Dithiadiazafulvalenes—New Strong Electron Donors. Synthesis, Isolation, Properties, and EPR Studies

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Abstract: Several dithiadiazafulvalenes, which are potent electron donors, were isolated as pure compounds for the first time. Solid charge-transfer complexes with TCNQ and also cation-radical and dication salts with perchlorate gegenions were obtained. Two of the TCNQ complexes are moderately conductive at room temperature (0.083 and 0.011 S/cm). A solution EPR study, combined with theoretical calculations, allowed the determination of the relative equilibrium cation-radical and anion-radical concentrations.

Introduction

The synthesis and redox properties of tetrathiafulvalene (TTF) **1**, its selenium and tellurium analogs, and their derivatives constitute a most significant sector of organic metals chemistry.[1] Modification of the heterocyclic core of TTF by replacing some or all of the four sulfurs by nitrogens should be expected to give rise to new classes of organic donors. Studies aimed at the synthesis and isolation of such compounds, especially tetraazafulvalenes and dithiadiazafulvalenes, have thus far met with only limited success.

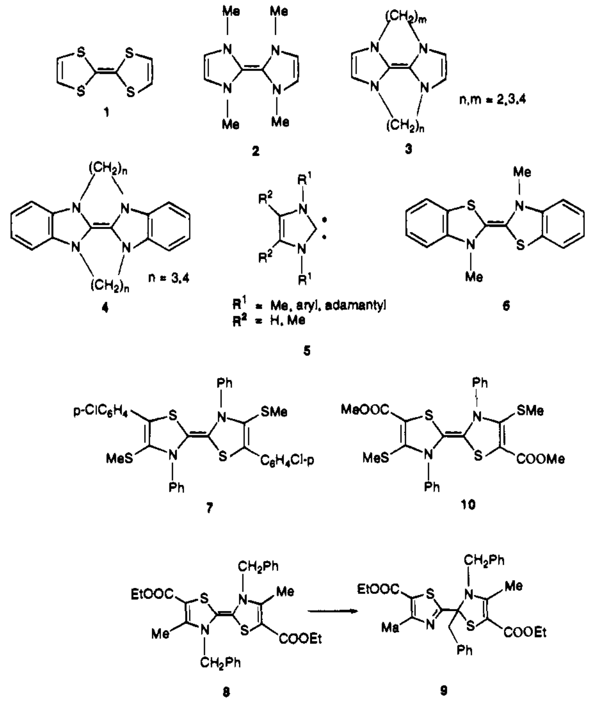
In 1989, Thummel and co-workers commented on the difficulty of preparing the TTF tetraaza analogs **2** and **3**.[2] Electrochemical studies of the dicationic oxidized salts of the desired compounds indicated extremely high donating properties for the neutral forms **2** and **3**, which made their isolation impossible. Moreover, even benzofusion proved to be barely sufficient to stabilize the neutral species **4**; these were extremely sensitive to oxygen but could be conclusively characterized by NMR.[3a,b]

Recently, Arduengo et al. prepared the first remarkably stable crystalline carbenes **5**.[4a] It has been also demonstrated that such carbenes have a very minimal tendency toward dimerization.[4b]

Bis(1,3-thiazoline-2)ylidenes (dithiadiazafulvalenes) and the related thiazolium carbenes have received considerable attention from both the chemical and biological points of view, as possible intermediates formed by the deprotonation of thiazolium salts.[5–7] The question of the function of these species as catalysts in the benzoin condensation has been the subject of some recent interests.[8]

In the last few years, dithiadiazafulvalenes (DTDAFs) have attracted attention as electron donors possessing TTF-like two-wave redox behavior,[7,9,10] making them potential components for the synthesis of conducting charge-transfer salts.[10] The first compound of this family, the air-sensitive benzannelated derivative **6**, was already reported by Metzger et al. in 1964.[11] Later attempts to isolate other examples lacking benzannelation led to compounds having very negative oxidation potentials; these were too sensitive to be conventionally isolated in crystalline form and characterized.[7,9] Robert and co-workers generated

Chart I



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[3] (a) Shi, Z.; Thummel, R. P. *Tetrahedron Lett.* **1994**, *35*, 33; (b) Shi, Z.; Thummel, R. P. *Tetrahedron Lett.* **1995**, *36*, 2741.

[4] (a) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530. (b) Arduengo, A. J. III; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812. Estimated ΔG_{298} for the dimerization obtained at the MNDO/AM1 level is close to 0 kcal/mol, which would predict that such dimers might not be even capable of existance or would be extremely reactive and an unstable species.

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[6] Doughty, M. B.; Risinger, G. E. *Bioorg. Chem.* **1987**, *15*, 1. Sigmatropic rearrangement was first documented in 1977: Baldwin, J. E.; Branz, S. E.; Walker, J. A. *J. Org. Chem.* **1977**, *42*, 4142.

[7] Bssaibis, M.; Robert, A.; Lemaguerès, P.; Ouahab, L.; Carlier, R.; Tallec, A. *J. Chem. Soc., Chem. Commun.* **1993**, 601.

[8] Breslow, R.; Kim, R. *Tetrahedron Lett.* **1994**, *35*, 699.

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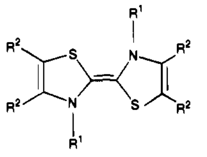
DTDAF **7** *in situ* and trapped it as a complex with tetracyanoquinodimethane (TCNQ).[7] Bordwell and Satish generated several unstable alkyl-substituted bis(1,3-thiazoline-2)ylidenes *in situ* and detected their existence electrochemically. However, an attempt to isolate one of these compounds led only to oxidation products.[9] Similar oxidation was also observed by Robert.[7] Doughty and Risinger observed the migration of a benzyl group on attempting to prepare DTDAF **8** from the corresponding 2-unsubstituted thiazolium salt and triethylamine, leading to the formation of the rearranged product **9**.[6] The only isolable noncondensed crystalline compound of this type reported to date, DTDAF **10**, has a first oxidation potential of 0.00 V (vs SCE), making it extremely labile to oxygen.[10]



11 R^1 = Me, R^2 = COOMe
12 R^1 = Ph, R^2 = COOMe
13 R^1 = Me, R^2 = CN

We now report the synthesis and properties of the new isolable DTDAF series **11**–**13**, in which stabilization is achieved by four electron-withdrawing substituents. These donors as well as the previously reported analog **10** have been converted into a series of conducting charge-transfer complexes by TCNQ. Experimental and calculated EPR coupling constants and g-values of these complexes are reported in solution.

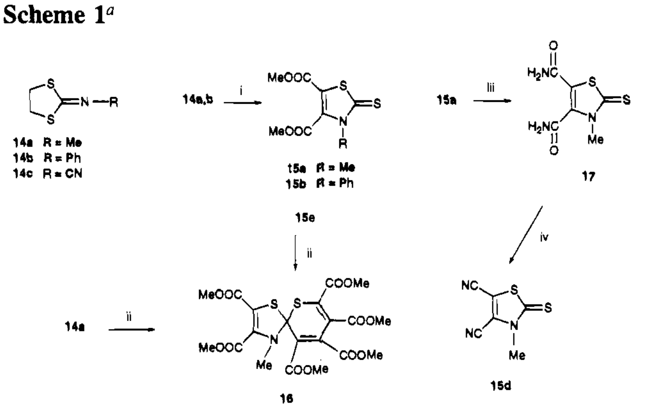
Synthetic Results

The target molecules **11**–**13**, having four electron-withdrawing groups in the 4,4′ and 5,5′ positions, were chosen in order to moderate the strong donating properties and high reactivity of the basic system toward oxygen.

The precursor 4,5-dicarbomethoxy-1,3-thiazoline-2-thiones **15a,b** were prepared by the [3 + 2] cycloaddition of the N-substituted imino-1,3-dithiolanes **14a,b** with dimethyl acetylenedicarboxylate (DMAD). Of the two reported procedures,[12] that of Vialle[12a] was modified by us and afforded **15a,b** in 72% and 84% yields, respectively (Scheme 1). The reactivity of imines **14a,b** was found to decrease considerably going from **14a** to **14b**. Thus, **14a** reacts smoothly with DMAD in the ratio of 1:1 to give **15a** as the major product, while the reaction with an excess of the acetylene derivative produced the known spiro compound **16**[12a] as the major product after refluxing for 15 h. In contrast, thione **15b** was the main product obtained from **14b** even after 30 h reflux with a twofold excess of DMAD. An attempt was made also to react DMAD with the *N*-cyanoimine **14c**, but the latter proved to be inert as a 1,3-dipole, and no reaction took place.

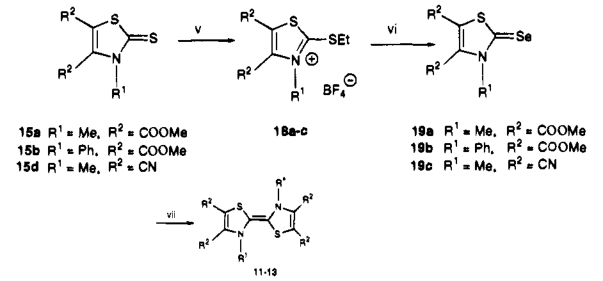
Treatment of diester **15a** with ammonia in saturated methanol solution gave diamide **17** in 78% yield. Dehydration of **17** was examined under a variety of conditions, i.e., with $SOCl_2$ or $POCl_3$ in anhydrous acetonitrile, with neat polyphosphoric acid, and with $SOCl_2$ or $POCl_3$ in tetramethylene sulfone. Only the dehydration with $POCl_3$ in sulfolane at 110 °C gave **15d** in good yield, while under the other conditions the reaction led to intractable mixtures.

Scheme 1[a]



[a] (i) DMAD, xylene, reflux, 72%, **15a**, 84%, **15b**; (ii) DMAD excess, xylene, reflux; (iii) NH_3 (gas), MeOH, 2 days, 78%; (iv) $POCl_3$, tetramethylene sulfone, 100 °C, 5 h, 69%.

Scheme 2[a]



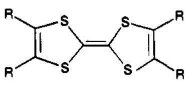
[a] (v) $HC(OEt)_3$, $Et_2O{\cdot}BF_3$, $CHCl_3$; (vi) NaHSe, EtOH, 96%, **19a**; 95%, **19b**, 79%, **19c**; (vii) $P(OEt)_3$, 100 °C, 84%, **11**; 91%, **12**; 58%, **13**.

Thiones **15a,b,d** were converted to the corresponding 2-(alkylthio)-1,3-thiazolium salts **18**, treatment of which with sodium hydrogen selenide afforded selones **19a**–**c**; the latter were coupled by treatment with triethyl phosphite to give DTDAF derivatives **11**–**13**. (Scheme 2).

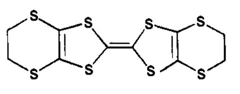
Cyclic Voltammetry

Compounds **11**–**13** proved to be excellent donors, and showed two quasi-reversible oxidation waves in accordance with Scheme 3.

The redox values of **11**–**13**, as determined by cyclic voltammetry, are outlined in Table 1 in comparison with the corresponding values of DTDAF **10** as well as TTF **1**, tetramethyltetrathiafulvalene (TMTTF) **20**, tetracarbomethoxy TTF (TTFE$_4$) **21**, and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, ET) **22**. The first oxidation potentials correlate well with the first ionization potentials calculated by AM1.



1 R = H
20 R = Me
21 R = COOMe



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The first oxidation potentials of **10**–**13** are considerably lower than those observed for major TTF systems. Tetracyanosubstituted **13** is the only compound of the DTDAF family with redox behavior comparable with the TTF family. Surprisingly,

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[12] (a) Gueden, C.; Vialle, J. *Bull. Soc. Chim. Fr.* **1973**, *1*, 270. (b) It should be noted that the later reported cyclization of iron pentacarbonyl derivatives with dimethyl acetylenedicarboxylate: Ngounda, M.; Le Bozec, H.; Dixneuf, P. *J. Org. Chem.* **1982**, *47*, 4000; where the authors describe the preparation of **15a** (32%, mp 78–80 °C), and **15b** (25%, presumably an oil), led to compounds **15a,b** with considerably different melting points. However, since the reported HRMS and ^{1}H NMR data correspond to the expected values, we assume, that the described thiones **15a,b** were not completely purified.

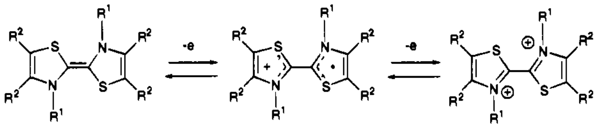
Table 1. Cyclic Voltammetry[a] for DTDAFs **10** and **11–13** and for other Compounds of Interest[b,c]

compd	solvent	E^p_1, V vs SCE	$E^{1/2}_1$, V vs SCE	E^p_2, V vs SCE	$E^{1/2}_2$, V vs SCE	ΔE, V	I_{calc}, eV
10	a	0.00	−0.05	0.48	0.43	0.48	6.86
	b	−0.02	−0.06	0.48	0.43	0.46	
11	a	0.10	0.06	0.45	0.41	0.35	7.36
	c	0.14	0.10	0.48	0.43	0.34	
	b	0.02	−0.02	0.26	0.23	0.24	
12	a	0.15	0.11	0.66	0.62	0.55	7.47
	c	0.18	0.14	0.66	0.61	0.48	
	b	0.13	0.09	0.61	0.57	0.48	
13	b	0.42	0.38	0.63	0.59	0.21	7.90
TTF, **1**[13]	a[13]	0.35		0.71		0.36	7.10
	b[14]	0.32		0.70		0.38	
TMTTF, **20**[13]	b	0.29		0.65		0.36	
BEDT-TTF, **22**	a	0.58		1.00		0.42	
TTFE$_4$, **21**[13]	b	0.83		1.10		0.27	

compd	solvent	E^p_1, V vs SCE	$E^{1/2}_1$, V vs SCE	E^p_2, V vs SCE	$E^{1/2}_2$, V vs SCE	ΔE, V	A_{exp}, eV
TCNQ	a	0.11	0.19	−0.49	−0.42	0.60	3.3[14]
	c	0.05	0.15	−0.54	−0.45	0.59	
	b	0.18	0.22	−0.40	−0.35	0.58	

[a] First and second oxidation peak potentials E^p_1 and E^p_2 (V vs SCE); estimated half-wave potentials $E^{1/2}_1$ and $E^{1/2}_2$ (V vs SCE; estimated as midway between oxidation and corresponding reduction). [b] For the electron acceptor TCNQ the entries are peak and half-wave potentials for reduction, rather than oxidation. Also given are the calculated difference $\Delta E = E^p_2 - E^p_1$, and the calculated first ionization potentials I_{calc} (vertical, AM1) for the electron donors, and the experimental gas-phase electron affinity A_{exp} for TCNQ. [c] Experimental conditions: concentration of **11–13** (ca. 1 × 10^{-3} M), electrolyte $Bu_4N^+PF_6^-$ (ca. 1 x 10^{-2} M), scan rate 70 mV/s. Solvent code: a = 1,2-dichloroethane, b = acetonitrile, c = methylene chloride.

Scheme 3



13 was extremely unstable in solutions of MeOH, CH_3CN, or $CHCl_3$ and decomposed within a few minutes. As noted before for TTF systems,[15] the redox potentials are moderately dependent (±0.1 V) on the polarity of the solvent. For compound **11**, the second oxidation potential E^2_{ox} shifts by an unusually large 0.22 V between acetonitrile and methylene chloride solutions.

Table 1 illustrates some interesting features. Although the $E^{1/2}_1$ values for DTDAFs **10**, **11**, and **12** are considerably lower than those observed for TTFs **1**, **20**, and **22**, they are positive for **11**, **12**, and **13**, in contrast to the negative literature values for DTDAFs **6**[11] and **7**.[7] On the other hand, for **11** and **12** the electron density balance achieved between electron donating nitrogen and four electron-withdrawing carbomethoxy groups is just perfect, while the TTF analog **21** possesses extremely high oxidation potentials (E^p_1 = 0.82, E^p_2 = 1.10 V vs SCE), making **21** useless for charge-transfer salt preparations.[1]

It has often been stated that, to form organic metals, both the cation-radical and the dication must be stable species and that the two oxidation waves in cyclic voltammetry must be well separated. For instance (Table 1), this difference $\Delta E = E^p_2 - E^p_1$, is 0.3 to 0.4 V for TTF, **1**, and for BEDT-TTF, **22**, both of which make exciting charge-transfer complexes and ion-radical salts. For the *N*-phenyl substituted donors **10** and **12** ΔE = 0.46 to 0.48 V, which is approximately twice the ΔE = 0.24 to 0.21 V for *N*-methyl substituted **11** and **13**. In phenyl-containing donors the greater charge delocalization probably gives added stability to the monocation-radical.

Table 2. Approximate Estimates of the Electrochemical Cell Potentials $E_{cell}(1)$ for Reaction 1 and $E_{cell}(2)$ for Reaction 2, for the case A = TCNQ[a]

donor (D)	solvent	$E_{cell}(1)$	$E_{cell}(2)$
10	a	0.11	−0.86
11	a	0.01	−0.93
12	a	−0.04	−1.19
13	b	−0.24	−1.25
TTF, **1**	b	−0.14	−1.24 δ
	a	−0.25	−1.43

[a] Solvent code: a = 1,2-dichloroethane, b = acetonitrile. (§) −1.24 = −0.32 − 0.70 + 0.18 − 0.40.

It is of some interest to consider the possible reactions:

$$\mathrm{D(soln)} + \mathrm{A(soln)} \rightleftarrows \mathrm{D^+(soln)} + \mathrm{A^-(soln)} \qquad (1)$$

$$\mathrm{D(soln)} + \mathrm{A(soln)} \rightleftarrows \mathrm{D^{++}(soln)} + \mathrm{A^{2-}(soln)} \qquad (2)$$

The spontaneity of eqs 1 and 2 is controlled by the Nernst equation. Since the activity coefficients for the various solute species are unavailable, and the concentrations of the cation-radical and anion-radical are not known in the voltammetric oxidation to D^{2+} and reduction to A^{2-}, therefore only an approximate estimate can be made as to the spontaneity of the reaction. Table 2 shows approximate estimates of the cell potentials, under the concentration conditions used to get the voltammetric data of Table 1.

As discussed previously,[15] the simultaneous oxidation of TTF to TTF^+ and reduction of TCNQ to $TCNQ^{\bullet-}$ is not spontaneous in solution: the electron transfer (partial) occurs only in the solid state complex. For the electron transfer reaction

$$\mathrm{TTF(CH_3CN)} + \mathrm{TCNQ(CH_3CN)} \rightleftarrows \mathrm{TTF^{\bullet+}(CH_3CN)} + \mathrm{TCNQ^{\bullet-}(CH_3CN)}$$

E° = −0.20 was estimated,[15] the calculated equilibrium constant was 6.3 × 10^{-3},[16] and the measured constant was 2.5 × 10^{-3}.[17] In dioxane, however, the equilibrium lies on the right-hand

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(13) Khodorkovsky, V.; Edzina, A.; Neilands, O. *J. Molecular Electronics* **1989**, *5*, 33.

(14) Jin, C.; Haufler, R. E.; Bashick, C. M.; Compton, R. N.; Puretzky, A. A.; Demyanenko, A. V.; Tuinman, A. A. *Science* **1994**, *263*, 64.

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Table 3. Room Temperature Conductivities of Complexes of **10**, **11**, and **12** with TCNQ (Measured on Compactions by the 2-Probe Method Using Gold Paste Contacts to Gold Wire)

donor	acceptor	ratio	conductivity σ, S cm^{-1}
10	TCNQ	1:1	1.6×10^{-7}
	TCNQ	1:4:2 CH_3CN	1.1×10^{-7}
11	TCNQ	1:4	8.3×10^{-2}
12	TCNQ	1:1	10^{-10}
	TCNQ	2:5	1.1×10^{-2}

side.[17] In acetonitrile, the driving force for the electron transfer is the formation of a solution complex, which may be followed by crystallization: the (partial) electron transfer in the crystal lowers the crystal lattice energy.

The data in Table 2 indicate that the donor **13** should act very much like TTF in its electron donating properties in solution, while donors **10** and **11** should spontaneously form the cation and TCNQ anion-radicals.

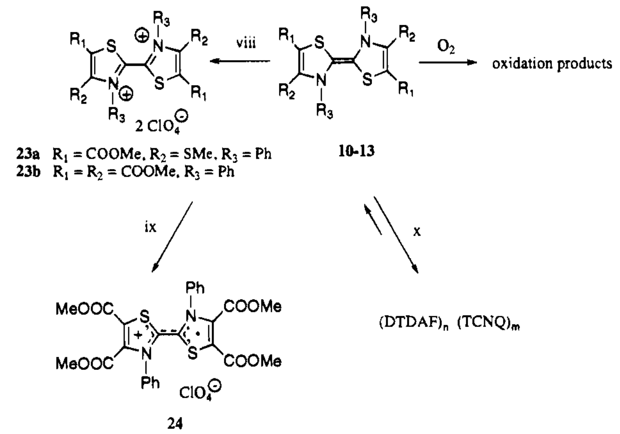
In the search for criteria of when given electron donors and electron acceptors will form a solid with high conductivity [which necessarily involves segregated stacking and a mixed valent partial electron transfer (ϱ)], one should use the gas-phase first ionization potential I_D for the donor (D) and first electron affinity A_A of the acceptor (A). For high $I_D - A_A$, the electrically insulating, mixed-stack DADADA complex will form, with low electron transfer (ϱ close to 0). If $I_D - A_A$ is very low, then the semiconducting ionic complex (ϱ close to 1) with mixed stacking $D^+A^-D^+A^-$ will result: this is the organic chemical equivalent of sodium chloride. Torrance[18] suggested that segregated stacking with mixed valence ($D^+DD^+D^+DD$ and/or $A^-AAA^-A^-AA$, ϱ between 0 and 1, usually $\varrho = 0.5-0.7$) with resultant high conductivity, will occur for "medium" $I_D - A_A$. Since A_A values are often unavailable, Torrance also proposed that differences between first solution oxidation potentials E_1 for the donor and reduction potentials E_1 for the acceptor ($E_1(D) - E_1(A)$) can be used instead.[19] Saito and Ferraris provided a numerical boundary, so that when $E_1(D) - E_1(A) > 0.02$, ionic insulators or semiconductors result; when $E_1(D) - E_1(A) < -0.34$, then neutral insulators will result.[20] By this criterion, donors **10** and **11** will tend to form ionic semiconductors with TCNQ.

There has been speculation whether solids of high conductivity are possible when the electron transfer ϱ is greater than 1, i.e., $1 < \varrho < 2$. The data of Table 2 show that, compared to TTF, donors **10** and **11** may be easier to coax into this high-ϱ state than TTF, but the reaction in solution is still not spontaneous.

Solid State Complexes and Salts

Donors **10**, **11**, and **12** form crystalline charge-transfer complexes with TCNQ which were precipitated from acetonitrile solutions at room temperature under nitrogen. Their ratios and room temperature conductivities are collected in Table 3. Crystals large enough for single-crystal conductivity measurements and X-ray analysis were not obtained. Attempted recrystallization of these complexes in all the cases resulted in the recovery of TCNQ and formation of noncrystalline black decomposition products. We assume that, upon redissolution of the complex, the equilibrium shifted to the neutral donor plus acceptor and that air oxidation of the donor occurred (Scheme 4). This is consistent with the observation that attempted recrystallization of the donors **10**−**13** in the presense of air led to extensive decomposition.

Scheme 4[a]



[a] (viii) $PhI(OAc)_2$, $HClO_4$, dioxane, 61%, **23a**; 59%, **23b**; (ix) **23b**, CH_2Cl_2, room temperature; (x) TCNQ, CH_3CN.

Donor **10** yields two solid TCNQ complexes with different stoichiometries and also the dication diperchlorate salt **23a** (as fine pale yellow needles stable for several weeks). Donor **11** yields only a single solid TCNQ complex. Donor **12** yields two solid TCNQ complexes with different stoichiometries as well as the dication diperchlorate salt **23b** (as fine pale yellow needles stable for several weeks), and also the cation-radical monoperchlorate salt **24**, stable for several days in solution, and obtained from mixing in 1:1 ratio dichloromethane solutions of neutral **12** and of the dication perchlorate **23b**. In the case of **13**, neither a solid complex nor any perchlorate salt could be isolated.

The relatively high conductivity (presumably semiconductivity) of the 1:4 complex of **11** with TCNQ, and of the 2:5 complex of **12** with TCNQ seems typical for segregated-stack TCNQ complexes, where the TCNQ species are not formally mixed-valent, and the cation functions as a counterion, rather than participating in the π electron conduction. The room-temperature compaction conductivity data are disappointing for both TCNQ complexes of **10** and the 1:1 TCNQ complex of **12**. The presence of the bulky phenyl groups in the donor **12** will make it nonplanar and impede π stacking of the donors. The donor **11** is more likely to be planar.

Robert and co-workers have solved the crystal structure of the related 1:5 complex of donor **7** with TCNQ: the nonplanar donor cation-radical functions as a counterion in the lattice, surrounding a TCNQ stack that exhibits π to π overlap between the TCNQ species; there are three crystallographically distinct TCNQ species, with formal charges estimated from the bond lengths as −0.14, −0.31, and −0.36.[21] The room-temperature single-crystal four-probe conductivity of $(\mathbf{7})_1(TCNQ)_5$ is 6×10^{-4} S cm^{-1},[7] which is typical for TCNQ complexes with stacking of mixtures of neutral TCNQ molecules and $TCNQ^{\cdot-}$ anion-radicals, without the benefits of mixed valence.

The solid 1:1 and 2:5 complexes of **12** with TCNQ were studied by EPR: the former showed a broader EPR signal (peak-to-peak line width $\Delta H_{pp} = 6.9$ G), while the 2:5 complex showed a sharper line ($\Delta H_{pp} = 2.3$ G) with significant g-factor anisotropy. The FTIR of the solid 1:1 complex showed two ν_{CN} bands at 2179 and 2151 cm^{-1}, while the 2:5 complex $(\mathbf{12})_2(TCNQ)_5$ had a broad band at 2196 cm^{-1} and a small shoulder at 2167 cm^{-1}. The position of the ν_{CN} can often be associated[22] with the charge ϱ on TCNQ ($\nu_{CN} = 2227$ cm^{-1} for neutral

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Table 4. Experimental and Calculated EPR Coupling Constants, *g*-Values, and Synthesis Conditions for the Cation-Radicals from the Donors **10–13**

radical cation	source	temp, K	atom	a_{expt}, mT	a_{INDO}, mT	*g*
10$^{\cdot+}$	1:1	295	N	0.3136(2)	0.3518	2.0055(1)
	TCNQ		H(o)		−0.0288	
	complex		H(m)		0.0244	
	CH_2Cl_2		H(p)		−0.0117	
			S	0.44(1)		
11$^{\cdot+}$	I_2	230	N	0.319(4)	0.376	2.0055(1)
	CH_2Cl_2		H(3)	0.309(3)	0.381	
12$^{\cdot+}$	1:1	295	N	0.3188(4)	0.419	2.0056(1)
	TCNQ		H(o)	0.0230(2)	−0.0342	
	complex		H(m)	0.01107(8)	0.0276	
	CH_2Cl_2		H(p)	0.0353(2)	−0.0189	
13$^{\cdot+}$	TCNQ	295	N	0.3394(15)	0.404	2.0053(1)
	complex		H(3)	0.3071	0.418	
	CH_3CN		CN	0.0381(5)	0.0105	

[a] Errors are given in parentheses and are 95% confidence intervals (the results are from eight replicate determinations for cation-radicals of **10**, **11**, and **13**, and from six replicate determinations for cation-radical of **12**).

TCNQ ($\varrho = 0$), 2183 cm^{-1} for K^+TCNQ ($\varrho = -1$); however, crystal electric fields can lead to considerable shifts,[23] and it is unwise and probably unwarranted to associate the features at 2167 or 2151 cm^{-1} to contributions from $TCNQ^{2-}$. In support of our caution, unpublished IR data from the group of Robert find similar shifted IR peaks for the complex $(\mathbf{7})_1(TCNQ)_5$,[24] while the crystal structure shows no bond length evidence for $TCNQ^{2-}$ dianions.[21]

Calculations and Simulations

The molecular geometries of the neutral donors **10–13** were obtained by geometry optimization using the AM1 semiempirical Hamiltonian[25] of computer program MOPAC;[26] the ionization potentials of the neutral molecule are listed in Table 1: these ionization potentials track well the solution first half-wave oxidation potentials of Table 1. The optimized geometry was then used with a INDO semiempirical Hamiltonian[27] to generate spin densities and calculated hyperfine tensors for the $S = 1/2$ cation-radicals of these donors as well as for the anion-radical of TCNQ.

Preliminary AM1 calculations show that the *E*-isomers are more stable than the *Z*-isomers (typically by 40–60 kJ / mol), as expected, given the degree of steric strain inherent in the cis forms. Accordingly it is reasonable to believe that it is the *E*-isomers that have been synthesized in this study.

Electron Paramagnetic Resonance Spectroscopy

The EPR spectra were measured for solution complexes of donors **10–13** with TCNQ. For the *N*-phenyl donors **10** and **12** solutions containing radicals were obtained by dissolving the solid TCNQ complexes, while for the *N*-methyl donors **11** and **13** solution radicals were obtained by adding the neutral donor to a degassed solution containing iodine or TCNQ as the acceptor.

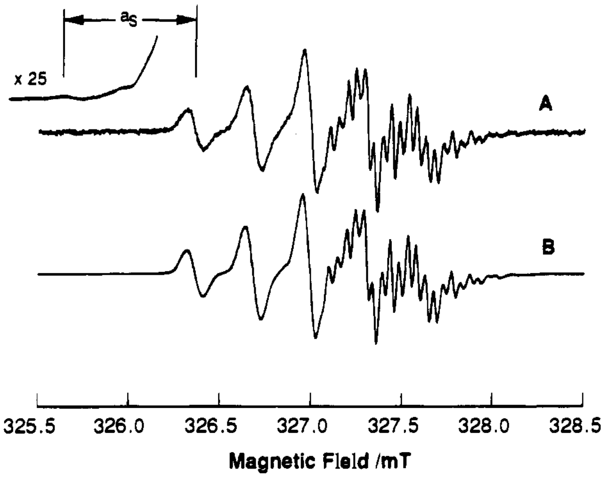

Figure 1. EPR spectrum of 1:1 Complex of **10**/TCNQ: (A) experimental; and (B) simulated Inset shows the ^{33}S coupling constant.

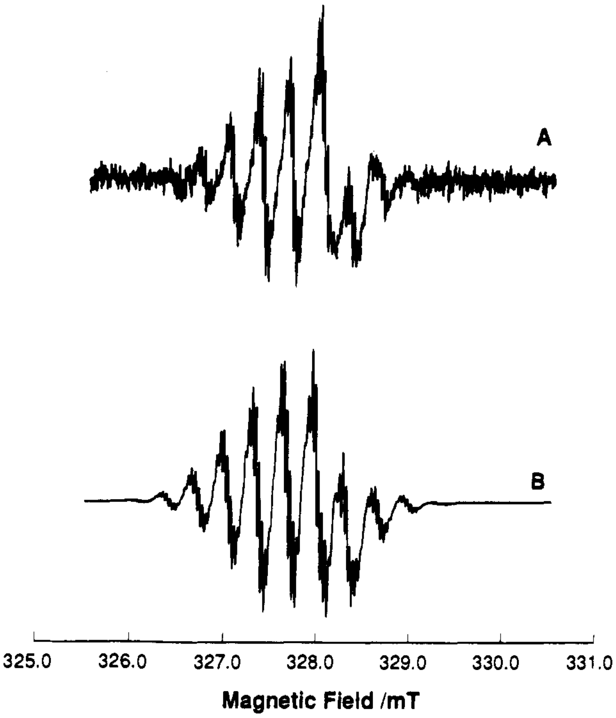

Figure 2. EPR spectrum of **13**/TCNQ: (A) experimental and (B) simulated.

Table 4 gives the experimental conditions, the *g*-values, and the EPR coupling constants determined by experiment and calculated by INDO for the cation-radicals derived from **10–13**. Figure 1 shows the EPR spectrum for the 1:1 solution complex of **10** with TCNQ, and the EPR spectrum simulated with the coupling constants given in Table 4. The EPR spectrum is made up of contributions from the cation-radical of the donor and the anion-radical form of the acceptor (TCNQ). The agreement between the experimental and fitted spectra is excellent. Figure 2 shows the EPR spectrum from donor **13** mixed with TCNQ and the simulated EPR spectrum. Again the agreement is excellent. In this case the TCNQ spectrum is not well resolved, because of broadening believed to be due to formation of the TCNQ dimer dianion.

The spectral assignments are straightforward for **10**$^{\cdot+}$ and **12**$^{\cdot+}$, but more problematic for **11**$^{\cdot+}$ and for **13**$^{\cdot+}$. For **11**$^{\cdot+}$ the coupling constants for the methyl protons and the ring nitrogens are almost interchangable. For **13**$^{\cdot+}$ the coupling constants of the methyl protons and the ring nitrogens are very close, while

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Table 5. Observed Ratios of EPR Signal Intensities Due to Donor Cation-Radical ($D^{\cdot+}$) and to Acceptor Anion-Radical ($A^{\cdot-}$)

donor	acceptor	solvent	mixing ratio	temp, K	ratio $D^{\cdot+}$:$A^{\cdot-}$ (EPR)
10	TCNQ	CH_2Cl_2	1:1	295	1:1.04(2)
	TCNQ	CH_2Cl_2	1:4:2CH_3CN	220	5.8(2):1
11	TCNQ	CH_2Cl_2	1:4	190	anion signal only
	I_2	CH_2Cl_2	excess A	230	cation signal only
12	TCNQ	CH_2Cl_2	1:1	280	1:1.03(16)
	TCNQ	CH_2Cl_2	2:5	298	1:0.96(7)
	I_2	CH_2Cl_2	excess A	290	cation signal only
13	TCNQ	CH_3CN	excess A	298	3.5(5):1
	I_2	CH_2Cl_2	excess A	298	no signal

the coupling constant of the cyano nitrogens is very small. When the nitrogen and methyl proton coupling constants were varied independently, a substantial decrease in χ^2 resulted; two minima were found, one with the nitrogen coupling constant larger than the methyl proton coupling constant, and the other with the nitrogen coupling constant smaller. The former case gave slightly better overall χ^2 values, and gives much better reproducibility in the fitted parameters. The INDO calculations predict the opposite assignment; however, the difference between the calculated coupling constants is not large, and we feel that the balance of evidence supports the assignments given in Table 4. Satellite lines due to ^{33}S were observed in the EPR spectra from $\mathbf{10}^{\cdot+}$. The value of the ^{33}S coupling constant found is similar to those reported for TTF and various derivatives which range from 0.370 to 0.470 mT.[28] Similar satellite lines were observed in the spectrum of $\mathbf{11}^{\cdot+}$ but were not well resolved. The EPR data show only one isomer present per donor, but it is not possible to determine unambigously if the *E*- or *Z*-isomers are formed.

Table 5 summarizes the observation of EPR signals from the various complexes prepared and a number of donor/acceptor pairings and gives the experimentally determined ratio of the amount of donor cation-radical ($D^{\cdot+}$) to acceptor anion-radical ($A^{\cdot-}$). In three cases this ratio is close to 1:1, and for the complexes of **12** this is irrespective of the ratio in the isolated solid complex. In the complex of **11** with TCNQ no cation-radical signal was observed, although a very strong $TCNQ^{\cdot-}$ anion-radical signal was observed. Presumably the donor is being oxidized to the dication. The cation-radical $\mathbf{11}^{\cdot+}$ was prepared using I_2 as an oxidizing agent and was stable for at least one day. The cation-radical $\mathbf{13}^{\cdot+}$ was very unstable in solution, decaying within 3−4 h (at best), hence little significance can be attached to the observed ratio of the EPR signals for the system $\mathbf{13}^{\cdot+}$ $TCNQ^{\cdot-}$.

These results on the solution phase redox properties are of some interest, because they are not always consistent with the redox properties of the donors and acceptors determined by cyclic voltammetry. The data in Tables 1 and 2 suggest that, in solution, TCNQ should easily oxidize **10**, **11**, and **12**, but not **13**, and should oxidize none of them to the dication. The EPR evidence shows that TCNQ can oxidize **10**, **12**, and even **13** to the cation-radical, but, surprisingly, not **11**. Maybe TCNQ oxidizes **11** to the diamagnetic dication, or the cation-radicals of **11**, which are expected to be fairly planar, form a diamagnetic $\pi-\pi$ solution dimer $(\mathbf{11}^{\cdot+})_2$, similar to what is known to occur in aqueous solutions of $TCNQ^{\cdot-}$.[29]

The observation of 1:1 cation:anion ratios from both the 1:1 and 2:5 complexes of **12** with TCNQ implies that the equilibria in solution are between D and D^+ and do not involve D^{2+}. One wonders why the cation-radical of **13** is unstable. The oxygen concentration in the EPR experiment is very low, so a reaction with O_2 is probably not the primary mode of decomposition of $\mathbf{13}^{\cdot+}$. It is possible that the decomposition pathway for this donor may in fact be through dimerization of the cation-radicals. In contrast to the results with donor **12**, the EPR cation:anion ratios for donor **10** are at variance with the stoichiometric ratios of donor and acceptor in the corresponding solid complexes.

Iodine oxidizes both **11** and **12**: this is understandable, since iodine, in the gas phase,[30] is as potent an electron acceptor as TCNQ.[14] However, iodine did not oxidize **13**.

The discrepancies between the voltammetric data of Tables 1 and 2 and the EPR data of Table 5 may be due to substantial shifts in redox potentials resulting from the differences in concentration, solvent, and the absence of supporting electrolyte in going from the conditions at which the redox potentials were measured to the conditions under which the EPR spectra were run.

There is no simple correlation between the ionicity ϱ in the solid state and the formal charges for the predominant species in the solution phase. The equilibria in solution are affected by temperature, the dielectric constant of the solvent, and the presence of supporting electrolyte. The various long-range and short-range contributions to the crystal cohesive energy (Madelung energy, dispersion energy, polarization energy) involve, and therefore affect, the ionicity ϱ in the crystal;[31] these contributions are not at play in solution.

In solution one should consider the existence of neutral molecules, anion-radicals and cation-radicals, and the EPR-silent dianions and dications; in addition, TCNQ anion-radical can also form diamagnetic solution $\pi-\pi$ "dimers".[29] Equilibria will limit the number of independent solute species that can be present simultaneously in large concentration. It should not matter whether the solution equilibria are approached from dissolving the solid (ionic) complexes or from dissolving the neutral solid donors and acceptors and then mixing the solutions.

Conclusions

A new family of powerful donors has been prepared and characterized. A variety of complexes with TCNQ have been prepared; some show appreciable conductivity. Solution-phase EPR studies of the complexes and the donors have determined the coupling constants of the cation-radicals of the four donors. The oxidation state of the donor was found to be only moderately well correlated with the redox potentials of the donor and acceptor.

Experimental Section

Melting points were determined on a MEL-TEMT II, Laboratory Devices, apparatus. NMR, mass, UV−vis, and IR spectra were obtained using Bruker AM 360, VG Autospec, Perkin-Elmer Lambda 4B, and Perkin-Elmer 781 infrared spectrophotometer, respectively. Elemental analyses were performed by the Atlanta Microlab, Inc., Atlanta, GA. 2-(Phenylimino)-1,3-dithiolane (**14b**), was prepared by the literature procedure.[32] 2-(Methylimino)-1,3-dithiolane (**14a**) was synthesized according to Addor.[33] Potassium cyanodithioimididocar-

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bonate was obtained by a modified Hantzsch procedure,[34] and was alkylated with dibromoethane to yield 2-(cyanoimino)-1,3-dithiolane (**14c**).[35]

4,5-Dicarbomethoxy-3-methyl-1,3-thiazoline-2-thione (15a). Dimethyl acetylenedicarboxylate (3.45 g, 24.28 mmol) was added to a solution of 2-(methylimino)-1,3-dithiolane (**14a**) (3.23 g, 24.24 mmol) in xylene (60 mL). After being stirred and refluxed for 15 h under nitrogen, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the resulting solid was recrystallized from methanol to give 4.30 g (72%) of colorless needles: mp 118 °C (lit.[12a] 118 °C); ^{1}H NMR ($CDCl_3$) δ 3.64 (s, 3H, Me), 3.85 (s, 3H, OMe), 4.02 (s, 3H, OMe).

4,5-Dicarbomethoxy-3-phenyl-1,3-thiazoline-2-thione (15b). A solution of 2-(phenylimino)-1,3-dithiolane (**14b**) (2.47 g, 12.65 mmol) and dimethyl acetylenedicarboxylate (1.80 g, 12.65 mmol) in xylene (32 mL) was warmed at 120 °C (bath temperature) for 25 h. Another portion of dimethyl acetylenedicarboxylate (1.80 g, 12.65 mmol) was added to the solution. After refluxing for an additional 5 h the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residual oil was chromatographed on a short silica column (eluent benzene) to give 3.29 g (84%) of pale yellow crystalline material. Recrystallization from methanol afforded 2.97 g (76%) of colorless plates: mp 136 °C (lit.[12a] 134 °C); ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 3 H, OMe), 3.87 (s, 3H, OMe), 7.31−7.34 (m, 2H, m-H_{Ph}), 7.51−7.53 (m, 3H, o- and p-H_{Ph}).

4,5-Dicarbamido-3-methyl-1,3-thiazoline-2-thione (17). Dicarbomethoxy derivative **15a** (1.61 g, 6.51 mmol) was dissolved in hot methanol (450 mL). The solution was cooled down to room temperature and immediately saturated with ammonia gas. The reaction mixture was stirred for 48 h and repeatedly saturated with NH_3. Methanol was removed under reduced pressure, and the residual yellow crystalline material was recrystallized from MeOH to give 1.1 g (78%) of white crystals: mp 257 °C (dec); ^{1}H NMR (DMSO-d_6) δ 3.54 (s, 3H, Me), 7.49 (s, 1H, NH_2), 7.72 (s, 1H, NH_2), 8.28 (s, 1H, NH_2), 8.41 (s, 1H, NH_2); HRMS calcd for $C_6H_7N_3O_2S_2$ 216.9980, found 216.9973.

4,5-Dicyano-3-methyl-1,3-thiazoline-2-thione (15d). To a warm solution of diamide **17** (0.50 g, 2.30 mmol) in tetramethylene sulfone (9 mL) was added an excess of phosphorus oxychloride (0.71 g, 4.60 mmol). After stirring the reaction mixture at 110 °C (bath temperature) for 4 h, it was poured into ice water (ca. 80 mL). The yellow precipitate was filtered off, washed with water, and dried. It was purified by chromatography (silica gel, benzene) to yield 0.34 g (81%) of yellow crystalline material. Recrystallization from hexane afforded 0.2 g (69%) of tiny tan needles: mp 151 °C; ^{1}H NMR ($CDCl_3$) δ 3.77 (s, NMe). Anal. Calcd for $C_6H_3N_3S_2$: C, 39.76; H, 1.67; N, 23.19; S, 35.38. Found: C, 39.68; H, 1.65; N, 23.29; S, 35.30.

4,5-Dicarbomethoxy-3-methyl-1,3-thiazoline-2-selone (19a). To a hot solution of thione **15a** (0.20 g, 0.81 mmol) in chloroform (10 mL) were added $HC(OEt)_3$ (0.4 mL) and $Et_2O{\cdot}BF_3$ (0.4 mL). The reaction mixture was refluxed for 10 min and left at room temperature overnight. The resulting 2-(ethylthio)-1,3-thiazolium fluoroborate **18a** was precipitated with ether (70 mL), filtered off, washed with ether (4 × 2 mL), dried, and dissolved in acetonitrile (30 mL). The resulting solution was transferred into a syringe and injected dropwise into a freshly prepared solution of sodium hydroselenide, prepared from powdered selenium (0.13 g, 1.62 mmol) and sodium borohydride (0.07 g, 1.78 mmol) in absolute ethanol (70 mL) under nitrogen. After stirring for 20 min, the reaction mixture was poured into 50 mL of 2% AcOH in water. The precipitate was filtered off, washed with water (4 × 2 mL), and dried. The resulting yellow solid was dissolved in benzene, (25 mL), and the solution was dried over $CaCl_2$ and filtered through silica gel, eluting with benzene. The solvent was removed under reduced pressure to give 0.25 g (96%) of yellow crystals of selone **19a**, mp 110 °C. An analytically pure sample was prepared by recrystallization from hexane: UV, λ_{max} ($\log_{10} \epsilon$), 316 (3.77), 373 (4.15) nm; ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 3H, Me), 3.86 (s, 3H, OMe), 4.03 (s, 3H, OMe). Anal. Calcd for $C_8H_9NO_4SSe$: N, 4.76; S 10.90. Found: N, 4.68; S, 10.98.

4,5-Dicarbomethoxy-3-phenyl-1,3-thiazoline-2-selone (19b). This was prepared from thione **15b** (1.00 g, 3.23 mmol) by the procedure described for **19a**: yield 1.00 g (95%) of yellow crystalline selone. Recrystallization from methanol afforded yellow prisms: mp 124 °C; UV, λ_{max} ($\log_{10} \epsilon$), CH_2Cl_2 323 (3.80), 379 (4.31); ^{1}H NMR ($CDCl_3$) δ 3.67 (s, 3H, OMe), 3.88 (s, 3H, OMe), 7.36−7.37 (m, 2H, Ph), 7.53−7.55 (m, 3H, Ph). Anal. Calcd for $C_{13}H_{11}NO_4SSe$: C, 43.83; H, 3.11; N, 3.93; S, 9.00. Found: C, 43.96; H, 3.05; N, 3.81; S, 8.87.

4,5-Dicyano-3-methyl-1,3-thiazoline-2-selone (19c). A solution of thione **15d** (0.15 g, 0.83 mmol), $HC(OEt)_3$ (0.3 mL), and $Et_2O{\cdot}BF_3$ (0.3 mL) in 10 mL of chloroform was refluxed for 5 h. The reaction mixture was cooled to room temperature, and the product was precipitated with ether (50 mL), filtered off, washed with ether (4 × 2 mL), dried, and dissolved in 3 mL of dry acetonitrile. The resulting solution was injected in one portion with vigorous stirring under nitrogen into a solution of NaHSe, obtained from selenium (72 mg, 0.91 mmol), and sodium borohydride (38 mg, 1.00 mmol) in 5 mL of absolute ethanol. An immediate color change from colorless to orange was observed. After 1 min, 1 mL of AcOH was injected via the septum to neutralize the excess of base. The reaction mixture was diluted with 50 mL of 2% aqueous AcOH, and the product was extracted into benzene (4 × 10 mL). The combined organic layers were washed with water (4 × 10 mL) and dried over $CaCl_2$. The solvent was removed under reduced pressure, and the residual yellow solid was purified by chromatography on silica (benzene) to give 0.15 g (79%) of fine yellow needles: mp 148 °C. Recrystallization from hexane afforded an analytically pure sample of **19c**: UV, λ_{max} ($\log_{10} \epsilon$), CH_2Cl_2 329 (4.9), 405 (3.65) nm; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, NMe). Anal. Calcd for $C_6H_3N_3SSe$: C, 31.59; H, 1.33; S, 18.42; N, 14.06. Found: C, 31.70; H, 1.39; N, 18.56; S, 13.85.

Bis(4,5-dicarbomethoxy-3-methyl-1,3-thiazoline-2-ylidene) (11). A suspension of selone **19a** (1.00 g, 3.40 mmol) in freshly distilled triethyl phosphite (1.75 mL, 10.20 mmol) was warmed to 100 °C in 5 min. The mixture was cooled down to room temperature, and 10 mL of methanol was added. The precipitate was filtered off, washed with methanol, and dried: yield 0.61 g (84%) of deep violet fine needles; mp 181 °C dec; MS m/e 415 (M-Me, 20) 399 (10), 247 (14), 231(12), 216 (40), 200 (25), 185 (14), 170 (29), 157 (20), 149 (42), 145 (100), 144 (96), 131 (36). Anal. Calcd for $C_{16}H_{18}N_2O_8S_2$: C, 44.64; H, 4.25; N, 6.51; S, 14.90. Found: C, 44.90; H, 4.32; N, 6.32; S, 14.71.

12: yield 91%; dark brown crystals; mp 235 °C; UV, λ_{max} ($\log_{10} \epsilon$), CH_2Cl_2 259 (4.28), 351 (3.86), 494 (3.86) nm; ^{1}H NMR (acetone-d_6) δ 3.64 (s, 12 H, OMe), 7.20−7.55 (m, 10 H, Ph); MS m/e 554 (M^+, 59), 477 (90), 419 (7), 308 (9), 293 (14), 278 (70), 262 (42), 246 (2), 218 (21), 77 (100). Anal. Calcd for $C_{26}H_{22}N_2O_8S_2$: C, 56.30; H, 4.00; N, 5.05; S, 11.56. Found: C, 56.33; H, 4.09; N, 5.03; S, 11.84.

13: yield 58%, black crystals; mp 91 °C dec. Solutions of **13** decomposed at a moderate rate, which did not allow obtaining ^{1}H NMR and UV spectra: MS *m/e* 298 (M^+, 12), 283 (100), 268 (17), 178 (8), 150 (26), 108 (35); HRMS calcd for $C_{12}H_6N_6S_2$: 298.0095, found 298.0100. The compound was not sufficiently stable for an elemental analysis.

Bis(1,3-thiazole)diperchlorates (23a,b). A solution of the donor **10** or **12** (9.02×10^{-2} mmol) in 3 mL of dioxane was mixed with a solution of phenyliodoso diacetate (9.02×10^{-2} mmol) in 2 mL of dioxane. Aqueous 70% $HClO_4$ (0.15 mL) was added, and the reaction mixture was warmed to boiling and then left at room temperature for 3 h. The dication salt was precipitated by ether (20 mL), filtered off, washed with ether and hexane, and dried.

23a: yield 61%. Anal. Calcd for $C_{24}H_{22}N_2O_{12}S_4Cl_2$: C, 39.51; H, 3.04; N, 3.84; S, 17.58. Found: C, 39.41; H, 2.81; N, 3.66; S, 18.02.

23b: yield 59% UV, λ_{max} ($\log_{10} \epsilon$), CH_2Cl_2 356 (3.87) nm. Anal. Calcd for $C_{26}H_{22}N_2O_{16}S_2Cl_2$: C, 41.44; H, 2.94; N, 3.72; S, 8.51. Found: C, 41.99; H, 2.34; N, 3.62; S, 8.41.

Cation-Radical 24. A CH_2Cl_2 solution of **24** (10^{-4} M) was obtained under nitrogen by mixing equivalent amounts of the donor **12** in CH_2Cl_2 (10^{-4} M) and the appropriate solution of dication salt **23b** (10^{-4} M). Cation-radical **24** was stable in the solution and no change in its UV spectrum was observed after 60 days: UV, λ_{max} ($\log_{10} \epsilon$), CH_2Cl_2

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436 (4.01) (sh), 465 (4.21), 641 (3.28) nm. Slow evaporation of the solvent resulted in a green gum.

Charge-Transfer Complexes. TCNQ Complexes of 10. A degassed, hot solution of donor **10** (0.3 g, 0.57 mmol) in dry acetonitrile (50 mL) under nitrogen was treated with a hot solution of TCNQ (0.3 g, 1.47 mmol) in dry acetonitrile. The resulting green solution was cooled to room temperature under nitrogen. The dark precipitated crystals were filtered off, washed with acetonitrile, and dried under nitrogen to give 0.17 g of dark blue-black complex. The filtrate was concentrated under nitrogen to give a second crop of the above complex (0.02 g): total yield 0.19 g (46%). Anal. Calcd for (**10**) (TCNQ), $C_{36}H_{26}N_6O_4S_4$: C, 58.83; H, 3.57; N, 11.44; S, 17.45. Found: C, 58.62; H, 3.59; N, 11.48; S, 17.39. The filtrate from the second crop was concentrated in vacuo to the crystallization point and filtered, and the needles which crystallized were collected separately, washed with hexane, and dried to give 0.19 g of dark green-black complex. Anal. Calcd for (**10**) $(TCNQ)_4(CH_3CN)_2$, $C_{76}H_{44}N_{20}O_4S_4$: C, 63.85; H, 3.10, N, 19.60; S, 8.97. Found: C, 63.56; H, 3.15; N, 20.30; S, 8.83.

TCNQ Complex of Donor 11. A degassed solution of donor **11** (30 mg, 0.07 mmol) in dry acetonitrile (4 mL) under nitrogen was treated with a hot solution of TCNQ (28.46 mg, 0.14 mmol) in dry acetonitrile (6 mL). The resulting dark green solution was concentrated under nitrogen to 2 mL, sealed under nitrogen and cooled in the refrigerator. The precipitated black crystals were filtered off, washed with acetonitrile, and dried to yield 40.73 mg of the complex. Anal. Calcd for (**11**) $(TCNQ)_4$, $C_{64}H_{34}N_{18}O_8S_2$: C, 61.63; H, 2.75; N, 20.22; S, 5.14. Found: C, 61.60; H, 2.91; N, 20.10; S, 4.81.

TCNQ Complexes of Donor 12. A degassed solution of donor **12** (81.49 mg, 0.14 mmol) in dry acetonitrile (7 mL) under nitrogen was treated with a solution of TCNQ (15.00 mg, 0.07 mmol) in dry acetonitrile (4 mL). The yellow precipitate was filtered off, and the filtrate was concentrated to 5 mL. The precipitate of complex was filtered off and washed with acetonitrile to give 17.18 mg (31%) of dark navy-blue crystals. Anal. Calcd for (**12**) (TCNQ), $C_{38}H_{26}N_6O_8S_2$: C, 60.15; H, 3.45; N, 11.08; S, 8.45. Found: C, 60.20; H, 3.45; N, 11.05; S, 8.39.

A solution of **12** (30 mg, 0.054 mmol) in dry acetonitrile (5 mL) was mixed with a solution of TCNQ (22.09 mg, 0.108 mmol) in dry acetonitrile (7 mL) under nitrogen and left overnight. The precipitate was filtered off, washed with acetonitrile, and dried: yield 40 mg (69%) of dark green-black crystals. Anal. Calcd for $(\mathbf{12})_2$ $(TCNQ)_5$, $C_{112}H_{64}N_{24}O_{16}S_4$: C, 63.15; H, 3.03; N, 15.78; S, 6.02. Found: C, 63.17; H, 3.07; N, 15.76; S, 6.10.

EPR. The EPR samples were prepared in custom-made 7 mm × 0.5 mm flat cells, which were connected to a vacuum line. The solvent (CH_2Cl_2, CH_3CN) was degassed to $<10^{-3}$ Torr in a side arm of the sample cell and then mixed with the complex. For those samples for which iodine or bromine was used as oxidant, a small amount of Br_2 or I_2 was added to the solvent, which was then degassed as above. For donor (**13**), the donor was mixed with the TCNQ as a solid, and the solvent (CH_2Cl_2) was degassed and then mixed with the donor and acceptor, as above. The EPR spectra were recorded on a hybrid system consisting of a Varian E-109 bridge, IBM ER 10 inch magnet with a Bruker BH-15 magnetic field controller, controlled by a MacIntosh IIcx computer. Spectra were fitted using the Simplex algorithm.[36] Data points of 1000 were used in the fitting procedure, except for donors **11** and **12**, where 2000 points were used. Low-temperature spectra were collected using a single walled 9 mm i.d. insert in the cavity, through which cooled nitrogen gas was passed. The *g*-values were determined against the perylene cation-radical,[37] using a Hewlett-Packard Model 5352B frequency counter to correct for changes in the frequency of the two samples.

Calculations. Alchemy III was used to generate and minimize a molecular mechanics of the starting structure of the donor cations, using a MacIntosh IIci microcomputer. The structure was then further refined on a Cray Y/MP supercomputer using AM1[25] semiempirical Hamiltonian, as implemented in the MOPAC Version 5.00 computer package.[26] The AM1 runs were done using UHF for the neutral molecules and for the cation-radicals. In preliminary calculations, with no symmetry imposed on the molecules and the cation-radicals, it was found that the INDO program,[27] run on the Cray Y/MP supercomputer, would not provide correct convergence: the two halves of the molecule would have very different electron densities. To overcome this, a symmetry constraint was imposed. It was found that the minimum energy in both $\mathbf{10}^{\cdot+}$ and $\mathbf{11}^{\cdot+}$ required inversion symmetry, rather than C_2 symmetry. Accordingly, inversion symmetry was imposed on the AM1 calculations used to generate the geometries for the INDO calculations. AM1 calculations run without the symmetry constraints confirmed that the geometries and energies found corresponded to a minimum. The INDO data given in Table 5 were obtained for cation-radicals with inversion symmetry.

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