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Electron Acceptors of the Fluorene Series. 7.[1] 2,7-Dicyano-4,5-dinitro-9-X-fluorenes: Synthesis, Cyclic Voltammetry, Charge Transfer Complexation with *N*-Propylcarbazole in Solution, and X-ray Crystal Structures of Two Tetrathiafulvalene Complexes

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The synthesis and physical properties of a series of novel fluorene π-electron acceptors (**7**−**9**) are described. Cyclic voltammograms of **7** and **8** exhibit three separate reversible (or quasi-reversible) one-electron redox waves, characteristic of strong electron acceptors. Spectroelectrochemical experiments show the appearance in the long-wavelength visible region of absorption bands at appropriate potentials which were attributed to the transformations $A \rightarrow A^{\bullet-}$ and $A^{\bullet-} \rightarrow A^{2-}$. Charge-transfer complexation with *N*-propylcarbazole in dioxane shows the formation of 1:1 complexes with parameters characteristic for other fluorene acceptors. The single-crystal X-ray structures of 1:1 charge-transfer complexes of tetrathiafulvalene with the electron acceptor **8** and with the strongest fluorene acceptor **1f** both show ··A···D···A···D·· stacking in the crystal.

Introduction

Polynitrosubstituted 9-fluorenones (**1a**−**c**)[2] and 9-dicyanomethylenefluorenes (**1d**−**f**),[3] synthesized some decades ago, are a unique class of electron acceptor molecules. They have been widely employed as acceptors for charge-transfer complex (CTC) formation,[4] as photosensitizers and electron transport materials,[5,6] in the preparation of π-complexing phases for HPLC[7] and TLC,[8] as complexing agents for optical resolution,[9] and as spray reagents for nondestructive detection of many classes of biologically active compounds, polyaromatics and heteroaromatics.[10]

Subsequently, fluorene acceptors containing cyano substituents in the benzene rings (**2**−**3**) were synthesized.[4c,11] They have been shown to form semiconducting CTC with electron donors and to sensitize poly-*N*-epoxypropylcarbazole (PEPC). It was also found that substitution of the nitro group in position 4 of 9-dicyanomethylene-2,4,7-trinitrofluorene (**1e**) by a cyano group leads to a more effective sensitizer (**3c**) of PEPC photoconductivity.[12]

For acceptors **1b**,**c**,**e**,**f**, and **3b** (Chart 1) the structures were determined by single-crystal X-ray analysis which revealed significant steric interaction of the substituents in positions 4 and 5.[13−15] However, very little X-ray

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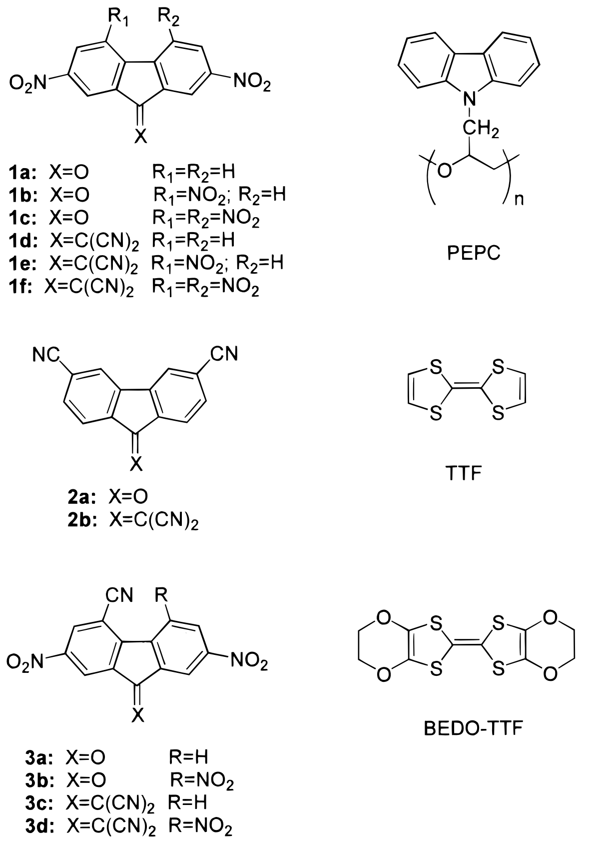
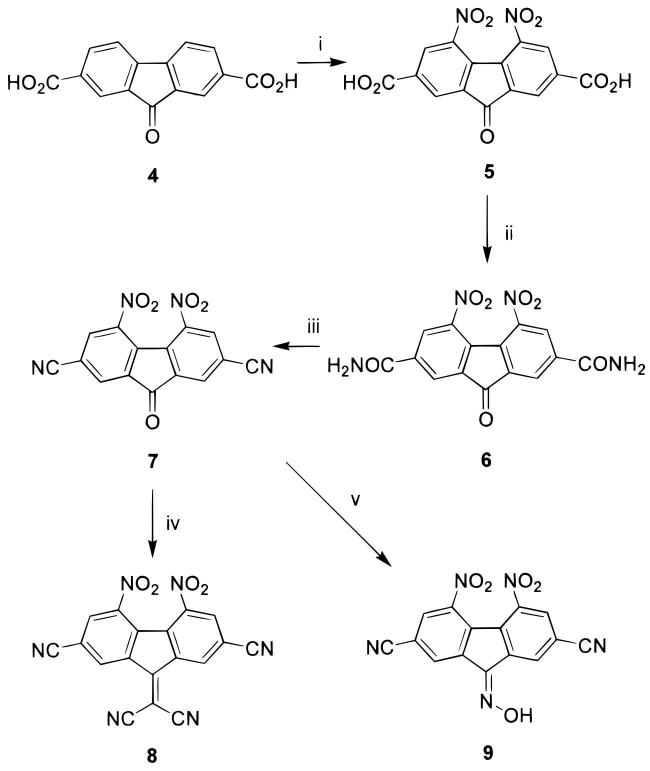
Chart 1



Scheme 1[a]



[a] (i) HNO_3/H_2SO_4, 80−85 °C, 6 h; (ii) $SOCl_2$, reflux, 3−4 h, then NH_4OH; (iii) $POCl_3$/DMF, reflux, 30 min; (iv) $CH_2(CN)_2$, DMF, rt, 40 min; (v) $NH_2OH-HCl$, DMF, 60 °C, 2 h.

structural data are known for their CTC. Most donors which have been used to form CTCs are of little interest for their solid-state electronic properties. Thus, single-crystal X-ray structures were determined for CTCs of **1b,e** with aromatic donors.[16−24] To our knowledge only one X-ray stucture has been reported[25] for a CTC of a fluorene acceptor and tetrathiafulvalene (TTF) donor: this is a 1:1 complex of the weak acceptor **1a** and TTF. This is surprising as TTF has been complexed with a wide range of other acceptors to provide materials with unusual electronic[26] and magnetic[27] properties. Recently it was reported[28] that bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) forms with **1e** and **1f** CTCs of 2:1 composition which showed (as compressed pellets) metallic-type electrical conductivity with σ_{rt} of 65 and 18 S cm^{-1} and $\sigma_{\max}$ of 390 (8 K) and 32 (94 K) S cm^{-1}, respectively (acceptors **1b** and **1c** gave semiconductive CTC with TTF of 1:1 compositions with σ_{rt} of ca. 10^{-10} S cm^{-1}), but no X-ray data were reported for the crystals. These observations prompt us to report our studies on CTC and radical ion salts (RS) of fluorene acceptors and TTF donors.

Herein we describe the synthesis of novel electron acceptors of the fluorene series, i.e., 2,7-dicyano-4,5-dinitro-9-X-fluorenes (**7**−**9**), investigations of their redox and spectroelectrochemical properties, CT complexation with *N*-propylcarbazole in solution, and single-crystal X-ray stuctures for **8**:TTF:C_6H_5Cl and **1f**:TTF complexes.

Results and Discussion

Synthesis. The synthesis of the acceptors is shown in Scheme 1. Fluorene-9-one-2,7-dicarboxylic acid **4**, readily accessible from 2,7-diacetylfluorene,[29] was nitrated by fuming HNO_3−concentrated H_2SO_4 mixture to yield diacid **5**, which was then converted into diamide **6**

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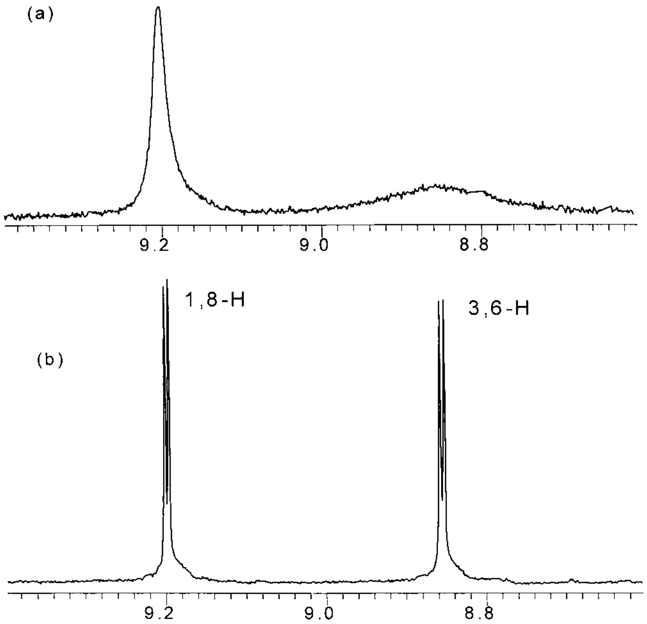

Figure 1. 250 MHz ^{1}H NMR spectra of acceptor **8** in acetone-d_6 at 25 °C: (a) original spectrum; (b) after 1 drop of CF_3COOD was added to solution a.

by subsequent action of thionyl chloride and ammonia. Dehydration of diamide **6** by $POCl_3$ gave 2,7-dicyano-4,5-dinitro-9-fluorenone (**7**) which was transformed into 9-dicyanomethylene derivative **8** and oxime **9** by reaction with malononitrile or hydroxylamine hydrochloride, respectively, in DMF.

^{1}H and ^{13}C NMR spectra were entirely consistent with their structures, by comparison with data for previous tetrasubstituted fluorenes.[1] We note one peculiarity in the spectra for acceptor **8**. Because of its strong electron acceptor nature, significant paramagnetic broadening of the aromatic protons is observed in the ^{1}H NMR spectrum (Figure 1a) as a result of possible interaction with donor solvent (acetone) or with traces of donor impurities. The protons in positions 3 and 6 are broadened much more than those in positions 1 and 8, confirming a higher spin density on C-3,6 atoms in the radical anion of **8**. In the ^{13}C NMR spectra of the compound, only C-1,8, CN, and C-3,6 signals are observable. Addition of trifluoroacetic acid completely restores the fine resolution of both the ^{1}H NMR (Figure 1b) and ^{13}C NMR (see Experimental Section) spectra of compound **8**. Broadening of the signals in the ^{1}H NMR spectra was previously observed for other strong electron acceptors of the fluorene series[1] in the presence of dipolar solvents.

Table 1. Cyclic Voltammetry Data for Fluorene Derivatives 1c,e,f, 3a,b, 7, 8, and 9 (V vs Ag/AgCl)[a]

compd	$E_{1red}^{1/2}$ (V)	$E_{2red}^{1/2}$ (V)	$E_{3red}^{1/2}$ (V)	K_{dispr}[b] (M^{-1})	EA (eV)
1c	−0.12	−0.41	−1.47	1.2×10^{-5}	2.42
1e	+0.02	−0.57	−1.37	1.0×10^{-10}	2.56
1f	+0.23	−0.31	−1.13	7.0×10^{-10}	2.77[c]
3a	−0.42	−0.74		3.8×10^{-6}	2.12
3b	−0.20	−0.49		1.2×10^{-5}	2.34
7	−0.27	−0.64	−1.33	5.4×10^{-7}	2.27
8	+0.17	−0.45	−1.04	3.1×10^{-11}	2.71
9	−0.38[d]	−0.73	−0.89		*e*

[a] Solvent acetonitrile; electrolyte 0.2 M $Et_4N^+BF_4^-$; scan rate 100 mV s^{-1}. All potentials given in the table were corrected using the Fc^0/Fc^+ couple as internal reference and recalculated to Ag/AgCl scale (Fc^0/Fc^+ couple showed +0.45 V vs Ag/AgCl in these conditions). [b] Calculated using equation $\Delta E_{1-2} = E_{1red}^{1/2} - E_{2red}^{1/2} = -0.059 \log K_{dispr}$. [c] Reference 11c. [d] Irreversible reduction peak. This value is for E_{1red}. [e] This value could not be reliably calculated as E_1 is an irreversible wave.

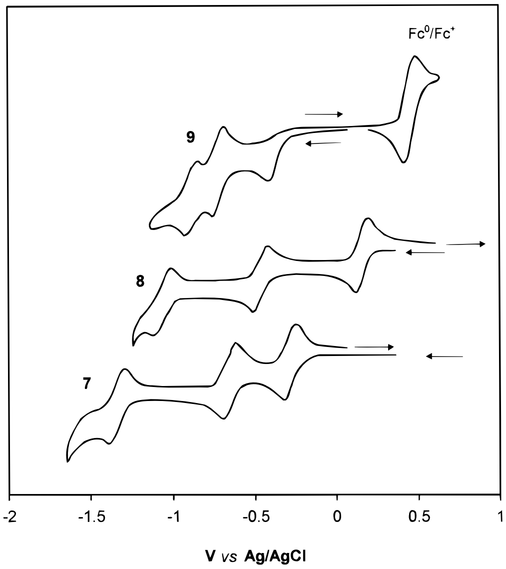

Figure 2. Cyclic voltammograms of compounds **7**−**9** (under the conditions stated in Table 1).

Electrochemistry. To study the redox properties of the novel acceptors **7**−**9**, we carried out cyclic voltammetry (CV) measurements in acetonitrile solution at room temperature with $Et_4N^+BF_4^-$ as supporting electrolyte. By analogy with nitrofluorenes **1a**−**f**, acceptors **7** and **8** show two, reversible, single-electron reduction waves resulting in radical anion and dianion species, respectively, followed at a considerably more negative potential by a third, quasi-reversible, single-electron reduction wave resulting in the radical trianion. The CV behavior of oxime **9** is anomalous: an irreversible reduction wave is followed by two reversible reduction waves. This suggests that the radical anion of **9** is converted into another compound which is a poorer electron acceptor than **9**. At this potential (−0.38 V) an electron could be lost (to the electrode or by reaction with neutral oxime **9**) and the second and third waves (at $E^{1/2}$ −0.73 and −0.89 V) are tentatively assigned to the first and second single-electron reductions of this reaction product, for which possible structures are the nitroso isomer of **9** or an azo compound containing two fluorene groups. Further studies on the electrochemistry of oxime **9** are planned. The results are summarized in Table 1 together with data for known acceptors **1c**,**e**,**f** and **3a**,**b** measured under the same conditions. The CVs of compounds **7**−**9** are shown in Figure 2.

Electron affinities (EA) were estimated (Table 1) by eq 1:

$$\mathrm{EA(ref)} - \mathrm{EA} = E_{1red}^{\ 1/2}\,(\mathrm{ref}) - E_{1red}^{\ 1/2} \qquad (1)$$

indicating that compound **8** is a rather strong acceptor (EA = 2.71 eV), comparable to the strongest known acceptor of the fluorene series, i.e., **1f**, which was used as the reference acceptor [EA(ref) = 2.77 eV[11c]]. Moreover, acceptor **8** is much more soluble than **1f**, especially in low polarity solvents, thereby making **8** more useful for CTC and RS preparation.

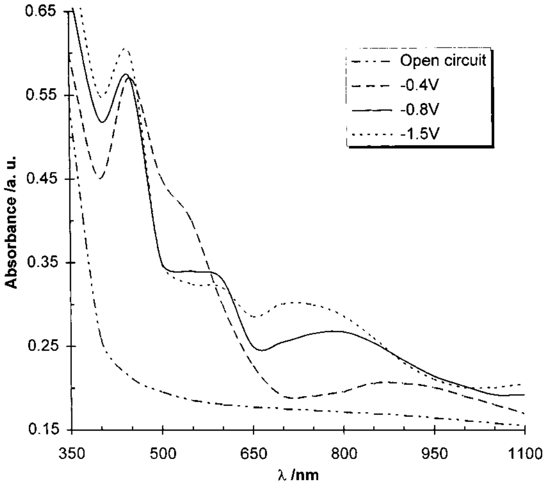

Figure 3. Electronic absorption spectra in visible and near-IR region for compound **7** at various applied potentials; solvent acetonitrile, electrolyte $Et_4N^+BF_4^-$ (0.2 M); potentials are given vs Ag/AgCl.

Disproportionation constants (K_{dispr}) in the equilibrium 2:

$$2A^{\bullet -} \xrightleftharpoons{K_{\mathrm{dispr}}} A + A^{2-} \qquad (2)$$

determined from the difference in potentials of the corresponding radical anion and dianion by the known equation[30] $\Delta E_{1-2} = E_{1\mathrm{red}}^{1/2} - E_{2\mathrm{red}}^{1/2} = -0.059 \log K_{\mathrm{dispr}}$ indicate thermodynamic stability of the radical anions from **7** and **8**, which is even higher than that for the corresponding tetranitrosubstituted fluorenes **1c**,**f**.

Spectroelectrochemistry. To study the effect of the transformations $A \rightarrow A^{\bullet -} \rightarrow A^{2-}$ on the electronic absorption spectra, we performed spectroelectrochemical experiments for acceptors **7** and **8**. (The stability of the electrode system was established in the 0 to −1.5 V potential range.) As seen from Figure 3, compound **7** has no absorption at $\lambda \geq 400$ nm. At a potential of −0.4 V vs Ag/AgCl an additional band at ca. 450 nm and a low-intensity broad band at 800−900 nm appear, as a result of the formation of the $A^{\bullet -}$ species in the solution. At more negative potentials of −0.8 and −1.5 V, when the formation of A^{2-} and $A^{\bullet 3-}$ species are expected, the short wavelength band does not change its position or intensity, whereas a hypsochromic shift and an increase in the intensity is observed for the long wavelength band.

If the potential is switched off (to open the circuit) after scanning to −0.8 V, the starting spectrum is fully restored, confirming the reversibility of the processes of radical anion and dianion formation. Turning off the potential after scanning to −1.5 V does not restore the original spectrum; instead absorption spectra of decomposition products are observed in the visible region.

We mentioned above that broadening of the aromatic protons in the NMR spectrum of compound **8** can be attributed to the formation of paramagnetic species $A^{\bullet -}$ due to electron transfer from donor solvent to acceptor molecule. Figure 4 reveals that acceptor **8** in acetonitrile at open circuit vs Ag/AgCl has a low-intensity broad band at ca. 800 nm which can be attributed to the existence of $A^{\bullet -}$ in solution. This agrees with the CV data ($A \rightarrow A^{\bullet -}$ for **8** occurs at $E_{1\mathrm{red}}^{1/2} = -0.28$ V vs $Fc/Fc^+ \equiv +0.17$ V vs Ag/AgCl). When a negative potential of −0.1 V is applied to the solution of **8**, this band increases in intensity, confirming its assignment to the radical anion species, and at −0.8 V the absorption at 800 nm almost disappeared due to the transformation $A^{\bullet -} \rightarrow A^{2-}$. (This spectrum was essentially unchanged when obtained at −1.5 V.)

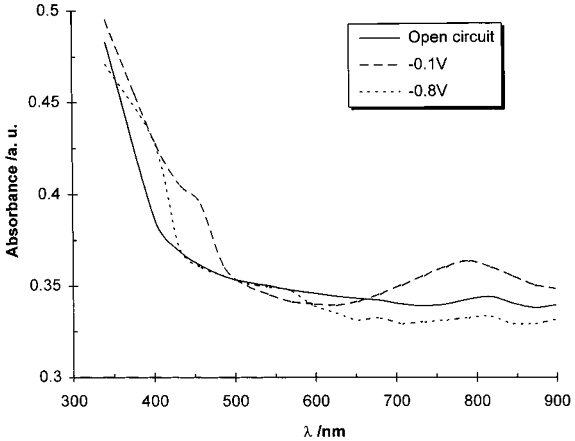

Figure 4. Electronic absorption spectra in visible and near-IR region for compound **8** at various applied potentials; solvent acetonitrile, electrolyte $Et_4N^+BF_4^-$ (0.2 M); potentials are given vs Ag/AgCl.

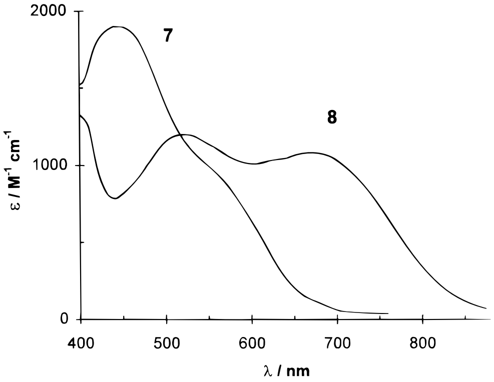

Figure 5. Electronic absorption spectra for CTC of acceptors **7** and **8** with *N*-propylcarbazole in dioxane, 25 °C.

CTC in Solution. The ability of fluorene acceptors to form molecular CTC with electron donors is well-known.[1−3,5,10,16−25] We investigated the formation of CTC of acceptors **7** and **8** with *N*-propylcarbazole in dioxane. This donor was chosen because it can be considered as a low-molecular-weight model of poly-*N*-vinylcarbazole (PVC) and poly-*N*-(2,3-epoxypropyl)carbazole (PEPC) which are both widely used as polymer photoconductors for optical storage media.[5] The formation of CTC between **7** or **8** and *N*-propylcarbazole was evident from the appearance of additional absorbance bands (CTC bands) in the visible region of the electronic spectra (Figure 5) which are absent in the spectra of both acceptors and donor. Isomolar series experiments (Figure 6) indicated the formation of CTC of 1:1 composition only.

Recently, we estimated equilibrium constants *K* for 1:1 CTC (eq 3) of a number of fluorene acceptors with *N*-propylcarbazole in dioxane[5a,31] and with anthracene in 1,2-dichloroethane[1] by nonlinear fitting of eq 4:

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Table 2. Equilibrium Constants (*K*) and Molar Extinction Coefficients (ϵ) for CTC of Fluorene Acceptors 7 and 8 with *N*-Propylcarbazole in Dioxane, 25 °C, Evaluated by Nonlinear Fitting (4) and Benesi−Hildebrand Method (5), and Their Comparison with Literature Data for 1b,c,e,f

			variation range of concntrtns							
compd	λ (nm)[a]	concn condtns	$C_A \times 10^3$ (M)	$C_D \times 10^2$ (M)	K (M^{-1})	ϵ ($M\ cm^{-1}$)	N[b]	R or r[c]	R_f or s_0[d]	method[e]
7	448	all data	0.86−18.4	0.48−32.8	1.07 ± 0.07	1930 ± 120	37	0.9996	1.33	(4)
		$C_D \geq 10C_A$	0.86−5.1	5.8−32.8	1.00 ± 0.09	2070 ± 160	20	0.9993	1.12	(4)
		$C_D \geq 10C_A$	0.86−5.1	5.8−32.8	0.96 ± 0.09	2130 ± 190	20	0.9994	7.2×10^{-5}	(5)
		$C_D < 10C_A$	6.10−18.4	0.48−7.7	0.99 ± 0.10	2080 ± 190	17	0.9991	1.19	(4)
8	525	all data	1.47−2.35	1.12−9.58	6.65 ± 0.90	1110 ± 110	26	0.9941	3.33	(4)
		$C_D < 10C_A$	1.47−2.35	1.11−2.31	7.45 ± 5.86	1020 ± 700	6	0.9917	1.88	(4)
		$C_D \geq 10C_A$	1.47−2.35	1.63−8.27	6.66 ± 1.23	1120 ± 150	20	0.9914	3.48	(4)
		$C_D \geq 10C_A$	1.47−2.35	1.63−8.27	7.13 ± 0.80	1060 ± 100	20	0.9952	1.8×10^{-4}	(5)
1b	588				1.68 ± 0.08	810 ± 30	20			(4)
1c	596				1.74 ± 0.07	860 ± 30	22			(4)
1e	633				6.11 ± 0.26	1120 ± 40	21			(4)
1f	704				8.38 ± 0.28	1430 ± 40	10			(4)

[a] Wavelength at which measurements were made. [b] *N* is quantity of points used in optimization procedure (4) or in correlation (5). [c] Multiple correlation coefficient (*R*) or correlation coefficient (*r*) is given for nonlinear (4) and linear (5) methods, respectively. [d] The misalignment factor (R_f) between experimental data and fitting is given for nonlinear method which is described as $R_f = [\sum(A_i^{exp} - A_i^{calc})^2/\sum A_i^{exp}] \times 100\%$ (where A_i^{exp} and A_i^{calc} are experimental and calculated values of a CTC absorbance for *i*th point, respectively) and indicates a mean percentage deviation of experimental A_{CTC} values from the fit according to eq 4. Standard deviation (s_0) is given for linear methods (5). [e] Enumeration of the methods corresponds to the number of an equation in the text.

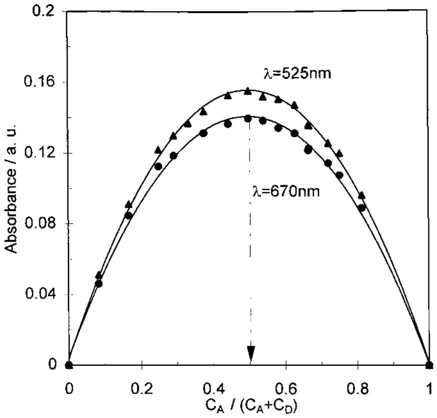

Figure 6. Effect of donor−acceptor ratio on absorbance of solution of CTC of 2,7-dicyano-4,5-dinitro-9-dicyanomethylenefluorene (**8**) with *N*-propylcarbazole in dioxane, 25 °C, at two CTC bands (λ = 670 and 525 nm); $C_A + C_D = 9.94 \times 10^{-3}$ M (method of isomolar series).

$$A + D \overset{K}{\rightleftarrows} [A^{\delta-}, D^{\delta+}] \tag{3}$$

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

where C_A and C_B are starting concentrations of a donor and an acceptor, ϵ_{CTC} is the molar extinction coefficient for CTC [$A^{\delta-}$, $D^{\delta+}$], and A_{CTC} is the equilibrium absorbance of the solution of the mixture of C_A and C_D.

Using this approach we estimated *K* values for 1:1 CTC of acceptors **7** and **8** with *N*-propylcarbazole in dioxane under the same conditions as in the previous study[31] (Table 2). Complexation constants for **7** and **8** (Table 2) are comparable with those for acceptors **1b**,**c**,**e**,**f**; the *K* value for **7** is ca. 1.6 times less than that for tri- and tetranitrosubstituted 9-fluorenones (**1b**,**c**) whereas for **8** it is similar to that for **1e**,**f** within experimental error. These data, together with $E_{1red}^{1/2}$ and $E_{2red}^{1/2}$ values for **7** and **8**, show that there are no significant changes in the electron acceptor and complexation abilities of the molecules, resulting from changing the nitro groups into cyano groups in positions 2 and 7. Treatment of the set of experimental data corresponding to a high excess of the donor [$C_D \gg C_A$ (or $C_A \gg C_D$) is a condition to transform eq 4 into approximation 5: in practice, usually a limitation of $C_D \geq 10C_A$ or $C_A \geq 10C_D$ is used] by the Benesi−Hildebrand method[32] (5):

$$\frac{C_A}{A_{CTC}} \cong \frac{1}{\epsilon_{CTC}} + \frac{1}{K\epsilon_{CTC}}\frac{1}{C_D} \tag{5}$$

gave *K* and ϵ values comparable within error with those obtained by eq 4 for both $C_D \geq 10C_A$ conditions and for the full set data we obtained (Table 2).

Single-Crystal X-ray Analysis for CTCs 1f:TTF, 1:1 (I) and 8:TTF:C_6H_5Cl, 1:1:1 (II). Single crystals of both complexes were grown from chlorobenzene solutions of equimolar amounts of TTF and the corresponding acceptors, i.e., **1f** or **8.** The unit cell of **I** is composed of TTF and fluorenone **1f** molecules in a 1:1 ratio; the unit cell of **II** is composed of TTF, acceptor **8**, and C_6H_5Cl molecules in the ratio of 1:1:1. Figure 7 shows the packing diagrams for **I** and **II**. It is seen that the donor and acceptor molecules alternate in stacks which is a characteristic motif for semiconducting CTC.[33]

Inclusion of the third component (solvent) in **II** does not significantly change the mode of stacking. In both complexes each TTF molecule in the stack is situated between the two translation-related (*c* in **I** and *a* in **II**) acceptor molecules; hence the mean planes of the acceptor molecules in the stack are rigorously parallel. In **I** and **II**, these stacks run along the *a* and *c* axes, respectively. Within the stacks, the dihedral angle between the TTF and the acceptor molecules is 2.9° in **I** and 4.1° in **II**. The

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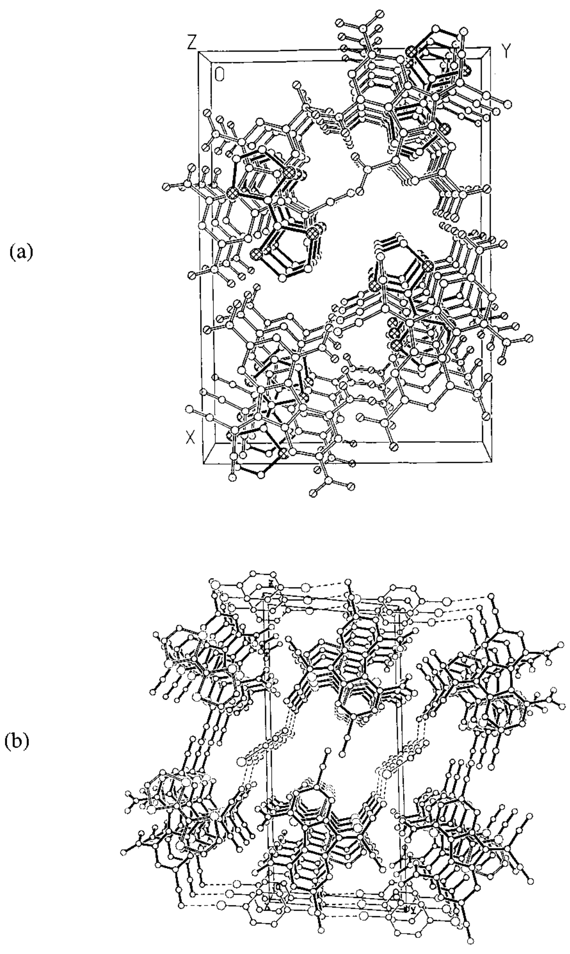

Figure 7. Packing diagram for **I** (a) and **II** (b) in the crystals.

mutual arrangement of the donors and acceptors in the stacks of **I** and **II** is qualitatively similar (Figure 8). In both cases, the central C=C bond of TTF is almost parallel to a bond of the C(9) atom with a benzene ring of an acceptor [C(9)−C(13) in **1f** and C(9)−C(10) in **8**]. One dithiole ring of TTF is packed between the cyclopentadiene rings of the two adjacent fluorene molecules, whereas the other dithiole ring is situated in the vicinity of a cyano group at C(14).

There are a number of short interatomic contacts between the donor and adjacent acceptors (A and B) in a stack of both **I** and **II** (Table 3) indicating dimerized stacks. The contacts between TTF and acceptor A in **I** and acceptor B in **II** (see Table 3) are shorter than contacts with the other acceptor molecule (i.e., B in **I** and A in **II**).

The single principal distinction in the stacking geometry in **I** and **II** is the occurrence of a very short interstack contact of 3.12 Å between S(2) and O(4) atoms in the dimer in **I**, which is not seen in **II**, due to a different rotation of the corresponding nitro group in the two structures.

The mutual arrangement of the stacks in crystals of **I** and **II** is different (Figure 9). Each acceptor molecule within a stack in **I** is connected with two translation *b* related TTF molecules from two adjacent stacks via specific S···O [atoms S(1) and O(3)] interactions and N···H−C (atoms N(2) and C(3′)) hydrogen bonds (Figure 9a). The S···O distance (3.10 Å) is rather short. The geometry of the C(1′)−S(1)···O(3)−N(4) contact [angle O(3)···S(1)−C(1′) is 162.3°] fills the σ−n orbital interaction between the S−C bond σ^* orbital and the oxygen atom lone pair on an sp^2 orbital as well as the π−n interaction of S(1) atom lone pair on the p orbital with the π^* orbital of the O−N bond.

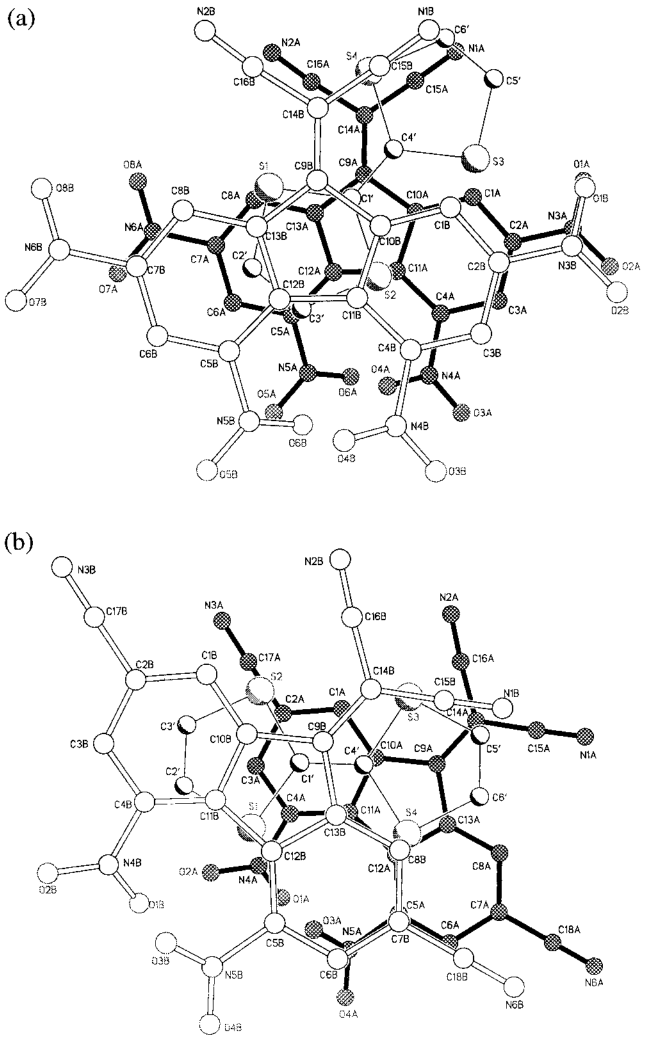

Figure 8. Mutual arrangement of two acceptor molecules and one TTF molecule in a stack of **I** (acceptor **1f**) (a) and in a stack of **II** (acceptor **8**) (b).

The packing of stacks in the crystal of **II** is more complicated due to the included solvent molecules. Two types of specific interactions between TTF and acceptor molecules in adjacent stacks are observed. The interaction C(1′)−S(2)···N(3) and C(4′)−S(3)···O(2) have the following parameters: S(2)···N(3) 3.08 Å, C(1′)-S(2)···N(3) 168°, S(2)···N(3)−C(17) 174° and S(3)···O(2) 3.04 Å, C(4′)−S(3)···O(2) 173° (Figure 9b). In the first case, the stacks related by translation *b* are considered. In the second case, the stacks are related by a symmetry center. In addition, the solvent molecules are involved in weak specific interactions with both TTF and the acceptor. Atom Cl(1) interacts with atom S(4) (Cl···S 3.69 Å) and atom Cl(2) interacts with atom O(2) (Cl···O 3.36 Å). The corresponding distances are rather long, although in both cases a lone pair of chlorine is oriented toward the corresponding heteroatom; C−Cl···S and C−Cl···O angles (98.1 and 97.5°, respectively) are close to 90°.

In **I** and **II**, TTF molecules manifest different types of out-of-plane deformations. In **I**, the most significant one

Table 3. Intrastack Short Contacts (Å) between TTF and Two Above (A) and Under (B) Molecules of Acceptors 1f and 8 in Structures I and II[a]

structure **I**				structure **II**			
molecule A		molecule B		molecule A		molecule B	
S(1)··C(8)	3.32	S(1)··C(9)	3.63	S(1)··C(4)	3.61	S(1)··C(11)	3.37
S(2)··C(11)	3.22	S(1)··C(13)	3.60	S(2)··C(2)	3.47	S(1)··C(12)	3.42
S(2)··C(12)	3.39	S(2)··C(10)	3.67	S(2)··C(17)	3.55	S(2)··C(10)	3.45
S(2)··O(4)	3.12	S(2)··C(11)	3.66	S(3)··C(10)	3.86	S(2)··C(1)	3.40
S(4)··C(14)	3.20	S(3)··C(1)	3.64	S(3)··C(1)	3.87	S(2)··C(9)	3.73
S(4)··C(16)	3.42	S(3)··O(1)	3.44	S(4)··C(11)	3.72	S(3)··C(14)	3.22
S(4)··C(15)	3.36	S(4)··C(15)	3.64	S(4)··C(12)	3.46	S(3)··C(15)	3.25
C(1′)··C(9)	3.29	S(4)··N(1)	3.78	S(4)··C(13)	3.65	S(4)··C(8)	3.25
C(1′)··C(13)	3.31	C(1′)··C(9)	3.66	C(1′)··C(2)	3.75	S(4)··C(13)	3.60
C(1′)··C(10)	3.60	C(1′)··C(10)	3.63	C(1′)··C(3)	3.74	C(1′)··C(9)	3.26
C(2′)··C(7)	3.52	C(2′)··C(13)	3.59	C(1′)··C(4)	3.79	C(1′)··C(10)	3.38
C(2′)··C(6)	3.67	C(2′)··C(12)	3.54	C(1′)··C(11)	3.84	C(1′)··C(13)	3.48
C(3′)··C(5)	3.51	C(2′)··C(13)	3.59	C(4′)··C(10)	3.55	C(2′)··C(4)	3.45
C(3′)··C(12)	3.45	C(3′)··C(11)	3.76	C(4′)··C(1)	3.82	C(2′)··C(11)	3.63
C(4′)··C(9)	3.27	C(3′)··C(12)	3.52	C(4′)··C(11)	3.72	C(3′)··C(1)	3.68
C(4′)··C(14)	3.42	C(6′)··N(1)	3.50	C(5)··C(14)	3.64	C(3′)··C(2)	3.63
C(6′)··N(1)	3.38			C(6′)··C(9)	3.69	C(4′)··C(13)	3.39
				C(6′)-C(13)	3.62	C(4′)··C(9)	3.29
						C(4′)··C(14)	3.48
						C(5′)··C(15)	3.39

[a] Enumeration of the atoms corresponds to Figures 8a and 8b for structures **I** and **II**, respectively.

is a twist of 7.1° around the central C═C bond. In **II**, the two dithiole rings are bent toward one another by an angle of 7.3° giving TTF a boat conformation. Such small distortions of planarity (within the range of 0−8°) are typical for TTF molecules included in the Cambridge Crystallographic Database (CCD).[34] In the two crystal modifications of TTF, no similar distortions have been observed.[35,36] Apparently, the distortions in **I** and **II** are determined by a compromise between tendencies to provide optimum molecular overlap and close packing in the crystals.

The double bonds of TTF are essentially localized. In **I** the central C═C bond length is 1.364(9) Å and the peripheral bonds are both 1.34(1) Å; in **II** these bonds are 1.359(6), 1.324(7), and 1.323(7) Å, respectively. These values are similar to but systematically longer (by approximately 2 esd) than the corresponding distances [1.337(4), 1.309(4), and 1.309(4) Å] in the structure of pure TTF where no plane-to-plane stacking occurs.[35] This effect can be attributed to charge transfer in **I** and **II**.

The S−C bond lengths vary within 1.725−1.747(6) Å in **I** and 1.731(5) −1.757(4) Å in **II**, whereas these bond lengths are 1.731(4) − 1.755(3) Å in the structure of TTF.[35] The molecules of unsubstituted TTF included in CCD (62 entries) reveal a wide variation of C−C and S−C bond lengths. The central C═C bond varies within the range 1.298−1.418 Å, the cyclic C═C bond within 1.260−1.404 Å, and S−C bonds within 1.626−1.798 Å.

The acceptor molecules **1f** and **8** have a boatlike distortion in both structures **I** and **II**, although each ring of the tricyclic system is planar. In **I**, the dihedral angle between the two benzene rings of **1f** is 11.2° and the angles between each benzene ring and the five-membered ring are 5.8 and 5.6°; in **II** these angles for **8** are 7.6, 3.2, and 4.4°, respectively. Such distortion was also observed in the structure of pure **1f**[15] and also in a fluorene acceptor with intramolecular charge transfer, viz. 2,4,5,7-tetranitro-9-(α-cyano-α-dimethylaminomethylene)fluorene (**10**),[37] where such distortion was attributed to steric hindrance and electrostatic repulsion between the two adjacent nitro groups in positions 4 and 5. In the complexes **I** and **II**, these nitro groups in **1f** and **8** are rotated from the planes of the corresponding benzene rings by 32−33° and 40−39°, respectively, whereas rotations of ca. 35° for **1f**[15] and 34° and 40° for **10**[37] were observed. For a number of other 4,5-dinitrosubstituted fluorenes, similar values (26.4−41.7°) were obtained.[13,14,38] It should be noted for comparison that for the nonhindered nitro groups in positions 2 and 7 the dihedral angles with the corresponding benzene rings in acceptor **1f** of complex **I** are only 13.5−14.9°, which is comparable with literature data for other 2,7-dinitrosubstituted fluorenes (7.4−20°).[39] In addition, out-of-plane displacements of nitrogens in positions 4 and 5 by 0.33 and −0.33 Å in **I** and 0.22 and −0.31 Å in **II**, respectively, and specific distortions of exocyclic angles at C(4) and C(5) atoms are observed.

The bond lengths in the acceptor molecules of **I** and **II** are basically similar to those in previously studied derivatives.[15,37] The exocyclic double bonds C(9)═C(14) of **1f** in complex **I** [1.389(8) Å] and of **8** in complex **II** [1.379(6) Å] are somewhat longer than that in the acceptor molecule **1f** [1.372(15) and 1.336(14) Å for two independent molecules[15]] and are close to that for acceptor **10** [1.388(4) Å] in which this bond is involved in intramolecular charge transfer (**10′**) which leads to decreasing bond order (Chart 2).

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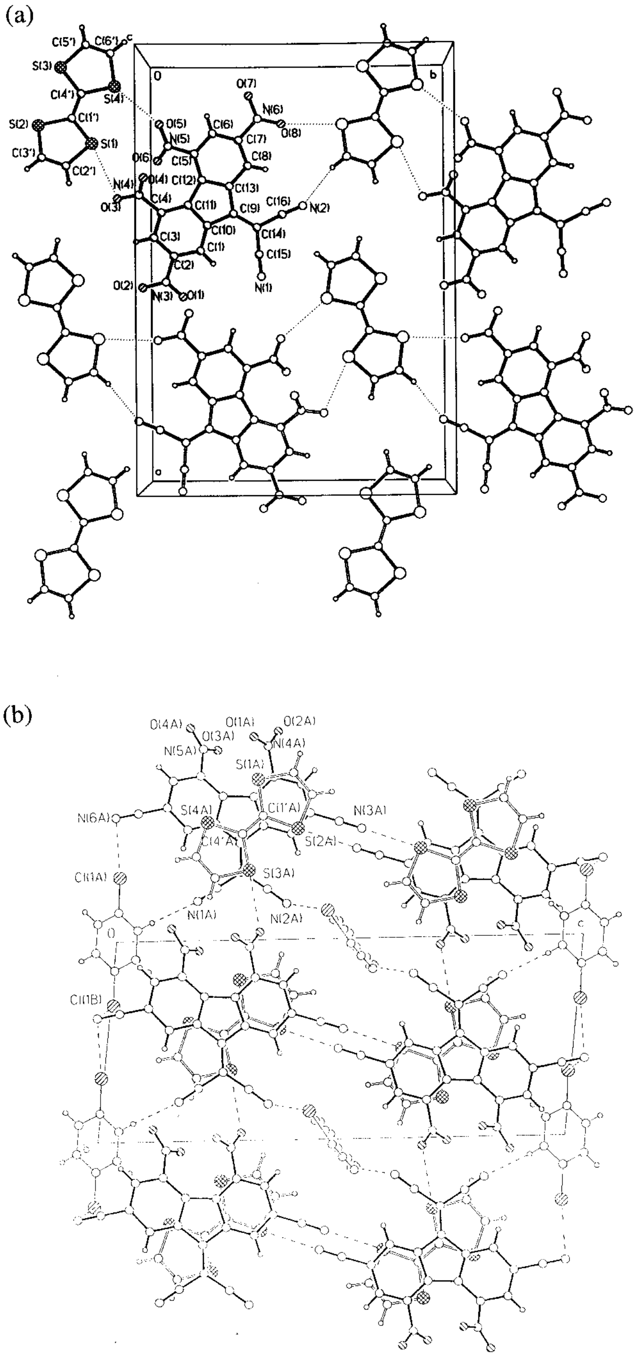
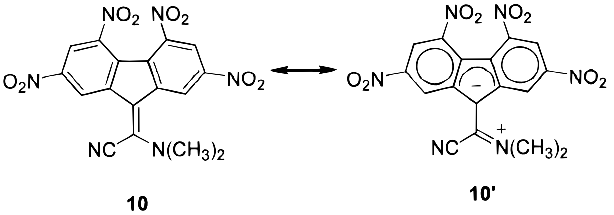


Figure 9. Specific intermolecular interactions in adjacent stacks of complexes **I** (a) and **II** (b).

Chart 2



10 **10'**

Conclusions

In summary, we have synthesized new strong electron acceptors **7**−**9** of the fluorene series. Cyclic voltammetric and spectroelectrochemical studies on **7** and **8** establish that these compounds undergo three separate reversible (or quasi-reversible) single-electron reduction processes. Single-crystal X-ray structures for two complexes of TTF with the aceptors **1f** and **8** have been obtained: they are characterized by mixed ··A···D···A···D·· stacking motifs and there is weak interplanar charge transfer. CTC formation of **7** and **8** with *N*-propylcarbazole has been demonstrated in solution. These studies establish that new fluorene derivatives are promising acceptor molecules for the development of organic semiconductors, conductors, and photoconductors.

Experimental Section

Electrochemical Measurements. Cyclic voltammetry experiments were performed on a EG&G PARC model 273 potentiostat with an Advanced Bryans XY recorder with *iR* compensation. Platinum wire, platinum disk (diameter 1.6 mm, BAS), and Ag/Ag$^+$ (AgNO$_3$ in acetonitrile) were used as counter, working, and reference electrodes, respectively. All potentials were corrected using the ferrocene−ferrocenium couple as internal reference and represented versus Ag/AgCl which showed in these conditions a potential of −0.45 V against the Fc^0/Fc$^+$ couple. CV experiments were performed in dry acetonitrile (Fluka, anhydrous) with Et$_4$N$^+$BF$_4^-$ (Fluka, puriss.) as supporting electrolyte (0.2 mol dm^{-3}) under N$_2$ flow; concentrations of acceptors were ca. 10^{-4} mol dm^{-3}. The scan rate was 100 mV s^{-1}.

Spectroelectrochemical Measurements. Spectroelectrochemistry was undertaken using a Perkin-Elmer Lambda 19 UV−vis−near-IR spectrophotometer with a Ministat (Thompson Electrochem. Ltd, Newcastle upon Tyne, U.K.). The spectroelectrochemical cell was based on a 1 cm thick cuvette; Pt wire was used as a counter electrode while Ag wire served as the quasi-reference electrode (all potentials were corrected to Ag/AgCl). A thin layer working electrode was constructed from glass and indium tin oxide conducting glass (sheet resistance is 30 Ohm cm^{-2}, from Balzers) held together with 0.1 mm thick PTFE spacer (from Goodfellow).

Single-Crystal X-ray Structure Determinations. Crystals of complexes of **1f**:TTF (1:1 stoichometry) and **8**:TTF:C$_6$H$_5$Cl (1:1:1 stoichometry) were obtained as long black needles by addition of a solution of TTF in chlorobenzene to a hot concentrated solution of the appropriate acceptor, i.e. **1f** or **8**, in the same solvent, followed by very slow cooling to room temperature.

Details of data collection, structure solution, and refinement are given in Table 4.

In the structure of **II**, two independent C$_6$H$_5$Cl solvent molecules were found to occupy the positions around different symmetry centers, resulting in disordering of the C$_6$H$_5$Cl molecules. For one of the molecules, the symmetry center coincides with the center of its benzene ring. As a result, the Cl substituent appears in two positions [C(1) and C(4)] of the benzene ring with a half occupancy for each position. For the second solvent molecule, the center of its benzene ring is shifted from the symmetry center, so the resultant appearance of the disordered molecule is more complicated. A pair of symmetrically related atoms C(5″) in sites 2 and 6 have the same coordinates for both disordered positions of the second solvent (site occupancy factor is 1). The other atoms have different coordinates (site occupancy factor is 0.5 for each atom).

The structures were solved and refined using SHELXS86[40] and SHELXL93[41] software. Software SHELXTL-Plus[42] was used for graphics and preparation of material for publication. Additional materials containing atomic coordinates, thermal

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Table 4. Crystal Data, Data Collection, and Structure Solution and Refinement Parameters for I and II

compd	**I** (**1f**:TTF, 1:1)	**II** (**8**:TTF:PhCl, 1:1:1)
empirical formula	$C_{22}H_8N_6O_8S_4$ $C_{16}H_4N_6O_8{:}C_6H_4S_4$	$C_{30}H_{13}ClN_6O_4S_4$ $C_{18}H_4N_6O_4{:}C_6H_4S_4{:}C_6H_5Cl$
form wt	612.58	685.15
color, habit	black, needle	black, needle
crystal size, mm	1.10 × 0.18 × 0.08	0.14 × 0.06 × 0.04
crystal system	orthorhombic	triclinic
space group	$Pna2(1)$	$P\bar{1}$
unit cell dimensions		
a, Å	21.958(4)	7.204(2)
b, Å	15.447(3)	9.500(2)
c, Å	6.8810(10)	21.660(5)
α, deg	90	96.25(2)
β, deg	90	92.72(2)
γ, deg	90	95.95(2)
volume, $Å^3$	2333.9(7)	1463.0(6)
Z	4	2
density (calcd), g cm^{-3}	1.743	1.555
abs coeff, mm^{-1}	0.474	0.466
$F(000)$	1240	696
diffractometer	Siemens SMART	Rigaku AFC-6S
temperature, K	150.0(2)	150(2)
radiation (λ, Å)	graphite monochromatized Mo Kα (0.71073)	graphite monochromatized Cu Kα (1.54184)
scan mode	ω	ω
scan step/width (in ω), deg	0.3	$1.0 + 0.15\tan(\theta)$
time/step (sec); scan rate, deg/min	15	8
θ range, deg	1.61–25.30	4.11–74.98
index ranges	$-24 \leq h \leq 21$ $-17 \leq k \leq 17$ $-8 \leq l \leq 7$	$-8 \leq h \leq 8$ $0 \leq k \leq 11$ $-27 \leq l \leq 26$
reflectns collected	9469	5697
indep reflectns	3721 [R(int) = 0.1125]	5367 [R(int) = 0.0245]
data reduction	Siemens SAINT (Siemens Analytical X-ray Instruments, 1995)	TEXSAN PROCESS (Molecular Structure Corporation, 1985)
absn corrctn	empirical (SHELXTL-Plus)	empirical (psi scan)
min and max transmission	0.6276 and 0.4944	1.0000 and 0.5472
solution method	direct methods (SHELX-86)	direct methods (SHELX-86)
refinement method	full-matrix l.s. on F^2 (SHELXL-93)	full-matrix l.s. on F^2 (SHELXL-93)
hydrogen treatment	H atoms were found from difference Fourier synthesis and refined with isotropic thermal parameters	All H atoms were placed in calculated positions and refined using riding model [$B_H = 1.2B_C$; d(C−H) = 0.93 Å]
data/restraints/parameters	3715/1/362	5367/15/434
goodness-of-fit on F^2	1.083	1.081
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0686$, $wR_2 = 0.1775$	$R_1 = 0.0588$, $wR_2 = 0.1294$
R indices (all data)	$R_1 = 0.0718$, $wR_2 = 0.1860$	$R_1 = 0.0982$, $wR_2 = 0.1520$
abs structure param	0.08(13)	
extinction coeff	0.0045(10)	0.0016(2)
largest diff peak and hole, e $Å^{-3}$	0.938 and −0.444	0.546 and −0.558

parameters, bond lengths and angles are available from the Cambridge Crystallographic Data Center.[43]

2,4,5,7-Tetranitro-9-dicyanomethylenefluorene (1f). This was prepared according to our modified procedure for condensation of fluoren-9-ones with malononitrile.[1,11c,12,37] 2,4,5,7-Tetranitrofluoren-9-one (**1c**) (1.80 g, 5 mmol) was dissolved in DMF (10 mL), malononitrile (0.73 g, 11 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h and diluted with propan-2-ol (40 mL). The yellow-green solid was collected by filtration, washed with propan-2-ol, and dried yielding compound **1f** (1.96 g, 96%). Recrystallization from dioxane gave analytically pure yellow crystals of **1f** (1.30 g, 64%), mp > 360 °C, which were identical to an authentic sample.[3b]

Fluoren-9-one-2,7-dicarboxylic Acid (4). 2,7-Diacetylfluorene[29] (60.0 g, 0.235 mol) was refluxed with 60% nitric acid (1200 mL) for ca. 5 h with water being distilled off water until the temperature of the distillate had reached 119 °C. The reaction mixture was left overnight, and the yellow solid was filtered off and washed with water. It was dissolved in a solution of sodium carbonate (ca. 500 mL) and filtered off from solid impurities, and the solution was poured into diluted nitric acid. The solid was filtered off and washed with water, yielding acid **4** (58.5 g, 92.8%), which can be used in the next step without purification; mp > 360 °C (lit.[29] mp 400 °C dec).

4,5-Dinitrofluoren-9-one-2,7-dicarboxylic Acid (5). Fluoren-9-one-2,7-dicarboxylic acid (**4**) (40.0 g, 0.149 mol) was refluxed with a mixture of fuming nitric acid (600 mL, d = 1.51 g cm^{-3}) and concentrated sulfuric acid (400 mL) for 2 h, cooled to room temperature, and poured into ice water (2 L). The pale yellow solid was filtered off, washed with water, and dried yielding crude acid **5**. The acid was extracted for 1.5 days in Soxlet apparatus by acetonitrile, yielding acid **5** (40.5 g, 75.8%), mp 357–360 °C (lit.[29] mp 285–294 °C). Alternatively, acid **5** can be purified by recrystallization from acetic acid.

4,5-Dinitrofluoren-9-one-2,7-dicarboxamide (6). Dicarboxylic acid **5** (11.0 g, 0.0307 mol) was refluxed with thionyl chloride (50 mL) for 3–4 h giving a dark yellow solution. The excess thionyl chloride was removed under low pressure, the residue was dissolved in dry dioxane (100 mL), and ammonia gas was passed through the stirred solution until pH 8 was reached (no excess NH_3). After cooling, the reaction mixture was diluted with water (100 mL) and the precipitate was filtered off, washed with water, and dried yielding crude diamide (9.5 g, 86.5%). Recrystallization from DMF (250 mL) gave **6** (8.05 g, 73.5%) as a yellow powder, mp > 300 °C dec:

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[43] The authors have deposited atomic coordinates for **I** and **II** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

^{1}H NMR (250 MHz; DMSO-d_6) δ 8.69 (2H, d, $J_{1,3}$ = 1.5 Hz), 8.60 (2H, d, $J_{1,3}$ = 1.5 Hz), 8.58 (2H, s, broad), 7.98 (2H, s, broad). Anal. Calcd for $C_{15}H_8N_4O_7$: C, 50.57; H, 2.26; N, 15.73. Found: C, 50.40; H, 2.16; N, 15.65%.

2,7-Dicyano-4,5-dinitrofluoren-9-one (7). A mixture of diamide **6** (0.56 g, 1.57 mmol), $POCl_3$ (2 mL), and DMF (0.1 mL) was refluxed for 30 min (complete disolution occurred in 5−7 min). The excess $POCl_3$ was removed in vacuo, the residue was thoroughly mixed with water (10 mL), and the precipitate was filtered off and washed with a large volume of water yielding a light-brown powder of crude dinitrile (0.52 g, ≈100%). This product was refluxed in toluene (18 mL), filtered through a 1 cm layer of Al_2O_3, and then washed with boiling toluene (4 mL). Pure **7** (0.16 g, 32%) crystallized on cooling the combined toluene solutions, mp 278−280 °C. An additional portion of the product (0.08 g, 16%) was obtained by evaporation of two-thirds of the mother liquor: ^{1}H NMR (400 MHz; acetone-d_6) δ 8.80 (2H, d, $J_{1,3}$ = 1.4 Hz), 8.60 (2H, d, $J_{1,3}$ = 1.4 Hz); ^{13}C NMR (63 MHz; acetone-d_6) δ 185.84, 147.27, 138.77, 137.15, 135.35, 132.50, 117.46, 116.43. Anal. Calcd for $C_{15}H_4N_4O_5$: C, 56.26; H, 1.26; N, 17.49. Found: C, 56.10; H, 1.31; N, 17.45%.

2,7-Dicyano-4,5-dinitro-9-dicyanomethylenefluorene (8). Malononitrile (31 mg, 0.47 mmol) was added to a solution of fluorenone **7** (127 mg, 0.397 mmol) in DMF (1 mL), and the reaction mixture was stirred for 40 min at room temperature (TLC monitoring). The reaction mixture was diluted with propan-2-ol (10 mL) and left to crystallize at 0−5 °C overnight. The precipitate was filtered off and washed with propan-2-ol yielding a dark yellow powder of **8** (100 mg, 69%). Recrystallization from toluene−dioxane mixture (3:1 v/v) gave pure product **8** (94 mg, 64%), mp 285−287 °C: ^{1}H NMR (250 MHz; acetone-d_6; 1 drop of CF_3COOD) δ 9.20 (2H, d, $J_{1,3}$ = 1.3 Hz), 8.86 (2H, d, $J_{1,3}$ = 1.3 Hz); ^{13}C NMR (63 MHz; acetone-d_6) δ 147.57, 139.28, 134.51, 134.26, 133.73, 129.16, 116.93, 116.53, 113.59, 113.16. Anal. Calcd for $C_{18}H_4N_6O_4$: C, 58.71; H, 1.09; N, 22.82. Found: C, 58.60; H, 1.10; N, 22.70%.

2,7-Dicyano-4,5-dinitrofluoren-9-one Oxime (9). Finely powdered dry hydroxylamine hydrochloride (123 mg, 1.77 mmol) was added to a solution of fluorenone **7** (196 mg, 0.613 mmol) in DMF (1.5 mL), and the reaction mixture was stirred at 60 °C for 2 h (TLC monitoring of the reaction). The reaction mixture was cooled to room temperature and diluted with water (2 mL), and the resulting precipitate was filtered off, washed with water, and dried yielding crude **8** (161 mg, 78.5%). Recrystallization from a dioxane−propan-2-ol mixture (1:5 v/v) gave pure oxime (150 mg, 73%), mp >300 °C: ^{1}H NMR (400 MHz; acetone-d_6) δ 9.27 (1H, d, $J_{1,3}$ = 1.5 Hz), 8.68 (1H, d, $J_{1,3}$ = 1.3 Hz), 8.63 (1H, d, $J_{1,3}$ = 1.5 Hz), 8.59 (1H, d, $J_{1,3}$ = 1.3 Hz); ^{13}C NMR (63 MHz; acetone-d_6) δ 147.67, 147.37, 147.20, 141.53, 136.24, 133.95, 132.36, 131.33, 131.09, 130.22, 129.88, 117.03, 116.97, 116.21, 115.65. Anal. Calcd for $C_{15}H_5N_5O_5$: C, 53.74; H, 1.50; N, 20.89. Found: C, 53.90; H, 1.62; N, 20.80.

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Supporting Information Available: X-ray crystallographic data for structures **I** and **II** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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