** result in a group of signals typical for the butyl substituent. In the case of sulfoxides **8** and **12** the asymmetrical sulfur atom leads to two sets of signals (corresponding to two isomers) from the methylene group directly linked to the sulfur atom with chemical shifts of δ 3.25 and 3.04 ppm.

For the strong acceptors **12**−**15** paramagnetic broadening of the aromatic proton signals was observed and their interaction with the polar solvent (and/or with trace amounts of donor compounds) can result in radical ion species in the solution. Such behavior of strong electron acceptors of the fluorene series was previously observed, and it was shown that the addition of a small amount of an acid resulted in reduction of the fine structure of the spectrum without changing the chemical shifts of the protons.[9,16] The considerably greater broadening of C(3)−H and C(6)−H signals, as compared to C(1)−H and C(8)−H, indicates significant localization of the spin density on the C-3 and C-6 atoms in the radical anion rather then on the C-1 and C-8 atoms.

Electrochemistry. The electrochemical behavior of these novel electron acceptor compounds was studied by cyclic voltammetry (CV) in acetonitrile at room temperature, using tetraethylammonium tetrafluoroborate as the supporting electrolyte. The redox potentials are summarized in Table 1.

The cyclic voltammograms of the compounds **2**−**15** exhibit three or four reversible (the last reduction waves were electrochemically reversible or quasi-reversible) single-electron reduction waves. It should be noted that the reversible two-step, single-electron, reduction to yield sequentially the radical anion and dianion is characteristic of 9-X-fluorene nitro derivatives.[1,9,14a,17,22,23] In our earlier investigation[14a] by CV at a graphite electrode only two first stages of the single-electron reduction were found to be reversible for compounds **1**, **16**, and related acceptors; further reduction processes were highly irreversible and involved three or four electrons. In some cases a third reduction wave resulting in radical trianion formation is also observed that is reversible, quasi-reversible, or irreversible.[1,9,17,22] However, when the potential is further increased, reduction of the nitro groups and subsequent reactions are observed; that is,

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Table 1. CV Data for Compounds 1−16[a]

compd	$E_1^{1/2}$ (V)	$E_2^{1/2}$ (V)	$E_3^{1/2}$ (V)	$E_4^{1/2}$ (V)	$\Delta E_{1-2}^{1/2}$ (V)	K_{SEM}[b] (M^{-1})	EA (eV)
1b[c]	−0.12	−0.41	−1.47		0.29	8.2×10^5	2.42
2	−0.41	−0.70	−1.44		0.29	8.2×10^5	2.13
3	−0.68	−0.96	−1.61		0.28	5.6×10^5	1.86
4	−0.65	−0.92	−1.60		0.27	3.8×10^5	1.89
5	−0.01	−0.57	−1.28		0.56	3.1×10^9	2.53
6	−0.23	−0.77	−1.35		0.54	1.4×10^9	2.31
7	−0.22	−0.75	−1.41		0.53	9.6×10^8	2.32
8	−0.32	−0.64	−1.42		0.32	2.7×10^5	2.22
9	−0.24	−0.57	−1.08		0.33	3.9×10^5	2.30
10	−0.30	−0.70	−1.25		0.40	6.0×10^6	2.24
11	−0.32	−0.71	−1.26		0.39	4.1×10^6	2.22
12	+0.07	−0.53	−1.25		0.56	3.1×10^9	2.61
13	+0.12	−0.43	−1.09	−1.49	0.55	2.1×10^9	2.66
14	+0.05	−0.47	−1.07	−1.39	0.52	6.5×10^8	2.59
15	+0.04	−0.47	−1.05	−1.41	0.51	4.4×10^8	2.58
16a[c]	+0.02	−0.57	−1.37		0.59	1.0×10^{10}	2.56
16b[c]	+0.23	−0.31	−1.13		0.54	1.4×10^9	2.77

[a] Solvent acetonitrile, electrolyte 0.1 M $\mathrm{Et_4N^+BF_4^-}$, scan rate 100 mV $\mathrm{s^{-1}}$; all potentials are given vs Ag/AgCl. [b] An error appeared in refs 28a,c: the sign "minus" was omitted when the disproportionation constants for the radical anion were calculated ($K_{\mathrm{dispr}} = 1/K_{\mathrm{SEM}}$); this resulted in wrong values of K_{dispr} tabulated in the papers which, in fact, are K_{SEM}. [c] From ref 9.

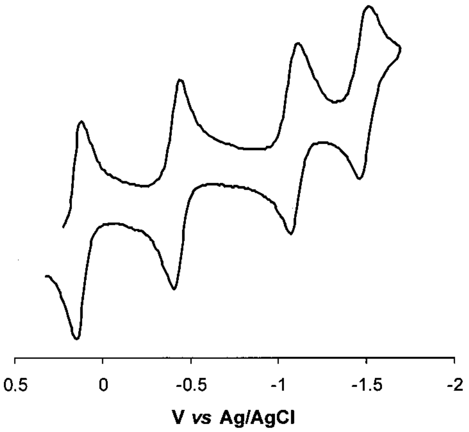

Figure 1. Cyclic voltammogram of compound **13** (under the conditions stated in Table 1).

the system becomes electrochemically irreversible. It is of interest, therefore, that fluorene derivatives **2**−**15** are capable of yielding not only radical anions and dianions but also fairly stable, reversibly formed radical trianions, and for compounds **13**−**15** even tetraanion formation is observed (Table 1, Figure 1).

9-Fluorenones with butylsulfanyl substituents (**2**−**4**) are relatively weak acceptors with reduction potentials $E_1^{1/2}$ ranging from −0.41 to −0.68 V vs Ag/AgCl. Oxidation of the sulfanyl group into the sulfinyl and sulfonyl analogues decreases the reduction potential by 0.09 and 0.17−0.19 V, respectively. Substitution of oxygen in the carbonyl group in 9-fluorenones (**2**−**4**, **8**−**11**) by the dicyanomethylene group (**5**−**7**, **12**−**15**) significantly increases the acceptor properties of the molecules, which result in an anodic shift in their reduction potentials by 0.35−0.45 V. Comparison of the reduction potentials for compounds **3**,**4** and **6**,**7** shows that the location of the BuS substituent on the fluorene nucleus (positions 2 or 4) does not exert a notable effect upon the electrochemical behavior of these compounds. This is in agreement with the approximate equivalence of positions 2 and 4 in fluorene derivatives in terms of their electronic effect upon the properties of the molecule, based upon UV and NMR studies of other derivatives.[17]

Compounds **13** and **14** are rather strong electron acceptors whose reduction to the radical anion is observed at positive potential values vs Ag/AgCl. They are only slightly weaker (i.e., by 0.09 to 0.16 V) than the strongest known electron acceptor of the fluorene series, i.e., 2,4,5,7-tetranitro-9-dicyanomethylenefluorene (**16b**). Electron affinities (EAs) of the acceptors **2**−**15** were estimated (Table 1) by eq 1[9,14a] using known acceptors **16a**,**b** as reference acceptors:

$$\mathrm{EA(ref)} - \mathrm{EA} = E_1^{1/2}(\mathrm{ref}) - E_1^{1/2} \tag{1}$$

As seen from Table 1, compounds **2**, **6**−**11** can be characterized as moderate acceptors (EA ≈ 2.1−2.3 eV), and the 9-dicyanomethylene derivatives **5**, **12**−**15** are rather strong acceptors (EA > 2.5 eV), comparable to strong fluorene acceptors **16a**,**b**.

The thermodynamic stability of the radical anions was determined from the difference in potentials of the corresponding radical anion and dianion using the equation $\Delta E = E_1^{1/2} - E_2^{1/2} = 0.059 \log K_{\mathrm{SEM}}$[24] (Table 1), where K_{SEM} is the equilibrium constant in eq 2:

$$\mathrm{A} + \mathrm{A}^{2-} \xrightleftharpoons{K_{\mathrm{SEM}}} 2\mathrm{A}^{\bullet-} \tag{2}$$

For electron acceptor compounds of the *p*-benzoquinone series, and substituted and π-extended analogues, the degree of charge delocalization in the radical anions increases in the following order: quinones < dicyanoquinodiimines < tetracyanoquinodimethanes, and the thermodynamic stability of the radical anions diminishes (due to a decrease in intramolecular Coulombic repulsion) in the same order.[25] This results in a decrease in the difference in the reduction potentials $E_1^{1/2}$ and $E_2^{1/2}$ and, hence, to a decrease in the equilibrium constant K_{SEM} in the range of the substituents C=O > C=N−CN > $\mathrm{C{=}C(CN)_2}$.[26−28] The characteristic feature of the least stable radical anion is represented by the observation

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that the first and second reduction waves coalesce into a single two-electron reduction wave.[25,28,29]

In the acceptors of the fluorene series the opposite tendency is observed; that is, in the transition from substituted 9-fluorenones to the corresponding 9-dicyanomethylenefluorenes the difference in the potentials for the first and second reduction waves increases and K_{SEM} grows from 4×10^5 to 6×10^6 for compounds **2**−**4**, **8**−**11** up to 4×10^8 to 3×10^9 for **5**−**7**, **12**−**15**, i.e., by 3 orders of magnitude (Table 1). Thus, in the fluorene acceptors, substitution of oxygen of the carbonyl group by a dicyanomethylene group does not decrease (as in benzoquinones and TCNQ derivatives) but, instead, increases the thermodynamic stability of the radical anion.

Intramolecular Charge Transfer (ICT). Intramolecular donor−acceptor interaction in compounds **2**−**4** was manifested in their electron absorption spectra: in the short-wave visible region additional bands corresponding to ICT from the donor sulfur atom onto the acceptor fluorene unit appeared {the ICT nature of the transition was corroborated by studies of concentration dependencies of its intensity, which showed good linearity $A = f([C])$}. Increasing the acceptor ability of the fluorene moiety by substitution of the carbonyl oxygen atom by the dicyanomethylene group (by 0.35−0.40 eV, according to CV data; Table 1) leads to an enhancement of ICT, which is manifested in a significant bathochromic shift of the ICT bands (from ~420−430 nm for **2**, **3** to ~510−560 nm for **5**−**7**; see Experimental Section).

Intermolecular CTC in Solution. The ability of the sulfonyl-containing acceptors **9**, **10**, **13**, and **14** to form intermolecular CTC with donors was studied in 1,2-dichloroethane (DCE) solution using anthracene as the π-donor. CTC formation is accompanied by the appearance of two additional bands in the visible region (CT bands), which are absent in the initial components (Figure 2). Isomolar series experiments gave A:D = 1:1 stoichometries for all CTC:

$$A + D \xrightleftharpoons{K_{CTC}} [A^{\delta -},D^{\delta +}] \qquad (3)$$

Complexation constants, K_{CTC}, and molar extinction coefficients, ϵ_{CTC}, are summarized in Table 2, together with literature data for related acceptors. The sulfonyl substituent is more bulky than the NO_2 group, which leads to some hindrance for CTC formation and, hence, a decrease in K_{CTC} and ϵ_{CTC} values (cf. **9** → **10**, **13** → **14** and also data for **17** and **18**; Table 2).

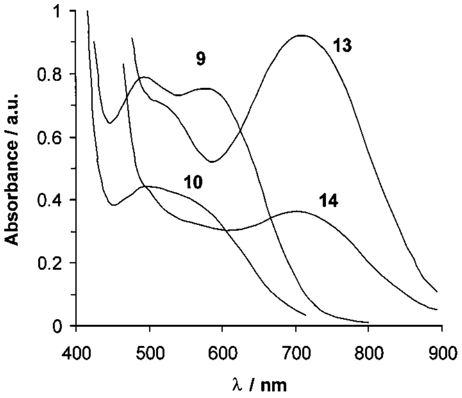

Figure 2. Electronic absorption spectra for CTC of acceptors **9**, **10**, **13**, and **14** with anthracene in 1,2-dichloroethane, 25 °C.

The electron affinities of acceptors **9**, **10**, **13**, and **14** were also estimated from the energies of their CTC by eq 4:

$$\mathrm{EA} - \mathrm{EA(ref)} = h\nu_{\mathrm{CTC}}(\mathrm{ref}) - h\nu_{\mathrm{CTC}} \qquad (4)$$

where $h\nu_{CTC}$(ref) and $h\nu_{CTC}$ denote charge-transfer energies in CTC of the reference acceptor and the acceptor under analysis in the same conditions. EA_{CTC} values (Table 2) for fluorene derivatives **9** and **10** are in good agreement with EA_{CV} values (Table 1), whereas for the dicyanomethylene derivatives **13** and **14** the CTC method gives somewhat higher electron affinities (by 0.08−0.12 eV) than CV. This can be explained by an accuracy in the estimation of the maximum of the longest-wavelength CT absorption, which can represent two or more overlapping CT bands.

X-ray Crystal Structures of CTCs 14:TTF, 2:3 Stoichiometry (I) and 17:TTF:PhCl, 1:1:0.5 Stoichiometry (II). The asymmetric unit of crystal **I** comprises one acceptor molecule **14** (A) and one complete TTF molecule (D) in general positions and a half of another TTF molecule (D′) located at a crystallographic inversion center (Figure 3). Thus the donor:acceptor ratio of 3:2 is the first example of this stoichiometry in TTF-fluorene complexes. Molecule D′ is rigorosly planar, whereas D is slightly puckered (±0.07 Å); their mean planes form a dihedral angle of 7° between them and are inclined, respectively, by 4° and 5° to the fluorene mean plane. The long axes of the D and D′ molecules are nearly perpendicular (88°) to each other. The packing motif is a mixed stack with ...DDAD′A... succession (Figure 4) with interplanar separations D−D ca. 3.6 Å, D−A 3.3 Å, and A−D′ 3.5 Å.

The acceptor molecule shows extensive disorder. Each nitro group is disordered over two positions, tilted out of the fluorene plane in opposite directions. The nitrogen atom [N(4) or N(5)] and one oxygen atom [O(42) or O(52)] of each nitro group are disordered, while the other oxygen atom [O(41) or O(51)] remains in the same position. In each single molecule the nitro groups can only be tilted in opposite directions from the fluorene plane, as the *cis*-disposition would cause improbably short O···O contacts. The observed planarity of the fluorene system is probably spurious, masking the overlap of two opposite-sense puckerings. Both *n*-butyl chains are also disordered.

The asymmetric unit of **II** (Figure 5) comprises one acceptor (**17**)[16] and one donor (TTF) molecule in general

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Table 2. CTC Formation between Acceptors 9, 10, 13, 14, 17, 18, and Anthracene in Dichloroethane, 25 °C

		variation range of concentrations							
compd	$\lambda_{max}{}^{CT}$ (nm)	$C_A \times 10^3$ (M)	$C_D \times 10^2$ (M)	K_{CTC} (M^{-1})	ϵ_{CTC} (M^{-1} cm^{-1})	n[a]	R_0[a]	R_f[a]	EA (eV)
9	581,[b] 495	5.75−46.0	0.25−4.03	4.98 ± 0.34	709 ± 42	23	0.9996	1.04	2.34
10	550sh,[b] 502	0.98−5.38	1.00−5.52	1.94 ± 0.22	544 ± 58	32	0.9995	1.26	2.22
13	716,[b] 515sh	0.61−4.91	0.25−4.00	14.05 ± 0.63	1127 ± 38	26	0.9996	1.74	2.74
14	705,[b] 500sh	0.28−3.64	0.84−5.52	5.22 ± 0.34	926 ± 53	22	0.9992	0.47	2.71
16a[c]	648								2.56
17[c]	725	1.26−7.57	0.32−5.07	8.17 ± 0.43	989 ± 42	33	0.9994	1.90	
18[c]	685	1.98−3.95	1.28−5.12	3.60 ± 0.71	878 ± 150	15	0.9992	2.05	

[a] n is a number of measurements: R_0 is multiple correlation coefficient; R_f is the misalignment factor between an experimental datum and a fit, $R_f = [\Sigma(A_{CTC(i)}{}^{exp} - A_{CTC(i)}{}^{calc})^2/\Sigma A_{CTC(i)}{}^{exp}] \times 100\%$, where $A_{CTC(i)}{}^{exp}$ and $A_{CTC(i)}{}^{calc}$ are experimental and calculated values of a CTC absorbance for ith point, respectively. [b] These λ_{max} were used for measurements A_{CTC} to estimate K_{CTC} and ϵ_{CTC} values (see Experimental Section). [c] From ref 16.

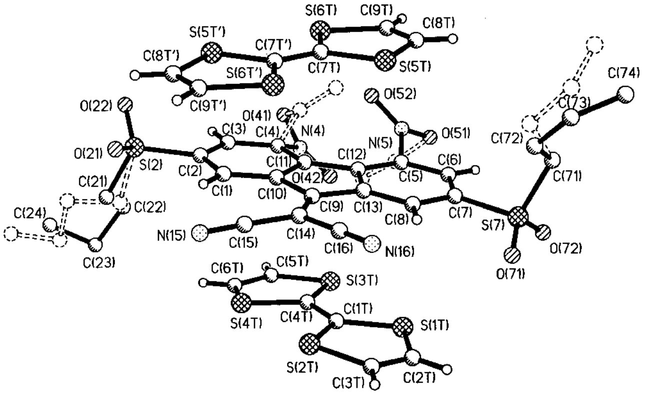

Figure 3. Molecules in structure **I** (showing the disorder). Primed atoms are related via the inversion center; butyl hydrogens are omitted for clarity.

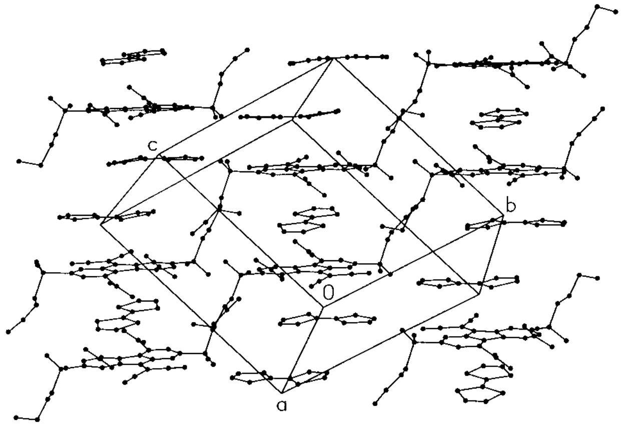

Figure 4. Crystal packing of **I** (disorder is not shown).

positions and a half of a chlorobenzene molecule, which is situated about an inversion center and disordered over two positions, related via this center. Molecule **17** is distorted in the usual way:[9,17,30] the nitro groups in positions 4 and 5 are tilted to opposite sides of the fluorene plane to avoid short O···O contacts, and the fluorene moiety itself is bent to follow the tilt. Both rings of the TTF molecule are planar, with a 6° twist around the central C(1T)=C(4T) bond. The donor and acceptor molecules lie approximately parallel, with extremely short contacts S(1T)···C(14) 3.18 Å, S(1T)···C(16) 3.26 Å, S(2T)···C(8) 3.20 Å, and S(3T)···C(1) 3.32 Å, cf. the normal van der Waals S···C contact distance[31] of 3.61 Å.

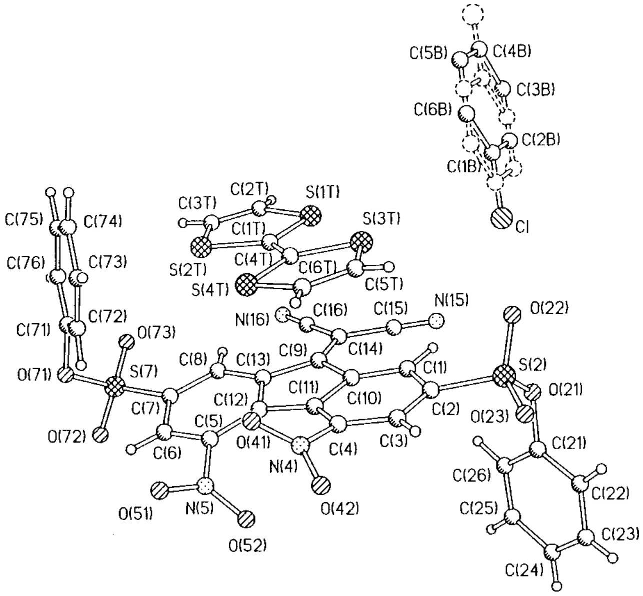

Figure 5. Molecular structure of **II** showing disorder of the chlorobenzene molecule (H atoms omitted).

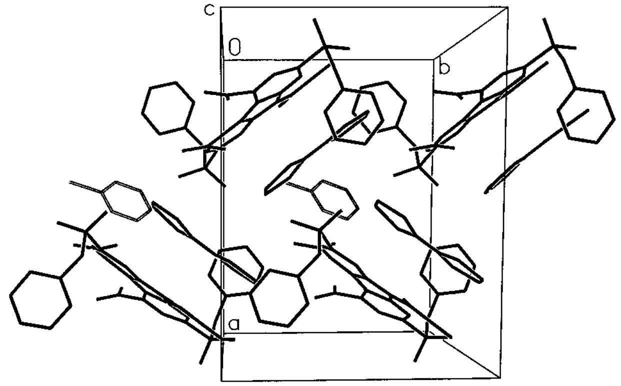

Figure 6. Crystal packing of **II**.

These CT pairs are packed in a herringbone motif (Figure 6), forming a layer parallel to the (0 0 1) plane. Chlorobenzene molecules and phenyl groups of **17** are approximately perpendicular to the donor/acceptor moieties and parallel to the layers that they separate from each other.

Certain bond distances in the **14** and **17** moieties of **I** and **II** (Table 3) differ appreciably from neutral molecules with a similar core.[30,32] Thus the C(9)=C(14) bond [1.374(4) Å in **I**, 1.379(4) in **II**] is longer than in **16b**,[30] **16b**·PhCl,[32] and **18′**(R = NH_2)[32] [1.354(15), 1.357(2), and

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Table 3. Selected Bond Distances (Å) and Torsion Angles around C(9)═C(14) Bond (τ, deg)

	I	II
C(9)−C(10)	1.461(4)	1.467(4)
C(9)−C(13)	1.459(5)	1.448(4)
C(9)−C(14)	1.374(4)	1.379(4)
C(14)−CN, av	1.426(5)	1.426(4)
τ	5.3	2.9

1.355(7) Å, respectively]. The C(9)−C(10) bond and C(9)−C(13) bonds are shorter, averaging 1.460(5) Å in **I** and 1.458(4) in **II**, vs 1.470(9), 1.480(2), and 1.474(7) Å in the neutral species **16a**, **16b**, and **18′**, respectively. The C(14)−CN bonds [mean 1.426(5) Å in both **I** and **II**] are also shorter than in the neutral species [1.436(9), 1.444(2), and 1.440(7) Å]. These differences can be attributed to an accumulation of negative charge on the acceptors in **I** and **II**. To envisage this, one can refer to metal π-complexes with the η^5-fluorenyl ligand,[33] wherein all C−C bonds of the five-membered ring are of similar length (1.43−1.44 Å). On the other hand, in **II** the central C(1T)═C(4T) bond of the TTF molecule [1.361(4) Å] is longer than in the crystal of pure TTF [1.349(3) Å][34] and the adjacent C−S bonds are shorter [mean 1.740(3) vs 1.757(2) Å], indicating[35] a positive charge of 0.4−0.5*e*. Thus a considerable CT interaction takes place in **II** and probably in **I**, although intense thermal libration (or disorder) of the TTF molecules in **I** precluded determining their bond lengths with sufficient precision.

Sensitization of PEPC Photoconductivity by Electron Acceptors 5 and 6. 2,7-Bis(butylsulfonyl)-9-dicyanomethylenefluorene has previously been used as a sensitizer in electrophotographic materials,[36] and recently, we showed that derivatives of 4,5-dinitro-9-X-fluorene-2,7-disulfonic acid can sensitize the PEPC photoconductivity and be used in photothermoplastic storage media (PTSM).[16] However, in both these cases the sulfur substituents in the acceptors were in the form of electron-withdrawing SO_2 groups.

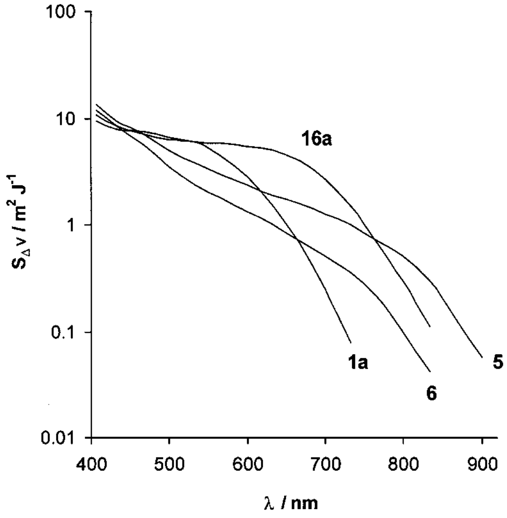
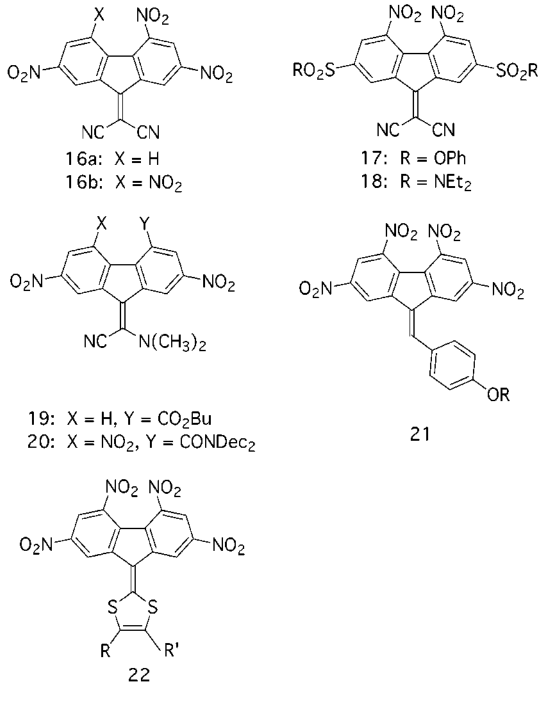


Figure 7. Spectral response of electrophotographic sensitivity ($S_{\Delta V}$, m^2 J^{-1}) for PEPC films sensitized by 2 mol % of acceptors **5**, **6**, **1a**, and **16a**.

Chart 2



We have now studied analogues containing electron-donating butylsulfanyl substituents, i.e., **5** and **6**, as sensitizers of photoconductivity in PTSM. Figure 7 demonstrates the spectral response of electrophotographic sensitivity (S_Δ, m^2 J^{-1}) of PTSM based on PEPC films sensitized by acceptors **5** and **6**, as well as by the known fluorene acceptors **1a** and **16a**, widely used as sensitizers of the photoconductivity of carbazole-containing polymers.[4,5a] In the short-wavelength visible region, both **5** and **6** show a lower level of electrophotosensitivity than sensitizer **1a** (the latter was the first fluorene acceptor introduced by IBM in its Copier 1 series in 1970[4]), although their electron affinities are higher than for **1a** (EA = 2.2 eV). However, the spectral responses for **5** and **6** have no such sharp decrease of S_Δ with increasing λ; thus in the long-wavelength region (>600 nm for **5** and >650 nm for **6**), these new acceptors show higher S_Δ values than **1a**, and in the near-infrared region (>750 nm) acceptor **5** shows even higher S_Δ values than an effective sensitizer **16a**. Despite ICT observed in these novel acceptors (see above) the spectral response of S_Δ does not show an increase of the photosensitivity in the ICT region of the acceptors, as was observed for other fluorene ICT acceptors (**19**, **20**,[5c,17a] **21**,[37] and **22**[38,39]). This can be explained by the low intensity of the ICT bands in acceptors **5** and **6** (ϵ_{ICT} 2600 and 1500 M^{-1} cm^{-1}, respectively), whereas acceptors **19**−**22** showed $\epsilon_{ICT} \approx$

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9000−10000 M^{-1} cm^{-1} or more. Nevertheless, acceptors **5** and **6** showed good rheological properties in PTSM films: the maximal diffraction efficiency, η_{max}, for planar light wave holograms was 16% and 18% for **5** and **6**, respectively, which allowed the attainment of real holographic sensitivity of PTSM by a visualized image $S_\eta \approx$ 60−90 m^2 J^{-1} (He−Ne laser, $\lambda = 632.9$ nm). This level of photosensitivity S_η makes these derivatives suitable for using in practice as sensitizers in PTSM for hologram recording.

Conclusions

New fluorene acceptors (**2**−**15**) containing BuS, BuSO, and $BuSO_2$ substituents have been synthesized. Nucleophilic substitution of the nitro groups in 2,4,5,7-tetranitro-9-fluorenone (**1b**) by butylsulfanyl groups proceeds selectively, giving 2- and 2,7-substitution (with the 2,5-isomer as a minor product, <1%). ICT observed in **3** and **4**, and more pronounced in **5**−**7**, is manifested in the appearance of the corresponding ICT bands in the visible region of the electronic absorption spectra. Cyclic voltammetry showed three or four reversible single-electron reduction waves for acceptors **2**−**15** (compounds **13**−**15** gave electrochemically stable tetraanions). The new acceptors readily formed charge-transfer complexes with electron donors, as demonstrated by the complexation of **9**, **10**, **13**, and **14** with anthracene in solution (dichloroethane) and by CTC of **14** and **17** with TTF in the solid state. Single-crystal X-ray analysis for two complexes, **14**:TTF (2:3 stoichiometry) and **17**:TTF:PhCl (1:1:0.5 stoichiometry), showed interesting packing motifs. Further studies on the electronic and optical properties of fluorene acceptors, with particular emphasis on inter- and intramolecular CT processes of relevance to optoelectronic devices, will be reported in due course.

Experimental Section

General Procedures. Acetonitrile for CV and UV−vis spectral measurements was twice distilled from P_4O_{10}, then from CaH_2. 1,2-Dichloroethane for CTC measurements was twice treated with concentrated sulfuric acid, washed with water, dried over $CaCl_2$, and twice distilled from P_4O_{10}.

TLC analyses were performed using Chemapol "Silufol UV 254" precoated silica aluminum backed sheets; eluents were benzene, benzene/dioxane, (4−8):1, or toluene/dioxane/heptane, (4−8):(1−3):1, mixtures. For column chromatography, Chemapol Silicagel (100−160 mesh or 40−100 mesh) was employed, with benzene or benzene/acetone, (2−5):1, as eluents.

Electrochemical Mesurements. Cyclic voltammetry experiments were performed on a BAS CV50W voltammetric analyzer and on a EG&G PARC Model 263A potentiostat, both with *iR* compensation and PC-controlled. Platinum wire, platinum disk [Ø 1.6 mm (BAS), Ø 2.0 mm (PARC)], and Ag/AgCl were used as counter, working, and reference electrodes, respectively. In all cases, CV experiments were performed in dry MeCN with $EtN_4^+BF_4^-$ as supporting electrolyte (0.1 M) under N_2 flow; concentrations of acceptors were ca. 10^{-4} M^{-1}. The scan rate was 100 mV s^{-1}.

CTC Spectral Measurements. Measurements of isomolar series and also absorption of CTCs for estimations of equilibrium constants were made at the maxima of CTC absorptions. Evaluation of K_{CTC} and ϵ_{CTC} values was performed by nonlinear fitting based on a complete solution of eq 5:[9,16,40]

$$A_{CTC} = \frac{\epsilon_{CTC}}{2}\left[\left(C_A + C_D + \frac{1}{K_{CTC}}\right) - \sqrt{\left(C_A + C_D + \frac{1}{K_{CTC}}\right)^2 - 4C_AC_D}\right] \quad (5)$$

where A_{CTC} is an absorbance of CTC (at $\lambda_{max}{}^{CT}$) for given concentrations of donor and acceptor, C_A and C_D.

X-ray Crystallography. The single-crystal X-ray diffraction experiment for **I** was carried out on a Siemens P4 four-circle diffractometer, using graphite-monochromated Mo Kα radiation; for **II** with a SMART 1K CCD area detector (mounted on a three-circle diffractometer) using Si-monochromated synchrotron radiation (Daresbury, station 9.8) and an Oxford Cryosystems open-flow N_2 gas cryostat. Analytical absorption correction was applied for **I** (six crystal faces indexed, ABSPSI program,[41] min. and max. transmission factors 0.79 and 0.87). For **II**, intensities were corrected for absorption and decline of the primary beam intensity, by semiempirical methods based on Laue equivalents and multiple measurements (SADABS program,[42] min./max. correction factors 0.72/1.00). The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data, using SHELXTL software.[43] In **I**, non-hydrogen atoms were refined with anisotropic displacement parameters (disordered carbon atoms in isotropic approximation), with all H atoms in a "riding" model. In **II**, non-hydrogen atoms were refined in anisotropic and H atoms in isotropic approximation, except for the disordered benzene ring (therein, non-hydrogen atoms isotropic, H atoms "riding"). Crystal data and experimental details are listed in Table 4; atomic coordinates, thermal parameters, and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.[44]

Photophysical Measurements of Sensitized PEPC Films. PTSM were prepared in the following way: anionic PEPC (0.5 g)[45] and a corresponding amount of the acceptor were dissolved separately in methyl ethyl ketone (both in 5 mL), and then the solutions were combined and filtered. The resulting solution was supported on an ITO-coated glass base. The final thickness of the photoconductive films was 1.2 ± 0.1 μm. The surface of the film was charged by a positive corona discharge grid, with the final potentials were $V_0 \approx 120-160$ V μm^{-1} (measured by the dynamic sonde method). The relative dark decay of the surface potential ($\Delta V \times 100/V_0$) was estimated for the time of 30 s ($\Delta V = V_0 - V_\tau$, where V_τ is the charge potential of the surface in the dark after $\tau = 30$ s) and lies in the range 10−15%. The electrophotographic sensitivity ($S_{\Delta V}$, m^2 J^{-1}) was estimated on the level of 20% decay of the initial potential under illumination with wavelengths of 400−900 nm and an intensity of 0.1 μWt cm^{-1}. Real holographic sensitivity (S_η, m^2 J^{-1}) was estimated at the level of 1% diffraction efficiency (η = 1%) of the visualized image by recording holograms of the planar light wave at the spatial frequency of $\nu = 450$ mm^{-1} with irradiation of a He−Ne laser ($\lambda = 632.9$ nm). The maximal diffraction efficiency, achieved without amplification of the hologram recording (η_{max}, %), was found as the ratio of the beam intensity diffracted into the first order of a diffraction to the intensity of the beam grazed on the hologram, when the ratio of the intensities of the integrated beams was 1:3.

2-Butylsulfanyl-4,5,7-trinitrofluoren-9-one (2). (a) 2,4,5,7-Tetranitrofluoren-9-one (**1**) (3.0 g, 8.4 mmol) was dissolved in

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(44) The coordinates for **I** and **II** can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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Table 4. Crystal Data an Data Collection for I and II

	I	II
formula	$C_{24}H_{22}N_4O_8S_2 \cdot 3/2C_6H_4S_4$	$C_{28}H_{14}N_4O_{10}S_2 \cdot C_6H_4S_4 \cdot 1/2C_6H_5Cl$
M	865.1	891.2
cryst size (mm)	0.4 × 0.35 × 0.32	0.16 × 0.04 × 0.02
T (K)	293	150
symmetry	triclinic	monoclinic
unit cell dimensions		
a (Å)	10.089(1)	14.370(3)
b (Å)	13.954(1)	10.772(2)
c (Å)	15.732(1)	24.156(5)
α (deg)	108.72(1)	90
β (deg)	98.44(1)	98.38(1)
γ (deg)	108.05(1)	90
U (Å^3)	1918.2(3)	3699(1)
space group	$P\bar{1}$	$P2_1/c$
Z	2	4
λ (Å)	0.71073	0.6849
μ (cm^{-1})	5.2	4.7
D_x (g cm^{-3})	1.50	1.60
scan mode	$2\theta/\omega$	ω (0.15° frames)
$2\theta_{max}$ (deg)	50	54
no. of total data	6873	20 499
no. of unique data	6474	7958
no. of data obsd, $I > 2\sigma(I)$	4551	5137
R_{int}	0.010	0.069
no. of variables	511	591
$wR(F^2)$, all data	0.173	0.120
$R(F)$, obsd data	0.058	0.049
$\Delta\rho_{max,min}$ (e Å^{-3})	0.59, −0.93	0.49, −0.56

HMPA (10 mL) at room temperature, *n*-butanethiol (4 mL, 37 mmol) was added dropwise, and the mixture was kept at room temperature for 2 days. Then it was poured onto 5% HCl (50 mL) and ice (50 g). The brown oil was separated from the aqueous solution and twice recrystallized from 50% acetic acid, yielding **2** (2.76 g, 82%) as orange crystals, mp 153−155 °C.

(b) 2,4,5,7-Tetranitrofluoren-9-one (**1**) (6.0 g, 16.7 mmol) was dissolved in DMSO (60 mL) at room temperature, *n*-butanethiol (5 mL, 47 mmol) was added, and the reaction mixture was heated with stirring at 80 °C for 30−60 min (TLC monitoring). After cooling to room temperature it was poured onto 5% HCl (200 mL) and ice (50 g). The solid was filtered off, washed with water and propan-2-ol, and dried, yielding compound **2** (4.8 g, 71%), mp 152−157 °C. This crude product was dissolved in hot dioxane (10 mL) and diluted with hot propan-2-ol (50 mL), yielding **2** (4.5 g, 67%) as orange crystals, mp 155−157 °C. R_f: 0.56 (benzene). ^{1}H NMR (200 MHz, acetone-d_6): δ 8.01 (1H, d, $J_{1,3} = 1.8$ Hz), 8.06 (1H, d, $J_{1,3} = 1.8$ Hz), 8.92 (1H, d, $J_{6,8} = 2.1$ Hz), 8.68 (1H, d, $J_{6,8} = 2.1$ Hz), 3.37 (2H, t, $J = 7.3$ Hz), 1.80 (2H, m), 1.58 (2H,m), 1.00 (3H, t, $J = 7.2$ Hz). UV−vis (MeCN), λ_{max}/nm: 423. IR (KBr): ν/cm^{-1} 3450, 3080, 2960, 2930, 2870, 1740 (C═O), 1605, 1590, 1540, 1530 (NO_2), 1460, 1420, 1360, 1340 (NO_2), 1290, 1250, 1220, 1185, 1070, 925, 915, 880, 805, 785, 775, 745, 730, 710. Anal. Calcd for $C_{17}H_{13}N_3O_7S$: C, 50.51; H, 3.34; N, 10.20; S, 7.94. Found: C, 50.62; H, 3.23; N, 10.42; S, 7.94.

2,7-Bis(butylsulfanyl)-4,5-dinitrofluoren-9-one (3). (a) 2,4,5,7-Tetranitrofluoren-9-one (**1**) (3.0 g, 8.4 mmol) was dissolved in DMSO (30 mL), *n*-butanethiol (4 mL, 37 mmol) was added, and the mixture was heated with stirring at 80 °C for 1 h. After cooling to room temperature it was poured onto 5% HCl (100 mL) and ice (50 g). The solid was filtered off, washed with water, and twice recrystallized from 50% acetic acid, yielding **3** (2.64 g, 71%) as orange crystals, mp 162−165 °C.

(b) 2,4,5,7-Tetranitrofluoren-9-one (**1**) (10.0 g, 27.8 mmol) was dissolved in HMPA (30 mL) at room temperature, *n*-butanethiol (10 mL, 93 mmol) was added, and the reaction mixture was left to stand at room temperature for 4 days. The solution was poured onto 5% HCl (300 mL) and ice (150 g), and the solid was filtered off, washed with water, and dried, yielding compound **3** (9.0 g, 73%), mp 160−168 °C. The crude product was dissolved in hot dioxane (50 mL) and diluted with hot propan-2-ol (150 mL), yielding **3** (8.1 g, 65%) as bright orange needles, mp 165−168 °C. R_f: 0.77 (benzene). ^{1}H NMR (200 MHz, acetone-d_6): δ 7.92 (2H, d, $J_{1,3} = 1.8$ Hz), 7.85 (2H, d, $J_{1,3} = 1.8$ Hz), 3.28 (4H, t, $J = 7.2$ Hz), 1.75 (4H, m), 1.56 (4H, m), 0.97 (6H, t, $J = 7.2$ Hz). UV−vis (MeCN), λ_{max}/nm: 428. IR (KBr): ν/cm^{-1} 3440, 3080, 2950, 2930, 2870, 2850, 1725 (C═O), 1600, 1535 (NO_2), 1460, 1430, 1410, 1360 (NO_2), 1320, 1270, 1250, 1230, 1195, 1100, 1070, 900, 880, 780, 765, 750, 740, 715. Anal. Calcd for $C_{21}H_{22}N_2O_5S_2$: C, 56.44; H, 5.05; N, 6.34; S, 14.29. Found: C, 56.50; H, 4.93; N, 6.28; S, 14.35.

2,5-Bis(butylsulfanyl)-4,7-dinitrofluoren-9-one (4). The HMPA mother liquor from the synthesis of sulfide **3** (method "b") was combined with the dioxane/propan-2-ol solution from its recrystallization; the solvents were evaporated under reduced pressure, and the residue was TLC-analyzed (benzene/acetone, 4:1), showing a minor orange spot running faster than the main orange spot of **3**. Flash chromatography on silica 100−160 mesh (benzene; 3 × 40 cm column) gave the crude product, which was then purified by repeated chromatography on silica 40−100 mesh (the same conditions), yielding sulfide **4** (0.11 g, 0.9%), mp 122−123 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 8.56 (1H, d, $J_{6,8} = 2.1$ Hz), 8.24 (1H, d, $J_{6,8} = 2.1$ Hz), 7.94 (1H, d, $J_{1,3} = 1.8$ Hz), 7.91 (1H, d, $J_{1,3} = 1.8$ Hz) 3.30 (2H, t, $J = 7.3$ Hz), 3.17 (2H, t, $J = 7.3$ Hz), 1.76 (2H, m), 1.56 (2H, m), 1.3−1.6 (4H, m), 0.97 (3H, t, $J = 7.2$ Hz), 0.86 (3H, t, $J = 7.2$ Hz). *m/z*: 446 (M$^+$, 100), 416 (7), 390 (13), 370 (9), 334 (12), 301 (55), 257 (11), 229 (9), 201 (9), 169 (9), 57 (63). Anal. Calcd for $C_{21}H_{22}N_2O_5S_2$: C, 56.61; H, 4.99; N, 6.30; S, 14.22. Found: C, 56.50; H, 4.93; N, 6.28; S, 14.35.

2-Butylsulfanyl-4,5,7-trinitro-9-dicyanomethylenefluorene (5). 2-Butylsulfanyl-4,5,7-trinitrofluoren-9-one (**2**) (0.64 g, 1.6 mmol) was dissolved in DMF (2.5 mL), malononitrile (0.21 g, 3.2 mmol) was added, and the reaction mixture was stirred at room temperature for 2 h and diluted with propan-2-ol (20 mL). The solid was collected by filtration, washed with propan-2-ol, and dried, yielding compound **5** (0.66 g, 92%), mp 199−202 °C. Purification by dissolution in hot dioxane and subsequent dilution with 5 times the volume of propan-2-ol yielded pure **5** (0.65 g, 91%) as black crystals, mp 200−202 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.61 (1H, d, $J_{6,8} = 2.0$ Hz), 8.97 (1H, d, $J_{6,8} = 2.0$ Hz), 8.77 (1H, d, $J_{1,3} = 1.7$ Hz), 8.15 (1H, d, $J_{1,3} = 1.7$ Hz), 3.31 (2H, t, $J = 7.3$ Hz), 1.82 (2H, m), 1.57 (2H, m), 0.97 (3H, t, $J = 7.3$ Hz). *m/z*: 451 (M$^+$, 27), 395 (8), 346 (2.5), 319 (4), 245 (6), 200 (5), 57 (100). UV−vis (MeCN), λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 260 (28 500), 320 (24 800), 420 (10 100), 510sh (2600). Anal. Calcd for $C_{20}H_{13}N_5O_6S$ (MW

451.41): C, 53.18; H, 3.00; N, 15.72; S, 7.14. Found: C, 53.21; H, 2.90; N, 15.51; S, 7.10.

2,7-Bis(butylsulfanyl)-4,5-dinitro-9-dicyanomethylenefluorene (6). 2,7-Bis(butylsulfanyl)-4,5-dinitrofluoren-9-one (**3**) (0.50 g, 1.1 mmol) was dissolved in DMF (4.0 mL), malononitrile (0.25 g, 3.8 mmol) was added, and the reaction mixture was stirred at 60−65 °C for 2 h and diluted with propan-2-ol (20 mL). The solid was collected by filtration, washed with propan-2-ol, and dried, yielding compound **6** (0.46 g, 83%), mp 127−129 °C. Purification by dissolution in hot dioxane (1 mL) and subsequent dilution with propan-2-ol (5 mL) yielded pure **6** (0.42 g, 76%) as long black needles, mp 131−133 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 8.63 (2H, d, $J_{1,3} = 1.7$ Hz), 8.00 (2H, d, $J_{1,3} = 1.7$ Hz), 3.25 (4H, t, $J = 7.3$ Hz), 1.78 (4H, m), 1.55 (4H, m), 0.96 (6H, t, $J = 7.2$ Hz). *m/z*: 494 (M$^+$, 63), 446 (7), 438 (5), 418 (6), 306 (10), 277 (5), 245 (4), 57 (100). UV−vis (MeCN), λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 275 (29 800), 334 (26 500), 432 (9000), 558 (1500). Anal. Calcd for $C_{24}H_{22}N_4O_4S_2$ (MW 494.58): C, 58.25; H, 4.34; N, 11.30; S, 12.84. Found: C, 58.28; H, 4.48; N, 11.33; S, 12.96.

2,5-Bis(butylsulfanyl)-4,7-dinitro-9-dicyanomethylenefluorene (7). This was obtained from sulfide **4** (50 mg, 0.11 mmol) similarly to compound **6** as dark red-brown crystals (45 mg, 81%), mp 129−131 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.18 (1H, d, $J_{6,8} = 1.9$ Hz), 8.68 (1H, d, $J_{1,3} = 1.6$ Hz), 8.59 (1H, d, $J_{6,8} = 1.9$ Hz), 8.02 (1H, d, $J_{1,3} = 1.6$ Hz), 3.26 (2H, t, $J = 7.3$ Hz), 3.17 (2H, t, $J = 7.2$ Hz), 1.79 (2H, m), 1.55 (2H, m), 1.3−1.6 (4H, m), 0.97 (3H, t, $J = 7.3$ Hz), 0.85 (3H, t, $J = 7.2$ Hz). UV−vis (MeCN), λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 261 (27 200), 278 (25 500), 333 (26 300), 401 (10 300), 529 (2100). Anal. Calcd for $C_{24}H_{22}N_4O_4S_2$ (MW 494.58): C, 58.35; H, 4.43; N, 11.41; S, 12.88. Found: C, 58.28; H, 4.48; N, 11.33; S, 12.96.

2-Butylsulfinyl-4,5,7-trinitrofluoren-9-one (8). 2-Butylsulfanyl-4,5,7-trinitrofluoren-9-one (**2**) (1.40 g, 3.47 mmol) was dissolved in hot acetic acid (120 mL), 27% hydrogen peroxide (0.85 mL, 7.4 mmol) was added, and the reaction mixture was stirred at 60 °C for ca. 2.5 h with TLC monitoring until the appearance of a spot from sulfone **9**. The reaction mixture was diluted with water (300 mL), and the solid was filtered off and washed with water. The crude product was purified by flash chromatography (3.5 × 40 cm column, silica 100/160 mesh). The first fraction eluted by benzene contained starting sulfide **2**; the second fraction eluted by benzene/acetone, 6:1, yielded pure **8** (0.58 g, 40%) as yellow crystals, mp 164−165 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.00 (1H, d, $J_{6,8} = 2.1$ Hz), 8.79 (1H, d, $J_{6,8} = 2.1$ Hz), 8.56 (1H, d, $J_{1,3} = 1.5$ Hz), 8.49 (1H, d, $J_{1,3} = 1.5$ Hz), 3.25 (1H, m), 3.04 (1H, m), 1.83 (1H, m), 1.62 (1H, m), 1.49 (2H, m), 0.92 (3H, t, $J = 7.3$ Hz). *m/z*: 403 (M$^+$ − O, 36), 347 (14), 98 (6), 84 (9), 64 (100). Anal. Calcd for $C_{17}H_{13}N_3O_8S$ (MW 419.37): C, 48.89; H, 3.02; N, 10.00; S, 7.72. Found: C, 48.69; H, 3.12; N, 10.02; S, 7.64.

2-Butylsulfonyl-4,5,7-trinitrofluoren-9-one (9). (a) 2-Butylsulfanyl-4,5,7-trinitrofluoren-9-one (**2**) (3.0 g, 7.4 mmol) was dissolved in hot acetic acid (100 mL), 27% hydrogen peroxide (5.2 mL, 45 mmol) was added, and the reaction mixture was stirred at 60−65 °C for 24 h. The reaction mixture was diluted with hot water (100 mL), and the solid was filtered off and washed with water, yielding sulfone **9** (3.2 g, 99%), mp 213-215 °C. The product was dissolved in hot dioxane and diluted with 5 times the volume of propan-2-ol, yielding analytically pure sulfone **9** (2.9 g, 90%) as pale yellow crystals with the same melting point.

(b) Sulfoxide **3** (0.50 g, 1.2 mmol) was oxidized under the same conditions as above, yielding sulfone **9** (0.51 g, 98%), mp 213.5−215 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.04 (1H, d, $J_{6,8} = 2.1$ Hz), 8.85 (1H, d, $J_{6,8} = 2.1$ Hz), 8.71 (1H, d, $J_{1,3} = 1.6$ Hz), 8.59 (1H, d, $J_{1,3} = 1.6$ Hz), 3.56 (2H, m), 1.76 (2H, m), 1.47 (2H, m), 0.91 (3H, t, $J = 7.5$ Hz). Anal. Calcd for $C_{17}H_{13}N_3O_9S$ (MW 435.36): C, 46.97; H, 3.05; N, 9.56; S, 7.38. Found: C, 46.90; H, 3.01; N, 9.65; S, 7.36.

2,7-Bis(butylsulfonyl)-4,5-dinitrofluoren-9-one (10). 2,7-Bis(butylsulfanyl)-4,5-dinitrofluoren-9-one (**3**) (1.00 g, 2,2 mmol) was dissolved in hot acetic acid (50 mL), 27% hydrogen peroxide (2.6 mL, 23 mmol) was added, and the reaction mixture was stirred at 100−108 °C for 6 h. After cooling to room temperature the solid was filtered off, washed with water, and dried, yielding sulfone **10** (1.05 g, 92%), mp 291−294 °C. Recrystallization from benzene gave pure compound **10** (0.81 g, 77%) as yellow needles, mp 292−294 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 8.70 (2H, d, $J_{1,3} = 1.7$ Hz), 8.57 (2H, d, $J_{1,3} = 1.7$ Hz), 3.55 (4H, m), 1.75 (4H, m), 1.46 (4H, m), 0.90 (6H, t, $J = 7.4$ Hz). Anal. Calcd for $C_{21}H_{22}N_2O_9S_2$ (MW 510.53): C, 49.23; H, 4.25; N, 5.46; S, 12.60. Found: C, 49.40; H, 4.34; N, 5.49; S, 12.56.

2,5-Bis(butylsulfonyl)-4,7-dinitrofluoren-9-one (11). This compound was obtained by the above procedure for compound **10**, from 2,5-bis(butylsulfanyl)-4,7-dinitrofluoren-9-one (**4**) (46 mg, 0.10 mmol) and 27% hydrogen peroxide (0.2 mL, 1.7 mmol) in acetic acid (2.50 mL). Reaction time was 3 h (TLC monitoring). Pale yellow crystals of sulfone **11** were isolated (49 mg, 93%), mp 192−194 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.02 (1H, d, $J_{6,8} = 2.1$ Hz), 8.76 (1H, d, $J_{6,8} = 2.1$ Hz), 8.67 (1H, d, $J_{1,3} = 1.7$ Hz), 8.52 (1H, d, $J_{1,3} = 1.7$ Hz), 3.72 (2H, m), 3.56 (2H, m), 1.86 (2H, m), 1.77 (2H, m), 1.60−1.40 (4H, m), 0.97 (3H, t, $J = 7.3$ Hz), 0.91 (3H, t, $J = 7.2$ Hz). Anal. Calcd for $C_{21}H_{22}N_2O_9S_2$ (MW 510.53): C, 49.45; H, 4.39; N, 5.60; S, 12.47. Found: C, 49.40; H, 4.34; N, 5.49; S, 12.56.

2-Butylsulfinyl-4,5,7-trinitro-9-dicyanomethylenefluorene (12). 2-Butylsulfinyl-4,5,7-trinitrofluoren-9-one (**8**) (50 mg, 0.12 mmol) was dissolved in DMF (0.25 mL), malononitrile (20 mg, 0.30 mol) was added, and the reaction mixture was stirred at room temperature for 4 h and diluted with methanol (1.5 mL). After standing at 0 °C for 3 h the solid was collected by filtration, washed with methanol, and dried, yielding compound **12** (41 mg, 74%) as pale brown crystals, mp 174−177 °C. ^{1}H NMR (300 MHz, acetone-d_6+1% CF_3CO_2D): δ 9.70 (1H, d, $J_{6,8} = 2.0$ Hz), 9.28 (1H, d, $J_{1,3} = 1.4$ Hz), 9.05 (1H, d, $J_{6,8} = 2.0$ Hz), 8.62 (1H, d, $J_{1,3} = 1.4$ Hz), 3.29 (1H, m), 3.05 (1H, m), 1.85 (1H, m), 1.63 (1H, m), 1.50 (2H, m), 0.92 (3H, t, $J = 7.3$ Hz). Anal. Calcd for $C_{20}H_{13}N_5O_7S$ (MW 467.41): C, 51.37; H, 2.95; N, 14.99; S, 7.02. Found: C, 51.39; H, 2.80; N, 14.98; S, 6.86.

2-Butylsulfonyl-4,5,7-trinitro-9-dicyanomethylenefluorene (13). 2-Butylsulfonyl-4,5,7-trinitrofluoren-9-one (**9**) (1.00 g, 2.3 mmol) was dissolved in DMF (3.0 mL), malononitrile (0.35 g, 5.3 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h and diluted with propan-2-ol (15 mL). The solid was collected by filtration and washed with propan-2-ol, yielding compound **13** (1.06 g, 95%), mp 291−294 °C. Recrystallization from toluene (170 mL) gave pure sulfone **13** (1.00 g, 90%), yellow crystals, mp 294−296 °C. ^{1}H NMR (200 MHz, acetone-d_6+1% CF_3CO_2D): δ 9.72 (1H, d, $J_{6,8} = 1.9$ Hz), 9.42 (1H, d, $J_{1,3} = 1.4$ Hz), 9.08 (1H, d, $J_{6,8} = 1.9$ Hz), 8.76 (1H, d, $J_{1,3} = 1.4$ Hz), 3.55 (2H, m), 1.82 (2H, m), 1.51 (2H, m), 0.95 (3H, t, $J = 7.2$ Hz). Anal. Calcd for $C_{20}H_{13}N_5O_8S$ (MW 483.41): C, 49.72; H, 2.71; N, 14.41; S, 6.59. Found: C, 49.69; H, 2.71; N, 14.49; S, 6.63.

2,7-Bis(butylsulfonyl)-4,5-dinitro-9-dicyanomethylenefluorene (14). 2,7-Bis(butylsulfonyl)-4,5-dinitrofluoren-9-one (**10**) (1.00 g, 1.96 mmol) was dissolved in DMF (15 mL), malononitrile (0.45 g, 6.8 mmol) was added, and the reaction mixture was stirred at 40−45 °C for 4 h and diluted with propan-2-ol (60 mL). The solid was filtered off and washed with propan-2-ol, yielding compound **14** (0.99 g, 90%), mp 323−326 °C. After two recrystallizations from benzene bright yellow crystals, mp 328−331 °C, were obtained. ^{1}H NMR (200 MHz, acetone-d_6+1% CF_3CO_2D): δ 9.39 (2H, d, $J_{1,3} = 1.4$ Hz), 8.74 (2H, d, $J_{1,3} = 1.4$ Hz), 3.54 (4H, m), 1.80 (4H, m), 1.49 (4H, m), 0.92 (6H, d, $J = 7.3$ Hz). Anal. Calcd for $C_{24}H_{22}N_4O_8S_2$ (MW 558.58): C, 51.45; H, 3.85; N, 9.89; S, 11.62. Found: C, 51.61; H, 3.97; N, 10.03; S, 11.48.

2,5-Bis(butylsulfonyl)-4,7-dinitro-9-dicyanomethylenefluorene (15). 2,5-Bis(butylsulfonyl)-4,7-dinitrofluoren-9-one (**11**) (30 mg, 0.059 mmol) was dissolved in DMF (0.3 mL), malononitrile (12.5 mg, 0.189 mmol) was added, the reaction mixture was stirred at 50 °C for 25 h and diluted with methanol (1.5 mL). After storage at 0 °C for 3 h the solid was collected by filtration, washed with methanol, and dried, yielding compound **14** (29 mg, 88%) as yellow crystals, mp 225−228 °C. ^{1}H NMR (300 MHz, acetone-d_6+1% CF_3CO_2D):

δ 9.61 (1H, d, $J_{6,8} = 1.9$ Hz), 9.32 (1H, d, $J_{1,3} = 1.4$ Hz), 9.04 (1H, d, $J_{6,8} = 1.9$ Hz), 8.69 (1H, d, $J_{1,3} = 1.4$ Hz), 3.69 (2H, m), 3.53 (2H, m), 1.78 (4H, m), 1.48 (4H, m), 0.96 (3H, t, $J = 7.3$ Hz), 0.91 (3H, t, $J = 7.2$ Hz). Anal. Calcd for $C_{24}H_{22}N_4O_8S_2$ (MW 558.58): C, 51.69; H, 3.95; N, 10.15; S, 11.41. Found: C, 51.61; H, 3.97; N, 10.03; S, 11.48.

Complex I: 2,7-Bis(butylsulfonyl)-4,5-dinitro-9-dicyanomethylenefluorene (14) and Tetrathiafulvalene (2:3). Acceptor **14** was dissolved in hot acetonitrile, TTF was added, and the reaction mixture was stirred until full dissolution and left in a flask for slow evaporation at room temperature for several days, during which time black crystals of the complex **II** were formed.

Complex II: 2,7-Bis(phenoxysulfonyl)-4,5-dinitro-9-dicyanomethylenefluorene (17) and Tetrathiafulvalene (1:1:0.5 PhCl). Acceptor **17**[16] (10 mg, 0.016 mmol) was dissolved in chlorobenzene (2 mL) at 80 °C, TTF (8 mg, 0.039 mmol) was added to this solution, and the mixture was stirred until full dissolution and left for very slow cooling to room temperature. Black crystals were collected, washed with a small portion of chlorobenzene, and dried at room temperature. Anal. Calcd for $C_{37}H_{20.5}Cl_{0.5}N_4O_{10}S_6$ (MW 891.21): C, 49.87; H, 2.32; N, 6.29; S, 21.59. Found: C, 50.02; H, 2.40; N, 6.20; S, 21.75.

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Supporting Information Available: Full crystallographic data for **I** and **II**. This material is available free of charge via the Internet at http://pubs.acs.org.

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