destruction of the starting material. Unchanged **11** and **12** were isolated by GLC on column B at 65 °C. NMR analysis showed a 65:35 ratio of **11** and **12.** Similarly, recovery of **11** and **12** from a reaction with sodium in ammonia (85% destruction of starting material) afforded a 65:35 mixture of these isomers.

Product Stability under Reductive Cleavage Conditions. To a solution of 0.17 g (7.4 g-atom) of sodium in 10 ml of ammonia was injected 50 μl (~0.3 mmol) of alkyl- or allylindene. After stirring for 1 h, the reaction was quenched and worked up as described above for the synthesis of alkylindenes. The products were analyzed on GLC column D at 65 °C. The product mixture from the treatment of **17a** consisted of 74% 1-isopropylindan (**16a**) and 26% **17a,** whereas the product mixture from the cleavage of **17c** consisted of 20% 1-*n*-propylindan (**16b**), 76% 1-allylindan (**16c**), 2% 3-allylindene (**17c**), and two unidentified products each formed in <2% yield. When lithium was substituted for sodium, **17a** produced 87% **16a** and 11% **17a,** whereas **17c** produced 21% **16b,** 72% **16c,** 5% **17c,** and 2% of an unidentified product.

Acknowledgment. We thank the National Science Foundation for support of this work.

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Synthesis of Electrically Conductive Organic Solids

R. C. Wheland* and J. L. Gillson

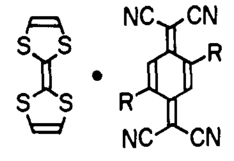
Contribution No. 2275 from the Central Research and Development Department,
Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898. Received July 7, 1975

Abstract: Over 80 electrically conductive charge-transfer complexes are reported. Donor structures include tetrathioethylenes, dithiodiaminoethylenes, dithiodiselenoethylenes, tetraaminoethylenes, azines, aromatic hydrocarbons, and aromatic heterocycles. Acceptor structures include substituted tetracyanoquinodimethanes, metal dithiolates, cyanocarbons, and nitro compounds. A novel dithiodiselenoethylene synthesis is reported. A rather general electrochemical technique for growing high-quality single crystals is discussed, and compaction resistivities are compared with corresponding single crystal values. Redox potentials are reported for a number of donors and acceptors.

Introduction

The room-temperature electrical conductivity of the tetrathiofulvalene–tetracyanoquinodimethan (TTF·TCNQ) charge-transfer complex **1** is comparable with that of graphite.[1,2] Lowering the temperature to roughly 60 K increases conductivity ten- to 500-fold,[1,2] the magnitude of this enhancement being a point of scientific controversy.[3-8]

In the context of materials analogous to TTF·TCNQ, the need for planar molecules capable of close, highly ordered packing and of stable radical ion configurations seems clear. But otherwise the detailed molecular requirements for high conductivity are poorly established and have been the subject of speculation in the literature. High symmetry,[1] high polarizability,[1,2,9,10] small molecular size,[10] high acceptor electron affinity,[10] low donor ionization potential,[10] partial electron transfer,[10,11-14] and small separation between first and second redox potentials[10] are among the factors felt to favor high conductivity. The roughly 80 conductive organics reported in



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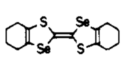
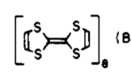

2,SSe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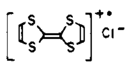
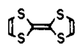
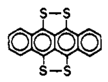
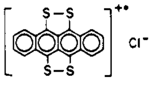
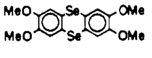
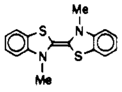

4[17]

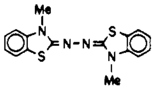

5[17-19]; TTF

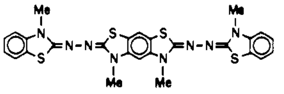

6[20,21]; TTN

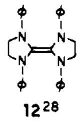

7[22,23]; TTN$^{+\cdot}$Cl$^-$

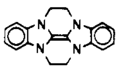

8[24]; TMSA

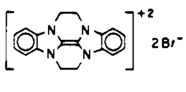

9[25]

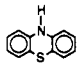

10[26]; AZ


11[27]; BAZ


12[28]


13, TAE


14[29]; TAE^{+2}(Br$^-$)$_2$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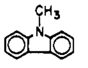
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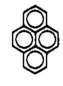
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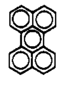
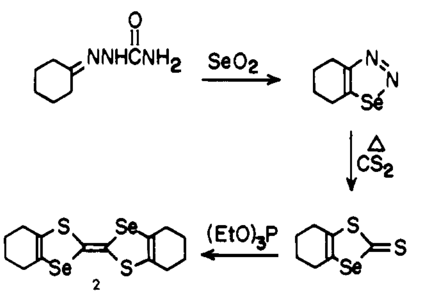
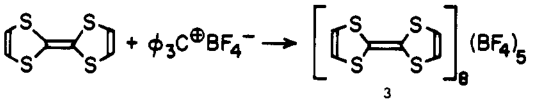

18

this paper form a starting experimental basis for the evaluation of these factors.

Synthesis

Donors. The novel dithiodiselenoethylene (**2**) was prepared in three steps. The distribution of cis-trans double bond isomers in **2** is unknown, the trans representation here being a convenience. Tetrathiofulvalene tetrafluoroborate (**3**) was





prepared by oxidation of TTF with trityl tetrafluoroborate.[16] Other donor and donor salts were either commercially available or prepared according to the literature. The donors used to prepare complexes are gathered in Chart I for later reference.

Acceptors. Acceptors and acceptor salts used to prepare complexes are gathered in Chart II.

Complexes. For compaction resistivity measurements a fine powder or gently crushed coarser crystalline material is suitable. Samples were prepared by direct combination of donor and acceptor or by metathesis between donor and acceptor salts, specific examples being shown, respectively, in the following equations:

$$\underset{\mathbf{6}}{\text{TTN}} + \underset{\mathbf{19a}}{\text{TCNQ}} \xrightarrow{C_6H_3Cl_3} \underset{\mathbf{6\cdot19a}}{(\text{TTN})(\text{TCNQ})} \qquad (1)$$

$$\underset{\mathbf{7}}{\text{TTN}^+\text{Cl}^-} + \underset{\mathbf{35}}{\text{Li}^+\text{TCNQ}^-} \xrightarrow{\text{MeOH}} \underset{\mathbf{6\cdot19a}}{(\text{TTN})(\text{TCNQ})} \qquad (2)$$

In the two examples above, the product precipitates immediately as a purple powder and may be filtered, washed, and dried.

Complex formation by metathesis occasionally affords control over stoichiometry as illustrated in the following equations:

$$\underset{\mathbf{7}}{\text{TTN}^+\text{Cl}^-} + \underset{\mathbf{26}}{(\text{Et}_4\text{N}^+)\text{PtC}_4\text{S}_4(\text{CN}_4)^-} \longrightarrow \underset{\mathbf{6\cdot23}}{(\text{TTN})\cdot[\text{PtC}_4\text{S}_4(\text{CN})_4]} \qquad (3)$$

$$\underset{\mathbf{7}}{\text{TTN}^+\text{Cl}^-} + \underset{\mathbf{25}}{(n\text{-Bu}_4\text{N}^+)_2\text{PtC}_4\text{S}_4(\text{CN})_4{}^{2-}} \longrightarrow \underset{(\mathbf{6})_2\cdot\mathbf{23}}{(\text{TTN})_2\cdot[\text{PtC}_4\text{S}_4(\text{CN})_4]} \qquad (4)$$

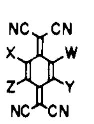
This method relies on the donor and acceptor moieties combining in a ratio that reflects their charges and thus can be affected if new redox reactions occur before precipitation.

A second method of altering stoichiometry is to react preformed complex with additional donor or acceptor. This technique has been particularly successful in onium ion systems (for example, ammonium and phosphonium) in the past[13] and is illustrated here in eq 5. Attempts to alter the stoichiometry of TTF·TCNQ (**1**) by crystallizing from a large excess of TCNQ have apparently failed.[1]

$$\begin{tikzcd}
 & & (\text{TAE})(\text{TCNQ})_{4-5} \; \mathbf{13}\cdot(\mathbf{19a})_{4-5} \\
\underset{\mathbf{14}}{\text{TAE}^{2+}(\text{Br}^-)_2} + \underset{\mathbf{35}}{\text{Li}^+\text{TCNQ}^-} \arrow[rr, "H_2O"] & & (\text{TAE})\cdot(\text{TCNQ})_2\cdot 2H_2O \; \mathbf{13}\cdot(\mathbf{19a})_2\cdot 2H_2O \arrow[u, "CH_3CN, TCNQ"'] \arrow[d, "CH_3CN"] \\
 & & (\text{TAE})(\text{TCNQ})_2 \; \mathbf{13}\cdot(\mathbf{19a})_2
\end{tikzcd} \qquad (5)$$

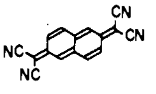
Only a small proportion of the complexes for which compaction resistivities are reported here have given mountable single crystals. TTF·TCNQ (**5·19a**), TTF·TCNQEt$_2$ (**5·19s**), and TTF·TCNQBrMe (**5·19l**) crystals were grown by diffusing an acetonitrile solution of acceptor into an acetonitrile solution of donor over several days. Crystals of TTN·TCNQ(OMe)$_2$ (**6·19c**) were grown as dendritic tussocks of black needles by allowing tetrathionaphthacene and TCNQ(OMe)$_2$ to sit in trichlorobenzene for a month. Slow cooling of acetonitrile solutions of TTF·TCNQI$_2$ (**5·19p**) and TTF·TCNQClMe (**5·19k**) gave crystalline needles.

Single crystals of TTF·TCNQBr$_2$ (**5·19o**), TTF·TCNQIMe (**5·19m**), and TTF·TCNQ were grown electrochemically and, in fact, relatively large numbers of such TTF·TCNQ crystals compared favorably under a polarizing microscope in perfection and size with the best solution grown crystals. Passing 1 μA for 2 weeks through an acetonitrile solution saturated in TTF·TCNQ, saturated in *N*-methylquinolinium tetracyanoquinodimethan (**39**), and 0.06 M in TTF results in a deposit of highly reflective TTF·TCNQ needles on the anode. Chemically speaking, *N*-methylquinolinium tetracyanoqui-

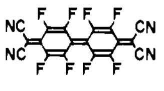


19,[30]; TCNQWXYZ

19a X=Y=Z=W, TCNQ
19b X=OMe, Y=W=Z=H, TCNQ(OMe)
19c X=Y=OMe, W=Z=H, TCNQ$(OMe)_2$
19d X=OMe, Y=OEt, W=Z=H, TCNQ(OMe)(OEt)
19e X=OMe, Y=O-i-Pr, W=Z=H, TCNQ(OMe)(O-i-Pr)
19f X=OMe, Y=O-iBu, W=Z=H, TCNQ(OMe)(O-i-Bu)
19g X=OMe, Y=O-i-C_5H_{11}, W=Z=H, TCNQ(OMe)(O-i-C_5H_{11})
19h X=OEt, Y=SMe, W=Z=H, TCNQ(OEt)(SMe)
19i X=Cl, Y=W=Z=H, TCNQCl
19j X=Br, Y=W=Z=H, TCNQBr
19k X=Cl, Y=Me, W=Z=H, TCNQ ClMe
19l X=Br, Y=Me, W=Z=H, TCNQ BrMe
19m X=I, Y=Me, W=Z=H, TCNQIMe
19n X=Y=Cl, W=Z=H, TCNQCl_2
19o X=Y=Br, W=Z=H, TCNQBr_2
19p X=Y=I, W=Z=H, TCNQI_2
19q X=OMe, Z=H, Y–W=OCH_2OCH_2, TCNQ(OMe)(OCH_2OCH_2)
19r X=Y=Me, W=Z=H, TCNQMe_2
19s X=Y=Et, W=Z=H, TCNQEt_2
19t X=Y=iPr, W=Z=H, TCNQ$i$$Pr_2$
19u X=Y=CN, W=Z=H, TCNQ$(CN)_2$
19v X=Y=W=Z=F, TCNQF_4



20[31,32]; TNAP



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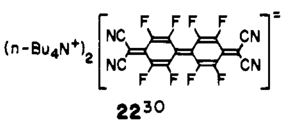
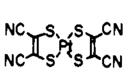
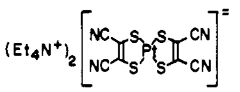


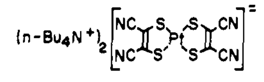
22[30]



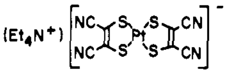
23; $PtC_4S_4(CN)_4$



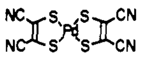
24[33]; $(Et_4N^+)_2PtC_4S_4(CN)_4^=$



25[34]; $(n\text{-}Bu_4N^+)_2PtC_4S_4(CN)_4^=$



26[35]; (Et_4N^+) $PtC_4S_4(CN)_4^-$



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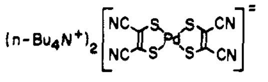
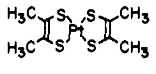
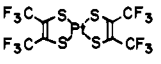


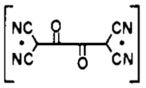
28[33]; $(n\text{-}Bu_4N^+)_2PdC_4S_4(CN)_4^=$



29[36], $PtC_4S_4(CH_3)_4$



30[37]; $PtC_4S_4(CF_3)_4$



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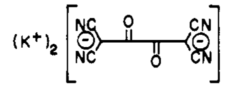
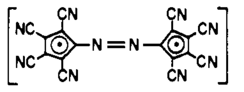
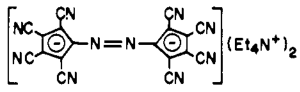


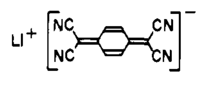
32[38]



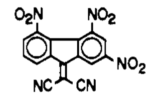
33



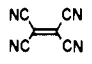
34[39]



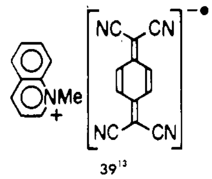
35[13]; $Li^+TCNQ^{-\bullet}$



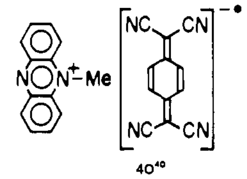
36



37, TCNE



39[13]



40[40]

nodimethan (**39**) serves to carry the electric current and is a source of TCNQ$\cdot^-$. At the anode this TCNQ$\cdot^-$ is oxidized to $TCNQ^0$ which reacts with TTF to form additional TTF·TCNQ. Since the solution is already saturated in TTF·TCNQ, the new complex generated nucleates and precipitates on the electrode. Originally, it had been hoped that the most conductive crystals would carry the greatest amount of current, generate the most TCNQ in their immediate vicinity, and thus select themselves out by growing the largest. Indeed many of the larger crystals seemed particularly well formed and rather uniformly comparable in conductivity to the best solution grown crystals.

The electrochemical crystal growing procedure may be of great generality, but it is already apparent that extending it to other systems will require much time spent with conditions and additives. For example, in the electrochemical growth of TTF·TCNQ, the *N*-methylquinolinium ion of **39** plays no electrochemical role and thus in principle *N*-methylphenazinium tetracyanoquinodimethan (**40**) or lithium tetracyanoquinodimethan (**35**) should be equally effective, whereas in fact they give much poorer crystals. In contrast $Li^+TCNQBr_2\cdot^-$ (**41**) seems to give better TTF·$TCNQBr_2$ crystals than do ammonium salts. In all cases the platinum electrodes must be soaked in nitric acid and then used to electrolyze 10% Na_2SO_4 before the crystals will adhere.

Compaction resistivity data are gathered in Table I, and single crystal resistivity data are plotted as a function of temperature in Figure 1. Five of these complexes have been described before and can be used to calibrate our data to that of other workers.[41,42] Compaction and single crystal resistivities are compared in Table II. Low resistivity compaction values are indeed associated with highly conductive single crystals and thus seem to be of use in evaluating materials for which single crystals are not available. From the data at hand, compaction resistivity values can probably be expected to be less than two orders of magnitude higher than the single crystal value. The low-temperature conductivity enhancement for TTF·TCNQ is notably larger than that shown by any of the other complexes in Table II. There seems to be no correlation between room-temperature resistivity and the magnitude of the enhancement, other than initial room-temperature resistivity must be quite low for any enhancement to be observed at all.

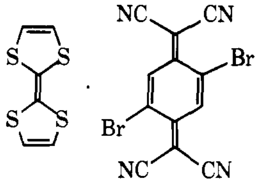
Handling of Data

Resistivities. Compaction resistivity measurement involves compressing milligram quantities of complex to a thin wafer between conductive electrodes. From the resistance (R) of the wafer under pressure, the thickness (l) of the wafer on removal, and the area (s) of the wafer, one may calculate the resistivity (ρ) of the complex from:

$$\rho = R\frac{s}{l} \tag{6}$$

There are various problems associated with compaction resistivity data, including the following. Desirable metallic behavior may be obscured because interparticle resistance and contact resistance are activated and cause ρ to increase with decreasing temperature. Compaction resistivities of anisotropic materials such as TTF·TCNQ[3-5] necessarily average conductivities along the various crystal axes and are influenced by any selective orientation that may occur during formation of the wafer. Powders used for compaction measurements force one to measure poor crystallites along with good ones and most frequently allow no estimation of crystallite quality at all.

Representative compaction resistivity data are shown below for TTF·TCNQBr$_2$ (**5·19o**).



5·19o

prep	
1	0.2, 0.2 Ωcm
2	0.4, 0.4 Ωcm
3	0.1, 0.08 Ωcm
4	0.1 Ωcm

Resistivities were measured on four independent preparations of TTF·TCNQBr$_2$. Two separate samplings from the first preparation of TTF·TCNQBr$_2$ gave resistivity measurements of 0.2 and 0.2 Ω cm while two samplings from the second preparation gave resistivities of 0.4 and 0.4 Ω cm and so on. The extent of variation shown over all four preparations is typical of our experience with compaction resistivities in that they are generally closely reproducible for measurements on an individual preparation but only reproducible within a factor of 2 to 5 for measurements on different preparations.

Relatively speaking, measurement of single crystal resistivity is more satisfactory although artifacts can arise.[5] One can select only the most attractive crystals and apply four silver paste or dag electrodes on in a line along the crystal axis of interest. Passing a constant current through the two outer electrodes and measuring the potential across the inner two allows resistance measurement independent of contact resistances between electrode and crystal. Using this resistance in conjunction with measurement of electrode separation and crystal dimensions allows calculations of ρ by eq 6. While simple and straightforward in principle, experimental difficulties are considerable: crystals as small as 1 × 0.2 × 0.03 mm must frequently be used, microvolt changes are involved, and real (in contrast to apparent) distances between electrodes are hard to estimate.

Elemental Analyses. Elemental analyses for many of the complexes reported here are admittedly outside normal error limits and occasionally even ambiguous with respect to stoichiometry. In such cases polarography, uv spectra, and mass spectra were frequently used to check for more fundamental changes than simple electron transfer. TTF·TCNQBr, for example, was prepared twice, and each time carbon and nitrogen were >0.3% away from calculated. Polarography, of an acetonitrile solution of TTF·TCNQBr affords TTF^0, TTF$^+$, TCNQBr^0, TCNQBr$^-$ concentrations from which one may calculate the ratio:

$$\frac{[\mathrm{TTF}] + [\mathrm{TTF}\cdot^{+}]}{[\mathrm{TCNQBr}] + [\mathrm{TCNQBr}\cdot^{-}]} = 1.05 \pm 0.03$$

Thus, in spite of its unfortunate elemental analysis, TTF·TCNQBr is essentially 1:1, and no reaction other than electron transfer seems to have occurred.

Elemental analysis for complex **12**·(**19a**)$_{4-5}$ falls between four and five TCNQ molecules per tetraaminoethylene. On the basis of uv absorption at 394 and 342 nm for TCNQ and LiTCNQ, the ratio of TCNQ/TCNQ$\cdot^-$ = 1.4. Hence, if the tetraaminoethylene donor has the expected +2 charge, **12**·(**19a**)$_{4-5}$ contains 4.8 TCNQ's per tetraaminoethylene consistent with elemental analyses.

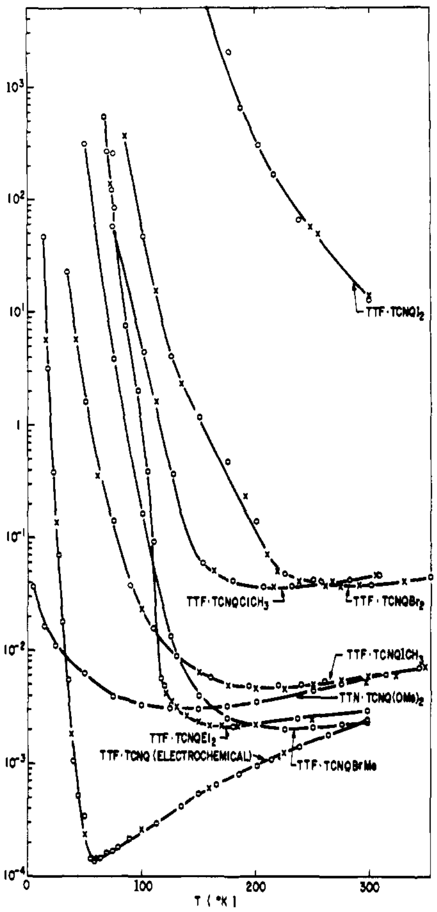


Figure 1. Single crystal resistivity vs. temperature.

Tetrathionaphthacene affords an interesting series of conductive materials that is admittedly poorly characterized by elemental analysis. Of the 28 tetrathionaphthacene based complexes in this report, only seven had a carbon analysis within 0.3% of calculated, compared with 20 with carbon too low and 1 with carbon too high. In the specific case of TTN·TCNQ (**6·19a**), parents of both TTN and TCNQ were apparent in the mass spectrum, suggesting no structural changes accompany complexation. Preparation of TTN·TCNQ by direct reaction gave complex with nitrogen 2.5% too high, whereas preparation by metathesis gave complex with nitrogen 1.3% too low—but resistivities were essentially indistinguishable, 1.5 and 1.8 Ω cm, respectively. Recrystallization of TTN·TCNQ from trichlorobenzene gave further apparently random variation in analysis as did gradient sublimation of the starting materials. Uv and polarographic analysis were not possible on account of the extreme insolubility of TTN complexes. Tetrathionaphthacene complexes have given analytical problems in the past.[43]

Cyclic Voltametric Data. Redox potentials for most of the donor and acceptors in this report are gathered in Tables III and IV. While redox potentials have been measured in the past for a number of these compounds (for example, TTF and TCNQ), many have been redetermined here to obtain a self-consistent set vs. SCE in acetonitrile. Whenever there is a choice between values, we have thus used our own for calculaton of the difference between first redox potentials of acceptor and donor, $E_{1\mathrm{A}} - E_{1\mathrm{D}}$, in Table III.

Rather surprisingly the E_1's of the TCNQ's plot very badly against σ_p^+ and σ_m values, rather poorly for σ_p, and marginally better against $(\sigma_p + \sigma_m)/2$.[44,45] A plot of E_1 vs. $(\sigma_m + \sigma_p)/2$[45] is shown in Figure 2 and suggests that OMe is considerably more inhibiting on solution electron affinity that would be predicted from its σ value.

Table I. Compaction Resistivities of Complexes

Complex	Analyses, %						Resistivity^a	$E_{1A} - E_{1D}$	Method^b	Solvent	Yield, %
	Calculated			Found							
	C	H	N	C	H	N					
5·19s, TTF·TCNQEt$_2$	56.87	3.47	12.06	56.73	3.57	11.92	0.1	−0.18	A	CH$_3$CN	50
5·19m, TTF·TCNQIMe	41.61	1.65	10.22	41.69	1.63	9.92	0.1	−0.05	A	CH$_3$CN	70
5·19l, TTF·TCNQBrMe	45.51	1.81	11.17	45.41	1.99	11.25	0.1	−0.04	A	CH$_3$CN	~100
5·19a, TTF·TCNQ							0.1	−0.13	A	CH$_3$CN	90
5·19k, TTF·TCNQClMe	49.94	1.99	12.26	49.69	2.27	12.02	0.2	−0.04	A	CH$_3$CN	60
5·19b, TTF·TCNQ(OMe)	52.04	2.30	12.78	52.40	2.43	12.71	0.2	−0.23	A	CH$_3$CN	80
5·19j, TTF·TCNQBr	44.36	1.45	11.49	44.32	1.72	10.86	0.2	−0.01	A	CH$_3$CN	50
5·19o, TTF·TCNQBr$_2$	38.18	1.07	9.89	38.16	1.17	9.86	0.2	0.11	A	CH$_3$CN	70
5·19r, TTF·TCNQMe$_2$	55.02	2.77	12.83	55.33	2.94	12.50	0.3	−0.20	A	CH$_3$CN	40
5·19i, TTF·TCNQCl	48.81	1.59	12.65	48.92	1.98	12.35	0.5	−0.01	A	CH$_3$CN	60
5·19p, TTF·TCNQI$_2$	32.74	0.92	8.48	32.79	1.09	8.64	45	0.05	A	CH$_3$CN	70
5·19n, TTF·TCNQCl$_2$	45.28	1.27	11.74	45.12	1.73	11.86	2900	0.11	A	CH$_3$CN	75
5·19v, TTF·TCNQF$_4$	45.00	0.84	11.66	45.19	1.02	11.91	3900	0.23	A	CH$_3$CN	65
(**5**)$_2$·(**19h**)$_3$, (TTF)$_2$·[TCNQ(OEt)(SMe)]$_3$	53.00	2.97	13.01	52.96	3.13	12.74	5000		A	CH$_3$CN	80
5·19t, TTF·TCNQ-*i*-Pr$_2$	58.51	4.09	11.37	58.68	4.11	11.54	2.10^5	−0.18	A	CH$_3$CN	50
5·19u, TTF·TCNQ(CN)$_2$	52.39	1.32	18.33	52.41	1.52	18.19	10^6	0.35	A	CH$_3$CN	30
5·37, TTF·TCNE	43.36	1.21	16.85	43.31	1.29	16.94	4.10^8	−0.15	A	CH$_3$CN	40
(**5**)$_2$·**21**	43.26	0.97	6.73	43.40	1.53	7.16	2.10^5		B	**3** + **22**, CH$_3$CN	15
5·20, TTF·TNAP	57.62	2.20	12.22	57.58	2.30	11.40	0.2	−0.10	A	CH$_3$CN	90
(**5**)$_2$·**23**, (TTF)$_2$·PtC$_4$S$_4$(CN)$_4$	27.19	0.91	6.34	26.39	0.84	6.35	6000		B	**4** + **24**, CH$_3$OH	15
(**5**)$_2$·**27**, (TTF)$_2$·PdC$_4$S$_4$(CN)$_4$	30.20	1.01	7.04	30.12	1.16	6.44	6.10^5		B	**4** + **28**, CH$_3$OH	
6·19p, TTN·TCNQI$_2$	44.89	1.33	7.10	44.57	1.25	6.93	0.1	0.23	A	C$_6$H$_3$Cl$_3$	90
6·19c, TTN·TCNQ(OMe)$_2$	62.32	2.62	9.08	62.02	2.65	8.84	0.2	−0.13	A	C$_6$H$_3$Cl$_3$	80
6·19b, TTN·TCNQ(OMe)	63.46	2.41	9.55	60.17	2.47	8.27	0.2	0.05	A	C$_6$H$_3$Cl$_3$	20
6·19m, TTN·TCNQIMe	53.45	1.89	8.04	53.03	1.90	7.59	0.3	0.13	A	C$_6$H$_3$Cl$_3$	80
6·19s, TTN·TCNQEt$_2$	66.64	3.29	9.14	66.34	3.36	8.78	0.3	0.05	A	C$_6$H$_3$Cl$_3$	95
6·19r, TTN·TCNQMe$_2$	65.73	2.76	9.58	65.39	2.79	9.05	0.4	−0.02	A	C$_6$H$_3$Cl$_3$	50
6·19l, TTN·TCNQBrMe	57.32	2.02	8.62	56.98	2.02	8.41	0.4	0.14	A	C$_6$H$_3$Cl$_3$	80
6·19q, TTN·TCNQ(OMe)(OCH$_2$OCH$_2$)	61.47	2.50	8.69	60.53	2.99	8.18	0.5	−0.07	A	C$_6$H$_3$Cl$_3$	70
6·19d, TTN·TCNQ(OMe)(OEt)	62.84	2.88	8.88	61.43	2.96	8.01	0.8	−0.14	A	C$_6$H$_3$Cl$_3$	70
6·19a, TTN·TCNQ	64.73	2.17	10.06	64.85	2.33	12.58	1.5	0.05	A	C$_6$H$_3$Cl$_3$	95
6·19a, TTN·TCNQ	64.73	2.17	10.06	63.53	2.40	8.72	1.8	0.05	B	**7** + **35**, CH$_3$OH	70
6·19o, TTN·TCNQBr$_2$	50.43	1.41	7.84	50.15	1.47	7.60	3	0.29	A	C$_6$H$_3$Cl$_3$	85
6·19k, TTN·TCNQClMe	61.53	2.17	9.26	59.28	2.16	8.62	4	0.14	A	C$_6$H$_3$Cl$_3$	85
6·19j, TTN·TCNQBr	56.69	1.74	8.81	55.74	1.78	8.61	12	0.17	A	C$_6$H$_3$Cl$_3$	95
6·19h, TTN·TCNQ(OEt)(SMe)	61.28	2.81	8.66	61.02	2.86	8.28	25	−0.14	A	C$_6$H$_3$Cl$_3$	40
6·19i, TTN·TCNQCl	60.96	1.88	9.48	58.87	1.90	8.90	45	0.17	A	C$_6$H$_3$Cl$_3$	70
6·19u, TTN·TCNQ(CN)$_2$	63.34	1.66	13.85	62.43	1.53	14.69	90	0.35	A	C$_6$H$_3$Cl$_3$	~100
6·19v, TTN·TCNQF$_4$	57.32	1.28	8.91	56.54	1.33	9.34	200	0.41	A	C$_6$H$_3$Cl$_3$	90
6·19n, TTN·TCNQCl$_2$	57.60	1.61	8.96	55.58	1.78	7.83	580	0.29	A	C$_6$H$_3$Cl$_3$	~100
(**6**)$_3$·(**37**)$_2$, (TTN)$_3$·(TCNE)$_2$	60.34	1.84	8.53	58.43	2.00	8.56	100		A	C$_6$H$_3$Cl$_3$	~100
(**6**)·(**20**), (TTN)·(TNAP)	67.30	2.33	9.23	67.18	2.57	9.89	0.3	0.08	A	C$_6$H$_3$Cl$_3$	70
6·36	57.06	1.83	9.78	56.39	2.17	9.58	4.10^5	−0.20	A	C$_6$H$_3$Cl$_3$	85
(**6**)$_2$·**23**, (TTN)$_2$·PtC$_4$S$_4$(CN)$_4$	44.77	1.37	4.75	42.18	1.42	4.96	3		B	**7** + **24**, CH$_3$OH	~100
6·23, TTN·PtC$_4$S$_4$(CN)$_4$	39.72	0.97	6.77	37.71	1.22	6.48	80	0.88	B	**7** + **26**, CH$_3$OH	50
(**6**)$_2$·**27**, (TTN)$_2$·PdC$_4$S$_4$(CN)$_4$	48.41	1.48	5.13	47.98	1.62	5.23	5000		B	**7** + **28**, CH$_3$OH	30
(**6**)$_3$·**29**, (TTN)$_3$·PtC$_4$S$_4$(CH$_3$)$_4$	50.01	2.44	34.45(S)	51.65	2.60	35.12(S)	5.10^4		A	C$_6$H$_3$Cl$_3$	65
(**6**)$_2$·**33·MeOH**	60.42	1.84	12.81	60.29	1.84	13.32	4.10^4		B	**7** + **34**, CH$_3$OH	70
(**6**)$_2$·**31·MeOH**	58.68	2.19	6.08	58.27	2.32	5.98	2.10^3		B	**7** + **32**, CH$_3$OH	15
8·19v, TMSA·TCNQF$_4$	47.61	2.28	7.93	49.97	2.48	7.81	10^5	$\sim -0.37^c$	A	CH$_3$CN	70
8·19u, TMSA·TCNQ(CN)$_2$	52.65	2.65	12.28	52.73	2.54	12.19	6.10^5		A	CH$_3$CN	73
8·19o, TMSA·TCNQBr$_2$	42.45	2.29	7.07	42.26	2.41	6.78	10^7	$\sim -0.49^c$	A	CH$_3$CN	
8·19n, TMSA·TCNQCl$_2$	47.82	2.58	7.97	47.85	2.71	7.71	10^7	$\sim -0.49^c$	A	CH$_3$CN	70
8·19j, TMSA·TCNQBr	47.15	2.68	7.85	47.36	2.89	7.43	10^8	$\sim -0.61^c$	A	CH$_3$CN	15
8·19a, TMSA·TCNQ	53.01	3.17	8.83	53.23	3.46	8.86	2.10^9	$\sim -0.73^c$	A	CH$_3$CN	40
(**2**)$_3$·(**20**)$_2$, (SSe)$_3$·(TNAP)$_2$	51.45	3.50	6.49	50.68	3.48	6.57	3.6		A	CH$_3$CN	~20

Table I. (*Continued*)

Complex	Analyses, % Calculated C	H	N	Found C	H	N	Resistivity[a]	$E_{1A} - E_{1D}$	Method[b]	Solvent	Yield, %
2·19a, SSe·TCNQ	51.15	3.30	9.18	51.33	3.45	8.72	4.10^5	−0.11	A	CH_3CN	65
2·19v, SSe·TCNQF$_4$	45.76	2.36	8.21	46.34	2.58	8.28	4.10^5	0.25	A	CH_3CN	50
9·(19c)$_2$	63.91	3.66	16.94	64.00	3.73	17.25	30		A	CH_3CN	65
9·(19a)$_3$	68.56	2.88	21.53	67.38	3.23	21.41	20		A	CH_3CN	70
9·29	30.16	3.16	1.76	31.89	3.60	2.11	2.10^6		A	CH_3CN	~75
10·19p, AZ·TCNQI$_2$	42.98	2.06	14.32	43.51	2.17	14.26	15	−0.11	A	$PhCH_3$	40
(10)$_2$·(19u)$_3$, (AZ)$_2$·[TCNQ(CN)$_2$]$_3$	62.76	2.45	25.72	62.91	2.21	25.08	30		A	$PhCH_3$	
10·19n, AZ·TCNQCl$_2$	56.10	2.69	18.69	56.37	2.81	18.53	5.10^4	−0.04	A	$PhCH_3$	60
10·19v, AZ·TNQF$_4$	55.81	2.34	18.60	55.97	2.42	18.02	10^5	0.07	A	$PhCH_3$	80
10·19o, AZ·TCNQBr$_2$	48.85	2.34	16.28	49.10	2.48	16.18	2.10^5	−0.04	A	$PhCH_3$	50
(10)$_2$·30, (AZ)$_2$·PtC$_4$S$_4$(CF$_3$)$_4$	36.95	2.17	8.62	37.00	2.28	8.22	300		A	$PhCH_3$	80
(11)$_5$·(19p)$_3$, (BAZ)$_5$·(TCNQI$_2$)$_3$	47.01	2.76	17.17	47.30	3.15	17.02	6		A	DMF	70
11·19v, BAZ·TCNQF$_4$	53.64	2.61	19.75	53.43	2.87	19.55	10		A	DMF	80
13·(19a)$_{4-5}$, TAE·(TCNQ)$_{4-5}$	71.64	2.84	25.53	71.29	3.19	24.33	60			C	
13·(19a)$_2$, TAE·(TCNQ)$_2$	72.40	3.49	24.12	72.23	3.37	24.35	600			C	
13·(19a)$_2$·2H$_2$O	68.84	3.85	22.94	68.91	3.43	23.00	9.10^4		B	**14 + 35**, H_2O	85
13·23, TAE·PtC$_4$S$_4$(CN)$_4$	40.89	2.11	14.67	41.00	2.40	14.19	10^{11}	~2.32	B	**14 + 25**, H_2O, CH_3CN	60
12·(19a)$_{4-5}$	74.00	3.40	22.60	73.44	3.72	22.07	30			C	
(12)$_2$·(19c)$_5$	70.64	4.38	17.74	70.79	4.60	17.99	800		A	CH_3CN	−60
12·(19s)$_3$	77.67	5.55	16.77	78.07	5.63	16.67	3.10^6		A	CH_3CN	~90
12·(19a)$_2$	76.04	4.25	19.71	75.85	4.47	19.71	2.10^7			C	
16·19v	65.65	2.42	15.31	65.43	2.60	15.09	10^{10}	~−0.6[c]	A	CH_3CN	60
16·19a	77.91	3.93	18.17	77.98	4.14	18.36	>10^{12}	~−0.9[c]	A	CH_3CN	50
15·19a	71.45	3.25	17.36	71.24	3.27	17.14	6.10^6	−0.41	A	CH_3CN	65
17·30	37.38	1.34		37.37	1.20		5.10^5		A	CH_2Cl_2	50
18·30	33.93	1.19		34.07	1.20		2.10^8		A	PhH	~100

[a] Resistivity in Ω cm for 2 probe, room-temperature compaction. [b] Method A, direct combination of donor and acceptor in solvent indicated; method B, metathesis of two salts indicated by number; method C, see Experimental Section. [c] $E_{1A} - E_{ox}$, where E_{ox} is the potential at which irreversible polarographic oxidation of the donor first occurs.

Table II. Comparison of Compaction and Single Crystal Resistivity

Complex	ρ, 300 K (Ω cm) Compaction	Single crystal[b]	Max enhancement rel to 300 K	Temp of max enhancement, K
5·19l, TTF·TCNQBrMe	0.1	2.3 × 10^{-3}	1.1	225
5·19a, TTF·TCNQ	0.1	2.4 × 10^{-3}	17	60
5·19s, TTF·TCNQEt$_2$	0.1	3.5 × 10^{-3}	1.6	175
5·19m, TTF·TCNQICH$_3$	0.1	5.4 × 10^{-3}	1.3	225
5·19c, TTN·TCNQ(OMe)$_2$	0.2	5.8 × 10^{-3}	1.9	150
5·19o, TTF·TCNQBr$_2$	0.2	3.4 × 10^{-2}	1.0[a]	275
5·19k, TTF·TCNQClCH$_3$	0.2	4.10^{-2}	1.2	210
5·19m, TTF·TCNQI$_2$	45	12	None[a]	

[a] Enhancements may be seen if resistivities for temperatures over 300 K are considered as, for example, TTF·TCNQBr$_2$ for which ρ350 K/ρ275 K = 1.2. [b] Single crystal resistivities were taken only in the direction of the longest crystal face and thus do not necessarily represent a maximum conductivity, although this is the case for solution and electrochemically grown TTF·TCNQ.

Experimental Section

Many of the synthetic procedures described in this report are of a highly repetitive nature. Typical examples of complex formation are set out in detail below and supporting data for these and other complexes gathered in Table I. Most complexes were prepared by direct reaction between donor and acceptor (procedure A in Table I) or by metathesis between donor and acceptor salts (procedure B in Table I). Rough melting points are given for many of the complexes, but accuracy may be poor since it is hard to follow the decomposition and melting of dark colored or black solids to equally dark fluids. KBr pellet ir spectra were taken for many of the complexes and are most often sharp for poor conductors and very broad for good conductors, two typical series being shown in Figure 3. A similar correlation with conductivity has been observed for series with other donors and between different stoichiometries of the same two reactants. Varying grinding times and suspending in mineral oil as well as KBr has little effect on the trend.

4,4′,5,5′,6,6′,7,7′-Octahydro-$\Delta^{2,2'}$-2*H*,-1,3-bibenzthiaselenole (2). Cyclohexanone semicarbazone (124 g) in 150 ml of dioxane was cooled in an ice bath and stirred mechanically while 180 g of selenium dioxide in 300 ml of water was added in 50-ml portions every 10 min.

Table III. Redox Potentials of Donors

Donor or donor salt	$E_1{}^a$	$E_2{}^b$	$E_1 - E_2$	Ref
14, $TAE^{2+}(Br^-)_2$	−1.32	−0.47	0.85	46
9	−0.17	−0.02	0.15	53
7, $TTN\cdot^+Cl^-$	0.12	0.49	0.37	47, 48
	0.24	0.73	0.49	49
2, SSe	0.28^d	0.63	0.35	47
5, TTF	0.30	0.66	0.36	47
	0.33	0.70	0.37	50
	0.37	0.78	0.42	51
10, AZ	0.46	0.78	0.32	47
	0.56	1.1	0.5	52
15	0.58			47
8, TMSA	0.90^c			47
16	$\sim 1.1-1.2^c$			47

[a] For reaction $D^+ + e^- \rightleftharpoons D^0$. [b] For reaction $D^{2+} + e^- \rightleftharpoons D^+$. [c] Irreversible, potential at which peak appears. [d] Quasi-reversible.

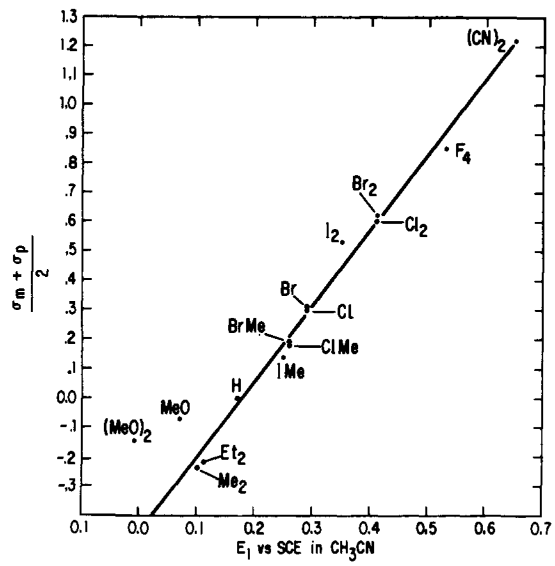


Figure 2. $(\sigma_m + \sigma_p)/2$ vs. E_1 for TCNQ's.

The reaction mixture was stirred overnight at room temperature. Vacuum filtration and washing with ether gave a filtrate that was reduced to a heavy brown residue at 40–55 °C on a rotary evaporator. This residue was mixed with 500 ml of ether and 500 ml of water and vacuum filtered through a 18.5-cm Buchner to remove additional solids. The ether layer was separated and later combined with three 500-ml extracts of the aqueous layer. This ether extract was dried over magnesium sulfate, filtered, and reduced to 68 g of red brown fluid on a rotary evaporator that was taken up in benzene and passed on 600 g of Mallinckrodt CC-7 SilicAR. The first 4–5 l. off the column was reduced to ~68 g of yellow-orange solution on a rotary evaporator. This residue was mixed with 250 ml of carbon disulfide and then heated at 140 °C for 1 h in a steel bomb. The reaction mixture was reduced to a thick red-brown semisolid on a rotary evaporator, taken up in a 200 ml benzene, and then passed through a chromatography column consisting of a 100-g layer of SilicAR CC-7 and a 20-g layer of Darco. The deeply colored fluid that came through was reduced to ~71 g of dark orange solid on a rotary evaporator. This solid was washed into a vacuum filter with several hundred milliliters of petroleum ether, giving ~50 g of sticky orange flakes. These flakes were taken up in ~750 ml of refluxing cyclohexane and cooled on ice. Vacuum filtration gave 38.72 g (19%) of brilliant orange flakes, mp 89–90 °C. Recrystallizing a small sample twice more affords yellow flakes: mp 93–94 °C; H^1 NMR ($CDCl_3$) δ 1.8–2.2 (4 H multiplet), 2.3–2.9 (4 H multiplet).

Table IV. Redox Potentials of Acceptors

Acceptor or acceptor salt	$E_1{}^a$	$E_2{}^b$	$E_1 - E_2$	Ref
28, $(n\text{-}Bu_4N^+)_2PdC_4S_4(CN)_4$	~1	0.44	0.6	54
24, $(Et_4N^+)_2PtC_4S_4(CN)_4$	~1	0.210	0.8	54
29, $PtC_4S_4(CH_3)_4$	0.982	0.051	0.93	55
30, $PtC_4S_4(F_3)_4$	0.819	−0.267	1.086	56
22	0.75	0.57	0.18	47, 57
19u, $TCNQ(CN)_2$	0.65	0.09	0.54	47
19v, $TCNQF_4$	0.53	0.02	0.51	47
	0.52	0.03	0.49	58
19o, $TCNQBr_2$	0.41	−0.08	0.49	57
19n, $TCNQCl_2$	0.41	−0.10	0.49	47
19p, $TCNQI_2$	0.35	−0.10	0.45	47
19j, TCNQBr	0.29	−0.22	0.51	47
19i, TCNQCl	0.29	−0.22	0.51	47
19l, $TCNQBrCH_3$	0.26	−0.22	0.48	47
19k, $TCNQClCH_3$	0.26	−0.23	0.49	47
19m, $TCNQICH_3$	0.25	−0.21	0.46	47
20, TNAP	0.20	−0.17	0.37	47
	0.21	−0.17	0.38	58
19a, TCNQ	0.17	−0.37	0.54	47
	0.13	−0.29	0.42	58
37, TCNE	0.152	−0.568	0.72	59
	0.15	−0.57	0.72	58
19t, $TCNQ(i\text{-}Pr)_2$	0.12	−0.35	0.47	47
19s, $TCNQEt_2$	0.11	−0.37	0.48	47
19r, $TCNQMe_2$	0.10	−0.38	0.48	47
19h, TCNQ(OEt)(SMe)	0.08	−0.36	0.44	47
19b, TCNQ(OMe)	0.07	−0.45	0.52	47
19q, $TCNQ(OMe)(OCH_2OCH_2)$	0.05	−0.33	0.38	47
19c, $TCNQ(OMe)_2$	−0.01	−0.47	0.46	47
19d, TCNQ(OMe)(OEt)	−0.02	−0.47	0.45	47
36	−0.08			60

[a] For reaction $A + e^- \rightleftharpoons A^-$. [b] For reaction $A^- + e^- \rightleftharpoons A^{2-}$.

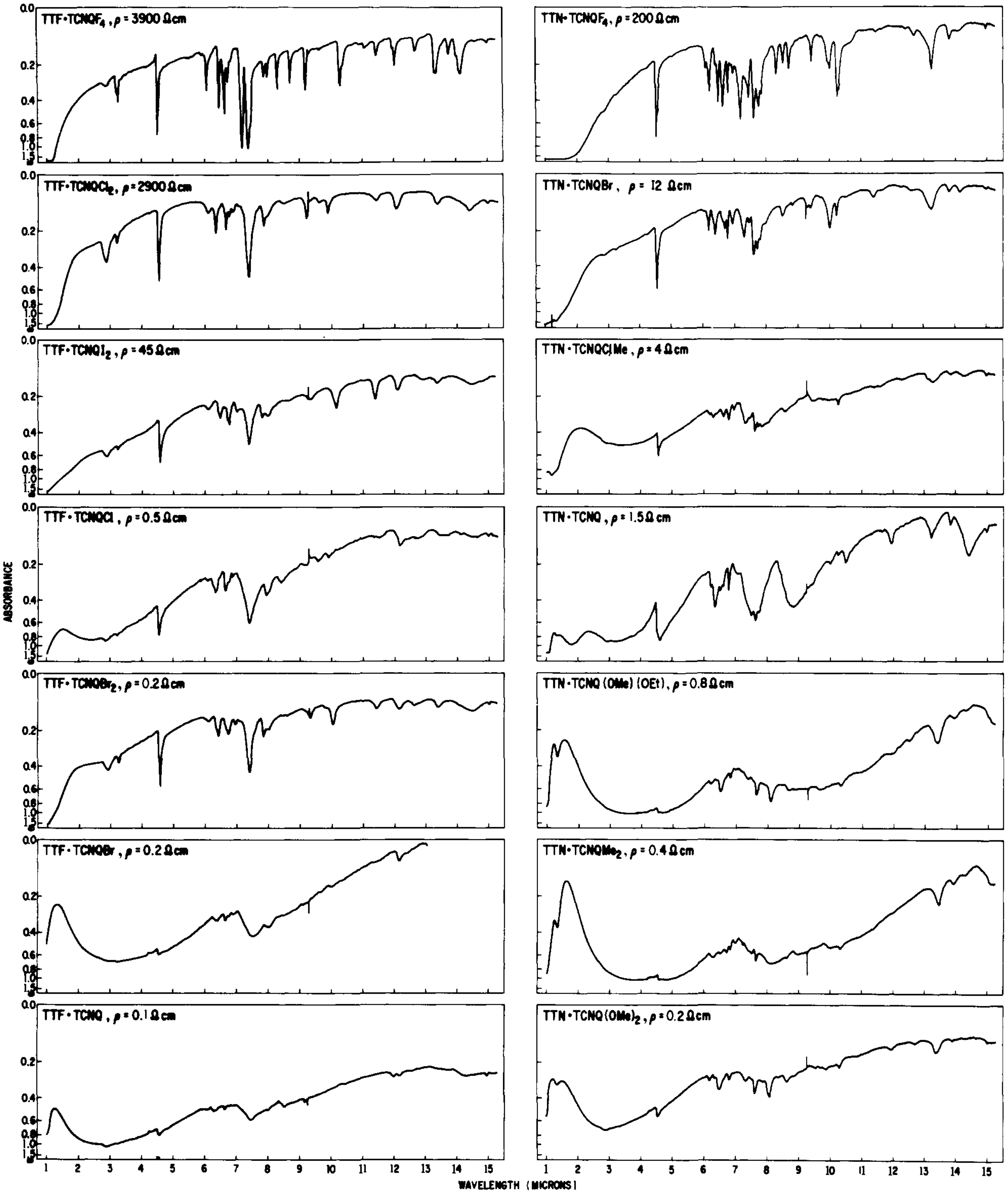


Figure 3. KBr pellet ir spectra.

Anal. Calcd for $C_7H_8S_2Se$: C, 35.74; H, 3.43. Found: C, 35.75; H, 3.57; C, 35.59; H, 3.34.

4,5,6,7-Tetrahydro-2H^1-3,1-benzothiaselenole-2-thione (10 g) prepared above and 100 ml of triethyl phosphite were refluxed for 1 h under nitrogen. Cooling on ice, adding 100 ml of petroleum ether, filtering, and washing with petroleum ether gave 0.42 g of crude product. The filtrate was stripped down at 70 °C and 15 mm on a rotary evaporator. Mixing with petroleum ether and filtering gave an additional 0.71 g of crude product. The combined crude product was vacuum sublimed over several days starting around 110 °C and 0.05 mm. Yellow solid coming over at first was discarded. Raising the temperature to 150–170 °C gave pink to red solid that sublimed slowly, 0.98 g (11%).

Anal. Calcd for $C_{14}H_{16}S_2Se_2$: C, 41.38; H, 3.97. Found: C, 40.86; H, 4.38; C, 40.92; H, 4.26.

Mass spectra show the parent at mass 407.9036 (calcd for $C_{14}H_{16}S_2Se_2$, 407.9013) and a peak at mass 248.0686 (calcd, for $C_{14}H_{16}S_2$, 248.0693).

Tetrathiofulvalene Tetrafluoroborate (3). A solution of 1.0 g of tetrathiofulvalene in 10 ml of methylene chloride and 25 ml of acetonitrile was stirred for 5 min at room temperature with 1.1 g of trityl tetrafluoroborate in 30 ml of acetonitrile. The black solid product, 0.87 g (69%), 211 °C dec, was filtered off and washed with methylene chloride. Recrystallization from acetonitrile gave an analytical sample.

Anal. Calcd for $C_{48}H_{32}S_{32}B_5F_{20}$: C, 27.86; H, 1.56; S, 49.58. Found: C, 27.91; H, 1.65; S, 49.48.

Tetrathiofulvalene–2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethan Complex (5·19v). A solution of 0.13 g of $TCNQF_4$ in 25 ml of refluxing dry Eastman acetonitrile was treated with 0.10 g of TTF in 25 ml of refluxing acetonitrile. The mixture was refluxed back to about 40 ml, cooled briefly, blanketed with N_2, stoppered, and set aside to cool. Several hours later, 0.15 g of brilliant purple needles (65%) were pressure filtered off under N_2, washed with acetonitrile, and blown dry, mp >360 °C.

Anal. Calcd for $C_{18}H_4F_4N_4S_4$: C, 45.00; H, 0.84; N, 11.66. Found: C, 45.19; H, 1.02; N, 11.91.

Tetrathiofulvalene–2,2′,3,3′,5,5′,6,6′-Octafluoro-7,7,7′,7′-tetracyanodiphenoquinodimethan Complex [(5)$_2$·21]. A solution of 0.09 g of $(n\text{-}Bu_4N^+)_2TCNDQF_8{}^{2-}$ (**22**) in 10 ml of acetonitrile was added dropwise with swirling to 0.10 g of $TTF_8(BF_4)_5$ (**3**) in 50 ml of acetonitrile. Pressure filtration under nitrogen gave 0.01 to 0.02 g (~15%) of purple solid, mp >360 °C.

Anal. Calcd for $C_{30}H_8N_4F_8S_8$: C, 43.26; H, 0.97; N, 6.73. Found: C, 43.16; H, 1.49; N, 7.10; C, 43.63; H, 1.56; N, 7.23.

Tetrathionaphthacene–2,5-Dimethoxy-7,7,8,8-tetracyanoquinodimethan Complex (6·19c). A solution of tetrathionaphthacene was prepared by heating 0.10 g of tetrathionaphthacene with 50 ml of trichlorobenzene and the cooling back to about 40 °C. A solution of 0.080 g of $TCNQ(OMe)_2$ in 45 ml of hot trichlorobenzene was added over several minutes. Slow cooling to room temperature, followed by pressure filtration under N_2, washing with trichlorobenzene and then benzene gave 0.14 g (~80%) of dark red-purple solid, mp >360 °C.

Anal. Calcd for $C_{32}H_{16}N_4O_2S_4$: C, 62.32; H, 2.62; N, 9.08. Found: C, 62.02; H, 2.65; N, 8.84.

Tetrathionaphthacene–Azotetracyanocyclopentadiene Complex [(6)$_2$·33]. A solution of 0.10 g of $TTN\cdot^+Cl^-$ (**7**) in 400 ml of refluxing methanol was gravity filtered into 0.10 g of **34** in room-temperature methanol. Pressure filtration under nitrogen, washing with methanol, and blowing dry gave 0.11 g (70%) of strikingly reflective dark brown solid, visible decomposition ~240 °C, mp >360 °C.

Anal. Calcd for $C_{54}H_{16}S_8N_{10}\cdot CH_3OH$: C, 60.42; H, 1.84; N, 12.81. Found: C, 60.26; H, 1.84; N, 13.29; C, 60.32; H, 1.84; N, 13.35.

1,1′,3,3′-Diethylene-2,2′-bibenzimidazolidene–Tetracyanoquinodimethan Complexes [13·(19a)$_2$·2H$_2$O, 13·(19a)$_2$, and 13·(19a)$_{4-5}$]. A solution of 0.094 g of LiTCNQ in 25 ml of water was filtered into 0.10 g of dibromide **14** in 25 ml of water. The flocculent blue precipitate was pressure filtered off under N_2, washed with water, and blown dry under N_2, giving 0.14 g (85%) of **13**·(**19a**)$_2$·2H$_2$O, mp 123–125 °C with decomposition.

Anal. Calcd for $C_{42}H_{24}N_{12}\cdot 2H_2O$: C, 68.84; H, 3.85; N, 22.94. Found: C, 68.89; H, 3.39; N, 23.13; C, 68.94; H, 3.47; N, 22.87.

13·(**19a**)$_2$·2H$_2$O (0.45 g), dissolved in 100 ml of refluxing acetonitrile, was refluxed down to 50 ml and rapidly filtered and cooled. Blowing the filtrate down further with nitrogen gave a small quantity of brilliant dark blue crystals **13**·(**19a**)$_2$, decomposition starting at ~200 °C.

Anal. Calcd for $C_{42}H_{24}N_{12}$: C, 72.40; H, 3.47; N, 24.12. Found: C, 72.23; H, 3.37; N, 24.35.

13·(**19a**)$_2$·2H$_2$O (0.48 g) and 0.42 g of TCNQ were refluxed under N_2 for 1 h in 100 ml of acetonitrile. Cooling and pressure filtration under nitrogen gave 0.42 g of **13**·(**19a**)$_{4-5}$ as a black powder, mp >360 °C.

Found: C, 71.38; H, 3.19; N, 24.45; C, 71.60; H, 3.18; N, 24.22.

$\Delta^{2,2'}$-Bis(1,3-diphenylimidazolidene)–Tetracyanoquinodimethan Complexes [12·(19a)$_2$ and 12·(19a)$_{4-5}$]. A solution of 3.06 g of TCNQ in 250 ml of refluxing acetonitrile under nitrogen was treated with 3.33 g of freshly prepared $\Delta^{2,2'}$-bis(1,3-diphenylimidazolidene) (**12**). After 1 h of refluxing the reaction mixture was allowed to cool slowly to room temperature. Pressure filtration under nitrogen gave 1.58 g of solid that could be mechanically separated into complex **12**·(**19a**)$_2$, mp 182–185 °C with decomposition, dark blue micaceous flakes, and complex **12**·(**19a**)$_{4-5}$, mp 215–225 °C with decomposition, coarse dark blue needles.

12·(**19a**)$_2$, Anal. Calcd for $C_{54}H_{36}N_{12}$: C, 76.04; H, 4.25; N, 19.71. Found: C, 75.85; H, 4.47; N, 19.71. **12**·(**19a**)$_{4-5}$, Found: C, 73.40; H, 3.74; N, 21.97; C, 73.48; H, 3.71; N, 22.17.

Tetramethoxyselenanthracene–2,5-Dichloro-7,7,8,8-tetracyanoquinodimethan Complex (8·19n). A solution of 0.11 g of $TCNQCl_2$ (**19n**) in 30 ml of refluxing acetonitrile was treated with 0.17 g of TMSA (**8**) in 10 ml of refluxing acetonitrile and cooled to room temperature. Pressure filtration under nitrogen, washing with acetonitrile, and blowing dry gave 0.19 g (70%) of blue-black needles, 150 °C dec, mp 230–234 °C.

Anal. Calcd for $C_{28}H_{18}N_4O_4Se_2Cl_2$: C, 47.82; H, 2.55; N, 7.97. Found: C, 47.89; H, 2.68; N, 7.79; C, 47.81; M, 2.73, N, 7.63.

4,4′,5,5′,6,6′,7,7′-Octahydro-$\Delta^{2,2'}$-2*H*,-1,3-bibenzthiaselenole–7,7,8,8-Tetracyanoquinodimethan Complex (2.19a). A solution of 0.13 g of **2** in 140 ml of refluxing acetonitrile was treated with 0.13 g of TCNQ in 10 ml of refluxing acetonitrile. Cooling and pressure filtration under nitrogen gave 0.12 g (65%) of black solid with a metallic sheen.

Anal. Calcd for $C_{26}H_{20}N_4S_2Se_2$: C, 51.15; H, 3.30; N, 9.18. Found: C, 51.29; H, 3.47; N, 9.07; C, 51.53; H, 3.48; N, 8.50; C, 51.18; H, 3.40; N, 8.61.

The mass spectrum gave peaks at 407.9020 (calcd SSe (**5**), 407.9023) and 204 (TCNQ). Cyclic voltametry found a concentration ratio of TCNQ/SSe = 1.04 assuming that TCNQ and SSe have equal diffusion coefficients.

Bis(3-methylbenzothiazolinyldene-2)–2,5-Dimethoxy-7,7,8,8-tetracyanoquinodimethan Complex (9·19c). A slurry of 200 ml of acetonitrile, 0.30 g of SN **9**, and 0.40 g of $TCNQ(OMe)_2$ (**19c**) was stirred under nitrogen overnight. Pressure filtration under nitrogen and washing with acetonitrile gave 0.42 g (65%) of dark blue complx, mp 190–215 °C.

Anal. Calcd for $C_{58}H_{38}N_{14}O_6S_2$: C, 63.91; H, 3.66; N, 16.94. Found: C, 64.00; H, 3.71; N, 17.25.

***N*-Methylbenzthiazolonazine–2,5-Dibromo-7,7,8,8-tetracyanoquinodimethan Complex (10·19o).** A solution of 0.06 g of AZ (**10**) in 20 ml of refluxing toluene was added to 0.078 g of $TCNQBr_2$ (**19o**) in 50 ml of refluxing toluene. The reaction vessel was flushed with nitrogen and cooled to room temperature. Pressure filtration under nitrogen the next day gave 0.07 g (50%) of shiny black crystals, mp >360 °C.

Anal. Calcd for $C_{28}H_{16}N_8Br_2S_2$: C, 48.85; H, 2.34; N, 16.28. Found: C, 49.01; H, 2.48; N, 16.18.

2,6-Bis(3′-methyl-2′,3′-dihydrobenzthiazolylidenhydrazono)-3,5-dimethyl - 2,3,5,6-tetrahydrothiazolo[4,5-*F*]benzthiazole–2,3,5,6-Tetrafluoro-7,7,8,8 - tetracyanoquinodimethan Complex (11·19v). A refluxing dimethyl formamide solution of 0.057 g of BAZ **11** under nitrogen was treated with 0.060 g of $TCNQF_4$. Refluxing was continued for 5 additional min and then the reaction mixture was cooled to room temperature. Pressure filtration under nitrogen 2 days later gave 0.07 g (80%) of turquoise-blue complex, discolors ~300 °C, mp >360 °C.

Anal. Calcd for $C_{38}H_{22}N_{12}S_4N_4$: C, 53.64; H, 2.61; N, 19.75. Found: C, 53.40; H, 2.90; N, 19.57.

***N*-Methylcarbazole–2,3,4,5-Tetrafluoro-7,7,8,8-tetracyanoquinodimethan Complex (16·19v).** A solution of 0.1 g of $TCNQF_4$ (**19v**) in 5 ml of refluxing acetonitrile was treated with 0.06 g of **16** in 2 ml of refluxing acetonitrile. The solution became extremely thick with precipitate on cooling to room temperature and was washed into a pressure filter with a small quantity of acetonitrile. Washing with acetonitrile and blowing dry gave 0.11 g (60%) of dark-purple needles, mp 190–198 °C.

Anal. Calcd for $C_{25}H_{11}F_4N_5$: C, 65.65; H, 2.42; N, 15.31. Found: C, 65.43; H, 2.60; N, 15.09.

Phenothiazine–7,7,8,8-Tetracyanoquinodimethan Complex (15·19a). A solution of 1.0 g of **15** in 25 ml of refluxing acetonitrile was added to 1.03 g of TCNQ (**19a**) in 100 ml of refluxing acetonitrile. Cooling gave 1.03 g (65%) of spectacular coal black needles, mp 234–238 °C.

Anal. Calcd for $C_{24}H_{13}N_3S$: C, 71.45; H, 3.25; H, 3.25; N, 17.36. Found: C, 71.35; H, 3.16; N, 17.23; C, 71.13; H, 3.38; N, 17.05.

Pyrene–Bis(*cis*-1,2-ditrifluoromethylethylene-1,2-dithiolato)platinum Complex (17.30). A solution of 0.05 g of pyrene **17** in 2 ml of benzene is treated with 0.05 g of $PtC_4S_4(CF_3)_4$ (**30**) in 10 ml of benzene. Pessure filtration the next day under nitrogen gave 0.1 g (~100%) of intensely blue solid, mp 286–292 °C.

Anal. Calcd for $C_{24}H_{10}F_{12}PtS_4$: C, 33.93; H, 1.19. Found: C, 34.00; H, 1.31; C, 34.14; H, 1.10.

Lithium 2,6-Dibromo-7,7,8,8-tetracyanoquinodimethanide (41). A solution of 1 g of 2,6-dibromo-7,7,8,8-tetracyanoquinodimethane in 400 ml of refluxing acetonitrile was treated with 1.12 g of lithium iodide in 25 ml of refluxing acetonitrile. The dark solution was refluxed back to 150–200 ml at which time solids started to appear. The reaction vessel was flushed with nitrogen and set aside to cool. Pressure filtration under nitrogen and washing with acetonitrile until the filtrate came through a light green gave 0.77 g (75%) of reflective blue-black crystals of $LiTCNQBr_2$, mp >360 °C.

Anal. Calcd for $C_{12}H_2Br_2N_4Li$: C, 39.07; H, 0.55; N, 15.15. Found: C, 38.98; H, 0.69; N, 15.08.

Electrochemical Growth of TTF·TCNQ (5·19a). Two electrodes were prepared by sealing 0.04 in. diameter of Pt wire in soft glass tubing with about 10–13 mm of wire protruding from the end. These electrodes were soaked in concentrated nitric acid for several hours, washed with distilled water, and then used to electrolyze 10% aqueous sodium sulfate for 5 min at 1 μA. The electrodes were washed with water and acetone and then allowed to air dry.

A slurry of 0.15 g of NMQ·TCNQ (**39**), 0.1 g of TTF, 0.05 g of TTF·TCNQ, and 80 ml of acetonitrile was stirred magnetically under nitrogen for 30–60 min and then pressure filtered into an electrolysis cell consisting of two arms separated by a fine glass frit. One electrode was placed in each arm of the electrolysis cell and the apparatus encased in a nitrogen filled glove bag. A 1-μA current was started keeping the electrode previously positive in the sodium sulfate electrolysis positive here too. The positive electrode was withdrawn 2 weeks later and immediately washed by dipping briefly in acetonitrile. Air drying revealed reflective black crystals 1–2 mm long on the electrode.

Anal. Calcd for $C_{18}H_8N_4S_4$: C, 52.92; H, 1.97; N, 13.71. Found: C, 53.10; H, 2.15; N, 13.90.

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