MHz) δ 1.56 (s, 6 H) and 7.2–7.7 (m, 20 H). The second fraction isolated from the column was identified as 1,2-dimethyl-3,4,5,6-tetraphenylbenzene (**13**) by comparison with an authentic sample.

A solution containing 128 mg of **15** and 50 mg of thioxanthone in 250 mL of benzene was irradiated for 1.25 h under an argon atmosphere with a 450-W Hanovia mercury arc lamp equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure and the resulting residue was subjected to silica gel chromatography using a hexane–benzene mixture as the eluent. The two components isolated from the column corresponded to the ortho (80%) and meta (20%) isomers.

Independent Synthesis of 1,2-Diphenyl-3-methyl-3-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)cyclopropene (24). To a solution containing 25 g of 1,4-diphenyl-1,3-butadiene in 1 L of anhydrous benzene was added 41.8 g of phenyl chlorodiazirine.[58] The mixture was heated at reflux for 4.5 h and cooled to room temperature, and the solvent was removed under reduced pressure. The pale yellow solid (31 g (56%)) that remained was identified as 3,3′-bi(1,2-diphenyl-1-chlorocyclopropane) on the basis of its characteristic spectral properties: mp 208–209 °C; NMR ($CDCl_3$, 90 MHz) δ 2.35–2.78 (m, 2 H), 2.89–3.20 (m, 2 H), and 6.8–7.7 (m, 20 H).

To a solution containing 15.0 g of the above material in 500 mL of anhydrous tetrahydrofuran under a nitrogen atmosphere was added 22.4 g of potassium *tert*-butoxide in one portion. The resulting reaction mixture was heated at reflux for 72 h. At the end of this time the reaction mixture was cooled to 25 °C and 100 mL of water was added. The resulting mixture was extracted with three 100-mL portions of ether. The combined ether extracts were washed with water and a saturated brine solution and were then dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 10.5 g (83%) of a tan solid which was identified as bi(1,2-diphenyl-1-cyclopropene) on the basis of its spectral properties: mp 164–165 °C; IR (KBr) 3080, 3020, 1820, 1680, 1600, 1500, 1450, 1270, 1070, 1020, 920, 690, 670 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.46 (s, 2 H), 7.1–7.6 (m, 20 H).

To a slurry containing 10.0 g of the above solid in 175 mL of anhydrous acetonitrile was added 20.5 g of trityl perchlorate. The resulting reaction mixture was stirred at 0 °C for 30 min and then 500 mL of anhydrous ether was added. The resulting slurry was filtered and the white amorphous solid that was obtained was washed with anhydrous ether. This solid was not allowed to dry completely. The material was stirred in 250 mL of anhydrous ether at −78 °C under a nitrogen atmosphere. To this mixture was added 34 mL of a 2.8 M solution of methylmagnesium bromide over a 30-min period. The resulting mixture was allowed to warm to 5 °C overnight. After quenching with a saturated ammonium chloride, the ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 6.65 g (62%) of a yellow solid, which was identified as 1,2-diphenyl-3-methyl-3-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)cyclopropene (**24**) on the basis of its characteristic spectral properties: mp 168–169 °C (lit.[35] mp 169–170 °C); IR (KBr) 3080, 3060, 3020, 2880, 1840, 1670, 1600, 1500, 1450, 1270, 1070, 1020, 920, 690, and 600 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.56 (s, 6 H) and 7.2–7.7 (m, 20 H).

Constant Potential Electrolysis of Diphenylmethylcyclopropenylium Perchlorate (5) in Acetonitrile. A solution containing 2.73 g of lithium perchlorate and 2.0 g of **5** in 200 mL of anhydrous acetonitrile was electrolyzed (1.35 V vs. the SCE and 500 A) to completion as indicated by a return to the background level of the current. The experimental setup consisted of a three-electrode system containing a mercury pool (instrumental grade) as the working cathode electrode, a standard saturated calomel reference electrode, and a silver auxiliary anode electrode which was separated from the solution by a fritted glass disk. The resulting solution was poured into a separatory funnel containing 100 mL of water and the mercury was removed. The reaction mixture was extracted with ether. The ethereal extracts were combined and washed repeatedly with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 1.32 g (98%) of a yellow solid, which was chromatographed on a 15 × 2.5 cm Florisil column using a 5% benzene–hexane mixture as the eluent. The first fraction isolated from the column contained 400 mg of 1,3-diphenyl-2-methyl-3-(1,2-diphenyl-3-methyl-2-cyclopropen-1-yl)cyclopropene (**15**). The second fraction contained 720 mg of 2,6-dimethyl-1,3,4,5-tetraphenylbicyclo[2.2.0]hexa-1,3-diene (**16**).

Dicyanoanthracene-Sensitized Irradiation of Bicyclopropenes 15 and 24. A solution containing 100 mg of **15** (or **24**) and 73 mg of 9,10-dicyanoanthracene in 450 mL of acetonitrile was irradiated for 8 h under an argon atmosphere with a 450-W Hanovia lamp equipped with a Uranium glass filter. Removal of the solvent left a yellow residue, which was subjected to thick-layer chromatography using a hexane–benzene mixture as the eluent. In the case of bicyclopropene **15** the only product isolated in 92% yield corresponded to 1,3-dimethyl-2,4,5,6-tetraphenylbenzene (**14**). The DCA-sensitized irradiation of **24** produced 1,2-dimethyl-3,4,5,6-tetraphenylbenzene (**13**) in 94% isolated yield.

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1,3,5,7-Tetrathia-*s*-indacene-2,6-dione Chemistry. Synthesis of New Multisulfur Donor Molecules and Nickel–Dithiolene Electron-Transfer Complexes

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The synthesis of 1,3,5,7-tetrathia-*s*-indacene-2,6-dione is reported. This versatile synthon is used to prepare a variety of new multisulfur tetrathiafulvalene-analogous donors and nickel–dithiolene complexes. Donor or acceptor properties are investigated, and new materials, in the form of charge-transfer solids or ion-radical salts, derived from the new compounds are either electrically insulating or semiconducting.

We report the synthesis of new donor molecules analogous to BEDT-TTF[1] (bis(ethylenedithio)tetrathiafulvalene) (**1**) (Figure 1). The latter has been used extensively in the preparation of new superconducting molecular

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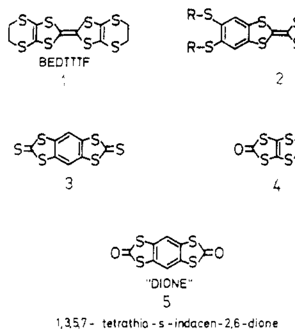
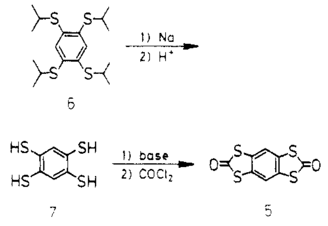


Figure 1.

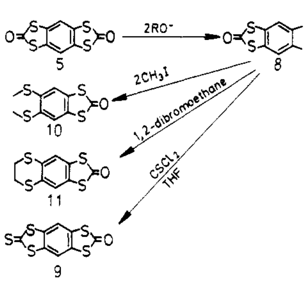
Scheme I



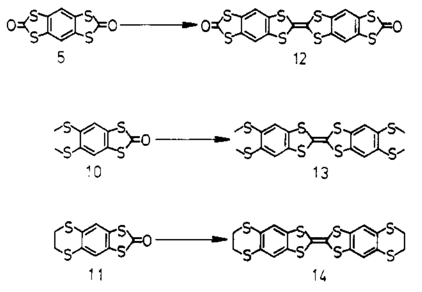
solids.[2-4] The molecules reported here are extensions of BEDT-TTF carrying two aromatic rings inserted in the basic framework. These new compounds (**2**) are somewhat longer than BEDT-TTF but are expected to give rise to solid-state structures close to those of the BEDT-TTF cation radical salts. The target molecules are prepared by phosphite coupling of the corresponding 4,5-benzo-annelated 1,3-dithiol-2-ones. Base-induced opening of the 1,3-dithiole rings also allows facile synthesis of "metal-dithiolene" complexes, in the present work exemplified by nickel complexes, which are potentially useful as acceptor molecules in conducting molecular solids.[5] Compound **3**, which is less versatile as a synthon than **5**, was recently reported.[6] We have extensively made use of reactions analogous to those of thiapen **4**, which was investigated in detail by Schumaker et al.[7,8]

Results and Discussion

Scheme II



Scheme III



Scheme IV

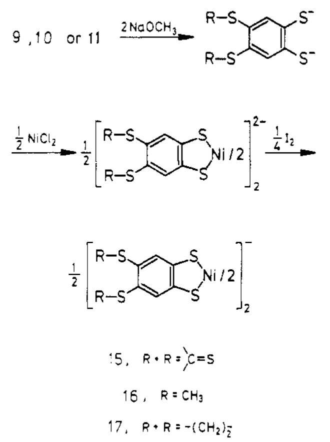


Table I. Cyclic Voltammetry of 13 and 14

compd	E_1, V[a]	E_2, V[a]
13	0.43	1.04
14	0.45	irrev

[a] V vs. SCE, Pt-button electrode; sweep rate, 200 mV/s; dichloromethane, n-Bu_4NPF_6 (0.1 M).

The versatile synthon exploited in this work is 1,3,5,7-tetrathia-*s*-indacene-2,6-dione (**5**), which can be prepared from 1,2,4,5-tetramercaptobenzene (**7**) and phosgene under basic conditions (Scheme I). The dione **5** can be opened sequentially by reaction with 2 equiv of sodium *tert*-amylate and thus give rise to the structures shown in Scheme II. The synthesis of the starting material, tetramercaptobenzene (**7**) has been reported by several authors. Tiecco et al.[9] used the reaction of 1,2,4,5-tetrachlorobenzene with sodium 2-propylmercaptide followed by cleavage with molten sodium in HMPTA. However, as also reported by Wudl et al.,[10] we found this procedure difficult to reproduce. We, for our purpose, found it unnecessary to isolate **7**. We instead prepared **6** using DMF as solvent, which in our hands facilitated isolation and purification of **6**. We cleaved **6** with sodium in hot pyridine[10] to give the tetraanion and treated the reaction mixture with phosgene. After two recrystallizations from toluene the dione **5** was obtained in 55% yield.

Reactions of the Dione 5. The opening of one of the 1,3-dithiol-2-one rings in **5** with 2 equiv of sodium *tert*-amylate proceeded smoothly to give the dianion **8**. Compound **8** could then be treated with thiophosgene to give **9**. Alkylation of the dianion **8** with iodomethane or 1,2-dibromoethane gave **10** and **11**, respectively (Scheme II). Compounds **5** as well as **10** and **11** were coupled to the tetrathiafulvalenes **12**–**14** in good yields by using triethyl

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Table II. Electrochemical Crystallization of 13 and 14 Salts[d]

compd	anion	solvent	stoichmtry	conductvty
13	BF_4^-	TCE[b]	1:1	ins.
13	I^- [a]	TCE	1:1 (I_3^-)	semicond.
13	I_3^-	TCE	1:1	ins.
13	$Re_6Se_5Cl_9^-$	PhCl[c]/THF	2:1	ins.
14	I_3^-	TCE	1:1	ins.
14	ReO_4^-	PhCl	3:2	ins.

[a] The supporting electrolyte is tetra-*n*-butylammonium iodide, but the salt contains triiodide ion. In this case a current of 50 μAmp was used. [b] TCE is 1,1,2-trichloroethane. [c] PhCl is chlorobenzene. [d] In the experiments, Pt electrodes and constant current in the 5–10-μAmp range were used.

Table III. Donor–Acceptor Complexes of the New Donors

donor	acceptor	solvent	stoichmtry	conductvty
12	I_3^-	1,2-dichlorobenzene	1:1	ins
13	I_3^-	1,2,4-trichlorobenzene	1:1	ins
13	I_3^-	chlorobenzene	1:1	ins
13	TCNQ	chlorobenzene	1:1	ins
14	I_3^-	1,2-dichlorobenzene	1:1	ins
14	TCNQ	1,2-dichlorobenzene	1:1	semicond

phosphite in refluxing toluene (Scheme III). Small amounts of **13** could also be obtained in rather impure form by treating **12** with 4 equiv of sodium *tert*-amylate followed by 4 equiv of iodomethane.

Nickel complexes were prepared by treating **5**, **9**, **10**, and **11** with 2 equiv of sodium methoxide in methanol and then adding 0.5 equiv of $NiCl_2$. After oxidation of the dianionic complex with 0.5 equiv of iodine, the monoanionic complex was isolated as the tetra-*n*-butylammonium salt (Scheme IV). A polymeric nickel complex was obtained by treating **5** with 4 equiv of $NaOCH_3$ followed by 1 equiv of $NiCl_2$. After iodine oxidation a black powder was isolated.

Properties of New Donors. The new donors **13** and **14** were sparingly soluble in most organic solvents. Cyclic voltammograms indicated a quasi-reversible one-electron oxidation corresponding to formation of the cation radical. The half-wave potential was somewhat higher than for BEDT-TTF as could be expected by comparison with benzo-annelated TTF's. At more positive potentials further oxidation occurred, presumably to produce the dications, but the waves are strongly distorted due to precipitation on the electrode. The results are collected in Table I. Compound **12** also exhibited donor properties. This was demonstrated by the formation of an iodine complex.

Cation Radical Salts and Charge-Transfer Salts of the New Donors. Electrochemical oxidation of the new donors in the presence of simple inorganic ions have so far mostly given 1:1 salts, which are electrically insulating. Also a few TCNQ[11] and iodine salts have been prepared directly. The results are collected in Tables II and III.

Metal–Dithiolenes. Monoanionic metal–dithiolenes were prepared as described above. Cyclic voltammograms indicated quasi-reversible one-electron oxidation to the neutral complex. Their analysis is, however, complicated by precipitation on the electrode. Also reversible one-electron reduction to the dianionic complex was observed. Results are given in Table IV. The polymeric complex was completely insoluble and microanalysis was not completely in accordance with the expected formula. In several cases, depending on experimental conditions, preparative electrochemical oxidation gave semiconducting nonstoichiometric crystalline *n*-butylammonium salts. Alternatively, oxidation lead to the formation of the neutral complex, which precipitated on the electrode. Results are given in Table V.

Table IV. Cyclic Voltammetry of Ni-Dithiolenes[a]

compound	peak potentials, V, for $0 \rightleftharpoons -1$	$E_{1/2}$, V, for $-1 \rightleftharpoons -2$
$Ni(8)_2$[a]	0.32 and 0.05	–0.37
15	0.26 and 0.04	–0.30
16	$E_{1/2}$, 0.21 (rev)	–0.52
17	0.24 and 0.08	–0.52

[a] V vs. SCE; Pt-button electrode; sweep rate, 200 mV/s; dichloromethane, n-Bu_4NPF_6 (0.1 M).

Table V. Electrochemical Crystallization of Ni–Dithiolenes

cation	compd	stoichmtry[a]	conductvty
n-Bu_4N^+	$Ni(8)_2$	0.09:1	semicond
n-Bu_4N^+	**15**	0.198:1	semicond
n-Bu_4N^+	**16**	0:1[b]	ins
n-Bu_4N^+	**17**	0:1[b]	ins

[a] Indicates cation/anion ratio. Solvent: dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate (0.1 M). [b] The 0:1 stoichiometry shows that instead of a mixed-valence salt, the neutral complex $Ni(L)_2^0$ is formed.

Conclusion. We have prepared several new donors and also potential "acceptor" metal–dithiolenes and ion–radical salts and charge-transfer solids derived therefrom. Preliminary results indicate that some new semiconducting materials are formed. Similarly to earlier experience for BEDT-TTF,[8] proper crystallization condition will have to be worked out. The results will be reported in a forthcoming paper.

Experimental Section

Analytical results were within ±0.3% of the theoretical values unless otherwise indicated.

The electrical resistivity of the new materials (Table II, III, and V) was estimated by pressuring to 0.1 GPa a few milligrams of the material between two gold plated steel pistons (2.7 mm i.d.) in a die made of reinforced Teflon. If the resistivity as measured by an Ohmmeter was in the MOhm range, the material was denoted "insulating", if in the kOhm range it was denoted "semiconducting".

1,2,4,5-Tetrakis(2-propylthio)benzene (6). A 2-L, round-bottom, three-necked flask equipped with reflux condenser and magnetic stirring was charged (under N_2) with 1 L of dry DMF and 190 mL of 2-propanethiol (2 mol) (stench!). Sodium (46 g, 2 mol) cut in small pieces was added and stirring continued overnight. After all the sodium had dissolved a light-yellow precipitate of sodium mercaptide had formed. The reaction mixture was cooled in an ice bath, and 1,2,4,5-tetrachlorobenzene (84.6 g, 0.4 mol) was added. The ice bath was removed, and the reaction mixture heated itself to reflux temperature in about 20 min. Reflux was then continued with an oil bath for 2 h. After cooling, the solution was poured on ice (1 kg), and the white precipitate was isolated by filtration, washed with water, and dried. recrystallization from methanol gave **6** as a white solid in 84% yield: mp 80–81.5 °C (lit.[9] mp 78–80 °C).

1,3,5,7-Tetrathia-*s*-indacene-2,6-dione (5). A dry four-necked flask, equipped with mechanical stirrer, a thermometer, a reflux condenser, and an addition funnel, was loaded (under N_2) with 300 mL of dry pyridine and 25 g (0.067 mol) of 1,2,4,5-tetrakis-(2-propylthio)benzene. After the mixture was heated to ca. 100 °C, sodium (8.3 g, 0.36 mol) cut in small pieces was added. The reaction mixture turned dark red, and the temperature increased to about 110 °C, where it was stabilized by occasional heating with an oil bath, until all the sodium had dissolved (1–2 h). The solution was cooled to –5 °C, and 60 mL of a phosgene solution (20% in toluene, excess!) (*toxic! use an efficient hood*) was added catiously from the addition funnel. After the initial violent reaction had ceased, the phosgene solution was added at such a rate that the temperature was kept between –5 and 0 °C. While the temperature was maintained below –10 °C, 400 mL of cold water was added, the first few milliliters dropwise. The brown pre-

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cipitated powder was filtered off quickly in order to prevent hydrolysis, washed extensively with ice–water followed by methanol, and dried. After two recrystallizations from toluene 9.5 g, 54%, of very fine, white needles were obtained: mp >320 °C; Anal. C, H, N, S.

2-Oxobenzo[*d*]-1,3-dithiole-5,6-dithiolate (8) and 5,6-Bis(methylthio)benzo[*d*]-1,3-dithiol-2-one (10). compound **5** (3 g, 0.0116 mol) was dispersed under N_2 in 100 mL of dry THF, and 12.5 mL of 1.85 M sodium *tert*-amylate in toluene was added. The solution immediately turned red, and after about 30 s a solid, presumably the disodium salt of **8** precipitated. After the mixture was stirred for 45 min, 1.46 mL (0.023 mol) of iodomethane was added, whereupon the solid dissolved. After the mixture was stirred for 30 min, the solvent was evaporated in vacuo. The semisolid residue was treated with 30 mL of dichloromethane, the solution filtered through a short alumina (neutral) or silica column, and the solvent evaporated. After recrystallization from ethyl acetate, a 48% yield of a white solid was obtained: mp 170–172 °C; Anal. C, H, N; NMR (Me_4Si internal standard) δ 2.43 (s, 6 H), 7.16 (s, 2 H).

6-Thioxo-1,3,5,7-tetrathia-*s*-indacen-2-one (9). A solution of **8** was prepared as described above. Thiophosgene (4.5 mL, 0.06 mol) (excess!) dissolved in 20 mL of dry THF was added slowly with ice cooling. After the mixture was stirred for 0.5 h, the precipitated solid was filtered off, dried, and recrystallized from xylene to give 63% yellow needles: mp >320 °C; Anal. C, H, N.

5,6-(Ethylenedithio)benzo[*d*]-1,3-dithiol-2-one (11). A solution of **8** was prepared as described above and treated with slight excess of 1,2-dibromoethane. After standing overnight the solution was cooled to −20 °C for several hours. The precipitated material was isolated by filtration, washed with water and methanol, and dried. The solid was then dissolved in 50 mL of dichloromethane and filtered through a short alumina (neutral) column. Evaporation of the solvent and recrystallization from ethyl acetate gave **11** in 35% yield as a white microcrystalline material: mp 199–201 °C; anal. C, H, N, S; NMR (Me_4Si internal standard) δ 3.16 (s, 4 H), 7.16 (s, 2 H).

6,6′-Dioxo-$\Delta^{2,2'}$-bi-1,3,5,7-tetrathia-*s*-indacene (12). Compound **5** (1 g, 0.0039 mol) was refluxed in 35 mL of dry toluene and 4 mL of triethyl phosphite for 4 h. The precipitated solid was filtered off, washed with warm toluene, and dried: yield, 96%. Recrystallization from 1,2,4-trichlorobenzene gave a yellow microcrystalline solid: mp >320 °C; Anal. C, H, N, S.

5,5′,6,6′-Tetrakis(methylthio)-$\Delta^{2,2'}$-bibenzo[*d*]-1,3-dithiole (13). Compound **10** (0.40 g) was refluxed in 10 mL of triethyl phosphite. After cooling, the precipitated material was filtered off and washed with ether. Recrystallization from xylene gave 45% yield of yellow-orange needles: mp 281.5–282.5 °C; Anal. C, H, N, S.

5,6:5′,6′-Bis(ethylenedithio)-$\Delta^{2,2'}$-bibenzo[*d*]-1,3-dithiole (14). Compound **14** was prepared similarly to **13**. Recrystallization from 1,2-dichlorobenzene gave a 73% yield of yellow powder: mp >320 °C; Anal. C, H, N, S.

Polymeric "Nickel–1,2,4,5-Benzenetetrathiolate". In a dry flask, under N_2, 0.47 g (0.0018 mol) of **5** was dispersed in 40 mL of absolute methanol and treated with 3.9 mL of 1.85 M $NaOCH_3$. After 30 min a clear solution was obtained, and 0.0018 mol of $NiCl_2 \cdot 6H_2O$ dissolved in a few milliliters of ethanol was added. The solution immediately darkened and after about 15 min became gelatinous. Dicloromethane (200 mL) containing 1 g of iodine was added and the solution stirred for 3 days. The solid was isolated by filtration, washed with dichloromethane, methanol, and water, and dried: yield, 450 mg. Anal. Calcd for $(C_6H_2S_4Ni)_n$: C, 27.61; H, 0.77; N, 0.00. Found: C, 29.12; H, 2.68; N, 0.11.

***n*-Bu_4N^+ Salts of Monoanionic Nickel Complex of 8.** A solution of **8** was prepared as described above. $NiCl_2$ (0.5 equiv) dissolved in ethanol was added, whereupon the solution turned black. After the mixture was stirred for 15 min, 0.5 equiv of iodine was added. After 20 min, 1 equiv of *n*-Bu_4NBr dissolved in a few milliliters of methanol was added. The product was isolated by centrifugation. After a washing with methanol, the product was redissolved in dichloromethane and any insoluble material removed by centrifugation. To the dark green solution was slowly added ethyl acetate, until precipitation started. After being stored in the freezer overnight, the product was isolated by filtration and further purified by an additional cycle of dissolving and precipitating: yield, 32%; mp 193–195 °C; Anal. C, H, N.

***n*-Bu_4N^+ Salts of Monoanionic Nickel Complexes 15, 16, and 17.** Starting from the appropriate precursors, these salts were prepared and purified as described above for the nickel complex of **8**. Properties were as follows. **15**: yield, 30%; mp 236–237 °C; Anal. C, H, N. **16**: yield, 52%; mp 214–217 °C; Anal. C, H, N. **17**: yield, 32%; mp 236–238 °C; Anal. C, H, N.

Preparation of Iodine and TCNQ Salts of 12, 13, and 14. The donor (10–20 mg) was dissolved in a minimal amount of the appropriate solvent (Table III) at boiling and mixed with a boiling solution of the acceptor, which was normally taken in 25% excess. After cooling, the precipitated material was filtered off, washed with cold solvent and ether, and dried. The stoichiometry of the resulting black solids was determined from the elemental analysis (C, H, N, S).

Electrochemical Crystallization of Salts of New Donors and Metal–Dithiolenes. A three-chamber electrolysis cell equipped with platinum wire electrodes was loaded, in the anode chamber, with a solution of 10^{-5} mol of the substrate dissolved in the indicated solvent containing the supporting electrolyte (0.1 M), as the tetrabutylammonium salt. After loading the cathode chamber with the same solvent, the cell was closed and the current switched on. After about 80% of the calculated amount of current had passed, the crystals, which normally had precipitated on the anode, were collected, washed with solvent, and dried. Yields varied from 50 to 80%. The stoichiometries indicated in Tables III and V are based on microanalysis (C, H, N, S).

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