Synthesis and Polymerization of 3-Vinylbisfulvalenediiron. Preparation and Conductivity of Its Polymeric [Fe^{II}Fe^{III}](TCNQ)$_2\cdot^-$ Salts

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Abstract: The synthesis of 3-vinylbisfulvalenediiron (**9**) in 0.02% overall yield from sodium cyclopentadienide was accomplished. This vinyl monomer was homopolymerized in using azobis(isobutyronitrile) initiation to give an 18–31% yield of homopolymer **10**, $\bar{M}_n$ = 5000. Styrene and **9** were copolymerized in 36% yield to copolymer **11**. Polymers **10** and **11** were oxidized with TCNQ to give their mixed-valence [Fe^{II}Fe^{III}](TCNQ)$_2\cdot^-$ polysalts **12** and **13**, respectively. The dark conductivity of **12** (71% of the bisfulvalenediiron units were monooxidized) was 6–9 × 10^{-3} Ω^{-1} cm^{-1}, one of the highest ever observed for an organic polymer. Bisfulvalenediiron, prepared as reported previously, was monoacylated (AlCl$_3$, CH$_3$COCl) in 8–10% yield (diacylation predominates), then reduced in 78% yield by NaBH$_4$ to 1-hydroxyethylbisfulvalenediiron (**8**) followed by dehydration to **9** over Al$_2$O$_3$ at 190° and 0.02 Torr in 14% yield.
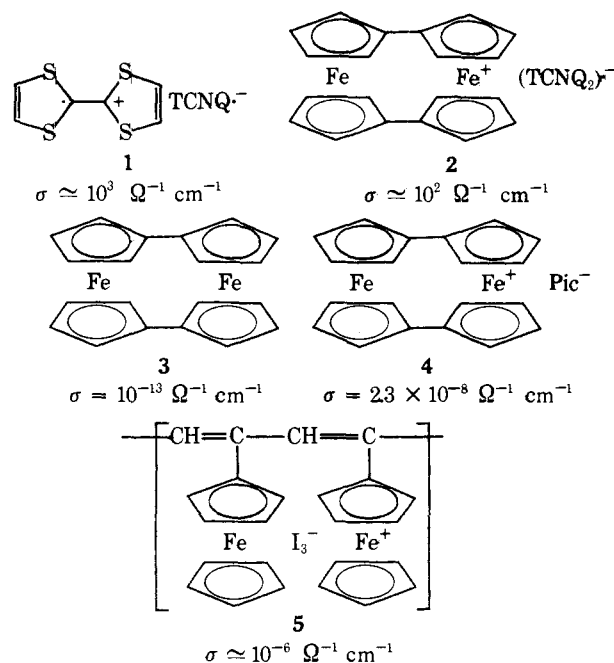
In general, organic compounds and their polymers are insulators. However, highly conjugated polymers and organic charge-transfer complexes have demonstrated that organic compounds need not necessarily be insulators and that suitable molecular and material design might lead to photoconducting behavior.[1-4] Indeed, the poly(N-vinylcarbazole)-trinitrofluorenone complex is an excellent photoconductor. Recently several organic salts have even been shown to exhibit metallic properties.[5] For example, the salt formed by tetrathiofulvalene and tetracyanoquinodimethan (TCNQ), **1**, has a room temperature conductivity of ∼10^3 Ω^{-1} cm^{-1}, a negative temperature coefficient, and a negative thermoelectric power which is linear with temperature above 100°K.[6-8] Similarly, the (bisfulvalenediiron)$^+$(TCNQ)$_2\cdot^-$ salt, **2**, has a high conductivity ($\sigma \simeq 10^2$ Ω^{-1}cm^{-1}).[9,10]

The introduction of mixed valence states can induce semiconductivity. Cowan and Kaufman[11,12] demonstrated that the conductivity of biferrocene [Fe^{II}Fe^{III}] picrate (**4**) was six orders of magnitude greater than biferrocene (**3**) itself. The synthesis of mixed-valence [Fe^{II}Fe^{III}] polyvinylferrocene and polyferrocenylene systems with significantly enhanced conductivities (10^{-7}–10^{-8} Ω^{-1} cm^{-1}) as compared to the [Fe^{II}] analogs (10^{-14} Ω^{-1} cm^{-1}) was previously reported by us.[13] Futhermore, mixed valence polyethynylferrocene iodide salts, **5**, were prepared[14] which exhibited conductivities up to ∼10^{-6} Ω^{-1} cm^{-1}.

Thus, it was of interest to prepare, polymerize, and copolymerize vinylbisfulvalenediiron and then convert the pendant BFD groups to mixed-valence TCNQ salts in order to examine the conductivity of the resulting polymers.
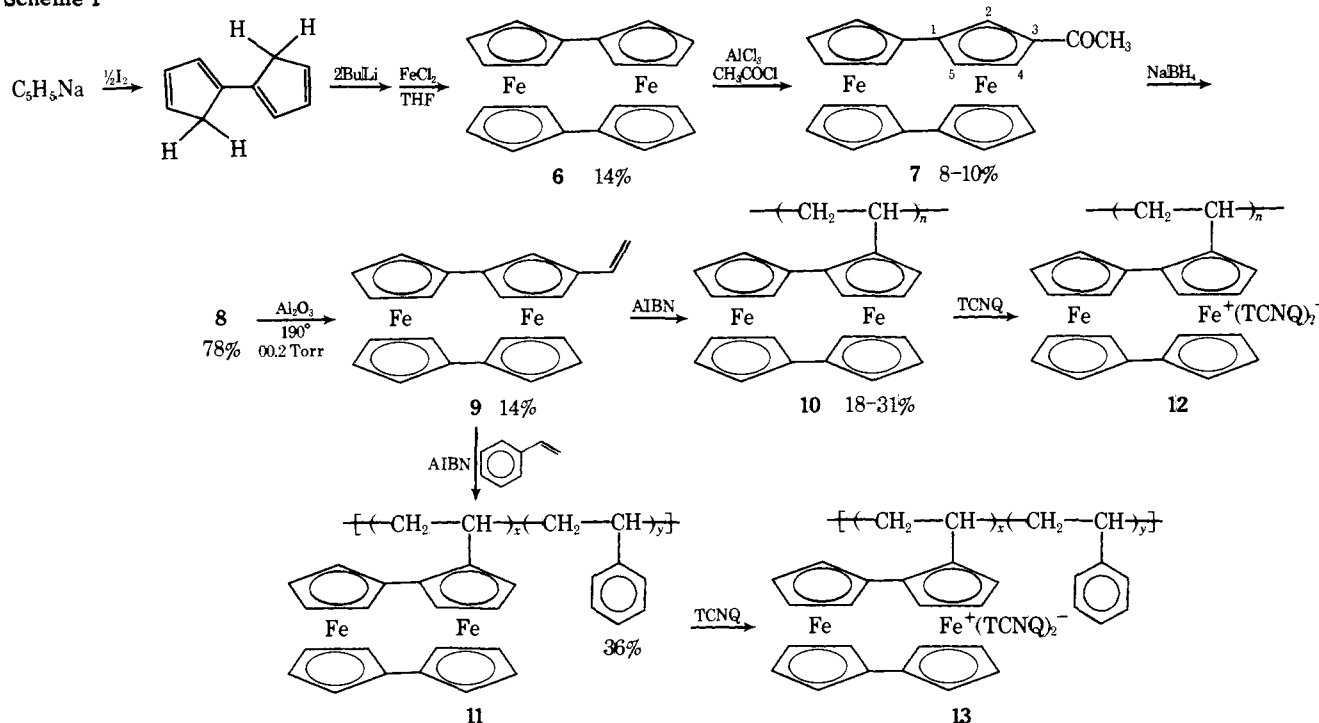
Results and Discussion

Bisfulvalenediiron (**6**) was prepared according to the improved method of Mueller-Westerhoff[10,15] in yields as high as 14% (see Scheme I). We were unable to reach the 18–22% yields previously reported. The nmr spectrum of **6** exhibited two triplets at τ 4.78 and 6.27 as reported, and its ir spectrum was identical with that of an authentic sample. Numerous attempts to monoacylate **6**, using a variety of conditions, failed in dilute CH$_2$Cl$_2$ solutions. Bisfulvalenediiron is only slightly soluble in benzene, CS$_2$, THF, CCl$_4$, acetone, CH$_2$Cl$_2$, and other organic solvents. This contributed to the difficulty in carrying out standard reactions with it. The use of acetic anhydride and BF$_3$-OEt$_2$, a method used successfully by Hauser on ferrocene,[16] failed as did the use of acetic anhydride-H$_3$PO$_4$ as employed by

1
$\sigma \simeq 10^3$ Ω^{-1} cm^{-1}

2
$\sigma \simeq 10^2$ Ω^{-1} cm^{-1}

3
$\sigma = 10^{-13}$ Ω^{-1} cm^{-1}

4
$\sigma = 2.3 \times 10^{-8}$ Ω^{-1} cm^{-1}

5
$\sigma \simeq 10^{-6}$ Ω^{-1} cm^{-1}

Graham.[17] Similarly, SnCl$_4$ and CH$_3$COCl in CH$_2$Cl$_2$ or benzene failed to give 3-acetylbisfulvalenediiron (**7**).

The heterogeneous reaction of **6**, AlCl$_3$, and CH$_3$COCl (2.5 mmol of each) in CH$_2$Cl$_2$ (30 ml) at 0°, then 24 hr at 22°, gave at least seven products from which a mixture of four diacetylferrocenes was isolated by dry column chromatographs in 22% yield, but **7** was not found. Acylation of **6** (7.5 mmol) with AlCl$_3$ (7.5 mmol) and CH$_3$COCl (7.5 mmol) at 0° in CH$_2$Cl$_2$ (350 ml) followed by 4 hr at 22° was successful and gave 0.41 g of crude CH$_2$Cl$_2$ soluble material. Evaporation followed by acetone extraction gave an insoluble product that was purified by dry column and high pressure liquid chromatography. Monoacetyl derivative, **7**, was isolated in 8–10% yield from a mixture of three diacetyl derivatives. The yields of **7** in six experiments were consistently in this range. A 16–22% yield of diacetylated derivatives and a 35–45% yield of unreacted **6** were also recovered. Purified **7** exhibited nmr bands (CDCl$_3$) at τ 4.5 (7 H, multiplet, ring H's at 3 and 4 positions), 6.02 (8 H, m, ring H's at 2 and 3 positions), and 7.62 (3 H, singlet, acetyl methyl), a parent ion at *m/e* 410, and its ir spectrum and analysis in agreement with the structure.

Scheme I

C_5H_5Na $\frac{1}{2}I_2$ 2BuLi $\frac{FeCl_2}{THF}$ Fe   Fe   **6**   14% $\frac{AlCl_3}{CH_3COCl}$ Fe   Fe   —COCH$_3$ **7**   8–10%   NaBH$_4$

8 $\frac{Al_2O_3}{190°}$ 78%   00.2 Torr   Fe   Fe   **9**   14%   AIBN   Fe   Fe   **10**   18–31%   TCNQ   Fe   Fe$^+$(TCNQ)$_2^-$ **12**

AIBN   (styrene)   Fe   Fe   36%   **11**   TCNQ   Fe   Fe$^+$(TCNQ)$_2^-$ **13**

Reduction of **7** to 1-hydroxyethylbisfulvalenediiron (**8**) in 78% isolated yield was accomplished using excess NaBH$_4$ in 10:10:1 CHCl$_3$:CH$_3$OH:H$_2$O at 22° for 4 hr followed by dry column chromatography (deactivated silica, CHCl$_3$). The dehydration of **8** was effected by heating a thoroughly mixed sample of **8** (0.08 g) with alumina (1 g) in a vacuum sublimator.[18] At 210–215° and 0.7 Torr only a 4% yield of the vinyl derivative **9** was obtained. Reducing the pressure and temperature to 0.002 Torr and 190° gave **4** in 14% yield. Thus **9** was prepared in 0.02% overall yield from NaC$_5$H$_5$. The ir spectrum of **9** exhibited a strong C=C stretch at 1630 cm^{-1}, a parent ion at m/e 394, and a satisfactory analysis.

Radical initiated polymerization of **9** in dilute degassed benzene solutions (40 mg of **9**, 25 ml of benzene) employing azobisisobutyronitrile (10 mol % of **9**) at 70° for 24 hr gave a 18% yield of low molecular weight (5000 via gel permeation chromatographic analysis) polymer, **10**. Yields to 31% were achieved by successive additions of **9** and initiator in more concentrated solutions. Polymer **10** was only slightly soluble in benzene and other solvents. This precluded kinetic studies of the polymerization and frustrated attempts to form higher molecular weight polymers. Solution copolymerizations of **9** with styrene (1:4 mole ratio) gave a 36% yield of copolymer **11** containing 28 mol % of **9**. Polymers **10** and **11** were purified by repeated precipitations into petroleum ether and methanol. Polymers **10** and **11** were then dissolved in excess benzene, CHCl$_3$, or benzonitrile and treated with excess TCNQ to give the mixed-valence [Fe^{II}Fe^{III}] polysalt precipitates, **12** and **13**. Analysis showed that 71% of the bisfulvalenediiron units in **12** (BFD) were oxidized to the mixed-valence form while 88% of those in **13** were oxidized in the most highly oxidized samples.

Nitrogen to iron weight ratios of 0.71 and 0.88 in **6** and **8**, respectively, established these ratios. The near-infrared of **12** and **13** possessed a broad absorption at 1000–2000 nm with a maximum intensity at 1400–1700 nm. This band in BFD$^+$ (TCNQ)$_2^-$ had previously been assigned to a photon-assisted intramolecular intervalence exchange[9,10] and it confirmed that monooxidation of BFD units to [Fe^{II}Fe^{III}]

occurred.[19] Absorption at 600 nm was also pronounced. The Mössbauer spectrum of **12** was dominated by a single symmetrical absorption with a quadrupole splitting of 1.73 mm/sec further confirming the BFD$^+$ structure. Neutral BFD's doublet was also seen.

It has also been suggested that BFD$^+$ could be a delocalized system with each iron atom formally Fe(2½) based on its Mössbauer spectrum, which shows only one type of iron present at 77°. Its ESCA spectrum was similarly interpreted.[20]

The room temperature bulk conductivity of compressed disks of **6** was 6–9 × 10^{-3} Ω^{-1} cm^{-1} while that of **13** was 2.5 × 10^{-5} Ω^{-1} cm^{-1}. Considering only 71% of the BFD units in **12** were oxidized, and realizing that **12** cannot pack in as orderly a manner as BFD$^+$(TCNQ)$_2$·$^-$, the conductivity of **12** is remarkably high. Preliminary microwave conductivity measurements on **12** appear to give results similar to bulk studies with disks. Figure 1 shows the increase in conductivity as the BFD$^+$/[BFD + BFD$^+$] ratio increases in polymer **12**. From the shape of the curve one might predict a conductivity of ∼0 when the polymer was completely oxidized.

Currently, attempts are underway to completely monooxidize **10** and to prepare block copolymers of **9** with 1,3-butadiene, followed by oxidation with TCNQ.

Experimental Section

Preparation of Bisfulvalenediiron (6). A sodium dispersion (57.5 g of 40% dispersion in mineral oil, 1.0 mol) and THF (300 ml) dried over sodium benzophenone were mixed in rigorously dried glassware under nitrogen, and freshly prepared cyclopentadiene (110 ml, 1.33 mol) was added at 0° over 6 hr. Copious gas evolution was noted. After stirring an additional 2 hr, the pale red solution of sodium cyclopentadienide was separated from excess sodium. The concentration was accurately determined by taking a 5-ml aliquot in water (25 ml) and titrating it against 0.229 M potassium biphthalate (duplicate titre was 49.8 ml, thus the molarity of the cyclopentadienide solution was 2.29).

Next an FeCl$_2$·2THF complex was prepared with all operations conducted in a nitrogen filled drybox. FeCl$_2$ (45 g, 0.355 mol) was weighed into a flask fitted with a condenser, serum cap, and nitrogen intet. Dry THF was added via syringe and an immediate exotherm was observed. The contents were stirred at THF reflux 2 hr
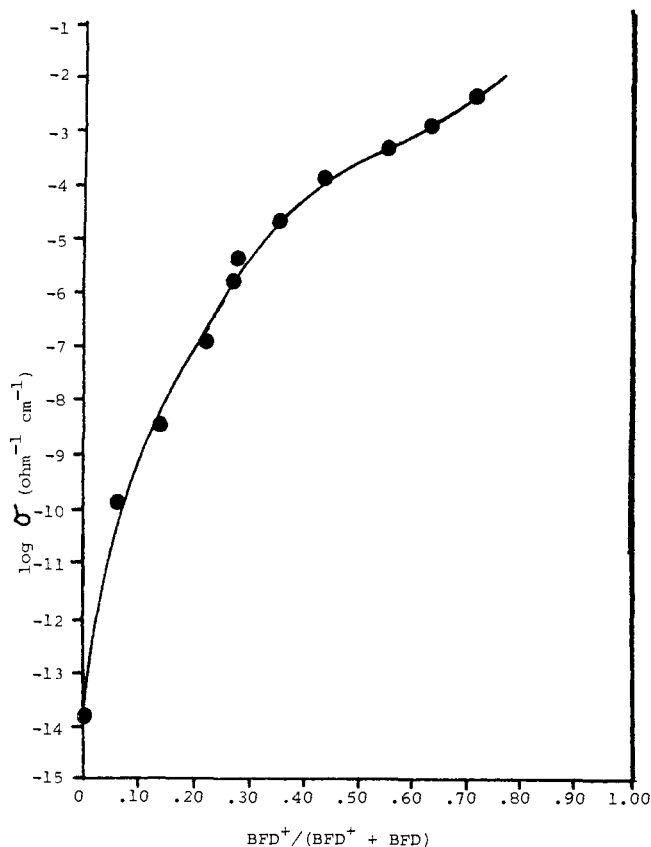
Figure 1. Variation of conductivity with increasing oxidation of polymer **12**.

and cooled by an external ice–methanol bath. The resulting $FeCl_2 \cdot$ 2THF complex was a pink sludge. It was extracted (soxhlet) with dry THF for 72 hr under nitrogen to give white $FeCl_2 \cdot 2THF$ crystals in the bottom flask. It should be emphasized that this entire operation should be kept free of air to prevent any oxidation of Fe^{2+} to Fe^{3+}. The $FeCl_2 \cdot 2THF$ crystals were washed once with dry THF, twice with anhydrous ether, and twice with dry pentane followed by drying under a stream of nitrogen. The pentane washing is desirable because traces of THF or ether accelerate the oxidation of Fe^{2+} to Fe^{3+}. Dried crystals (30.0 g) were stored under nitrogen in an amber bottle.

To a mixture of sodium cyclopentadienide (0.2 mol) and THF (500 ml) at $-78°$ under nitrogen, iodine (27.5 g, 0.11 mol) was added as a solution in THF (100 ml). The addition was carried out dropwise over a 1-hr period with rapid stirring. The mixture was further stirred 1 hr at $-60°$, after which, n- butyllithium in hexane (100 ml, 0.21 mol) was added dropwise by syringe. The reaction was warmed to $-30°$ and $FeCl_2 \cdot 2THF$ (30 g, 0.15 mol) in THF (200 ml) was added under a vigorous nitrogen flow. The reaction was then stirred at 25° for 24 hr after which the contents were poured into a solution of water (1000 ml) and methanol (750 ml). Vacuum filtration gave a residue which was washed three times with water, three times with methanol, and finally several times with benzene until the benzene came over yellow. The residue was air dried and extracted after 72 hr with benzene (Soxhlet). After cooling, bisfulvalenediiron (3.50 g) was obtained as a black powder. This crude product was reextracted with benzene and crystallized from benzene to give 2.34 g (13.1% yield) of pure bisfulvalenediiron as a deep red powder: mp dec above 280°; ir(KBr) 3080, 1418, 1380, 1270, 1105, 1048, 1032, 1000, 852, 840, 830, 810 cm^{-1}; mass spectral (60 eV) m/e 368 (parent ion), 184, 128, 102, 56;[21] ^1H nmr (C_6D_6) τ 4.78 (8 H, t, hydrogens at 3,4 positions), 6.27 (8 H, t, hydrogens at 2,5 positions).

Preparation of 3-Acetylbisfulvalenediiron (7). The heterogeneous reaction of **6**, $AlCl_3$, and acetylchloride (2.5 mmol of each) in CH_2Cl_2 (30 ml) at 0° followed by 24 hr at 22° was carried out. Hydrolysis with H_2O followed by routine work-up resulted in a brown-black crude product mixture from which **6** was recovered in 47% yield. At least six other products were formed from which a

mixture of four different diacetylferrocene isomers was isolated by dry column chromatography (5 ft, activated or various grades of deactivated silica). Analytical tlc proved four components were present, but these proved very difficult to separate. Even high pressure liquid chromatography over 4 ft of Corasil-I at a $CHCl_3$ flow rate of 1 ml min^{-1} did not achieve a separation of the four isomers. Similarly, the use of 4 ft of Carbowax on silica or glass (and $CHCl_3$ as the moving phase) proved unsuccessful as did solvent programming with $CHCl_3$ and isooctane. The mixture of isomers exhibited a strong broad ν_{CO} absorption at 1660 cm^{-1} and the mixture's mass spectrum gave a parent ion at m/e 452 consistent with diacetyl derivatives. *Anal.* Calcd for $C_{24}H_{20}O_2Fe_2$: C, 63.72; H, 4.42; Fe, 24.78. Found: C, 62.92; H, 4.84; Fe, 24.42.

Successful synthesis of **7** was achieved by the following procedure. To bisfulvalenediiron (2.76 g, 7.5 mmol) in CH_2Cl_2 (350 ml) at 0°, a solution of anhydrous $AlCl_3$ (1.0 g, 7.5 mmol) and acetylchloride (0.60 ml, 7.5 mmol) in CH_2Cl_2 was added dropwise over 15 min. The mixture was stirred 4 hr and then extracted with distilled water (violet to green color change). The water layer containing particulate matter was stored. The methylene chloride layer was water washed repeatedly, dried (Na_2SO_4), and evaporated giving 0.41 g of crude product. Extraction with acetone (30 ml) followed by dry column chromatography of the insoluble fraction over 4.5 ft of deactivated silica ($CHCl_3$) gave a long red streak which was cut and extracted to give 0.18 g of red powder. Tlc analysis indicated four fractions. High pressure liquid chromatography over Corasil-I using reverse flow programming (70% $CHCl_3$ and 30% isooctane to 100% $CHCl_3$) separated the monoacetyl fraction from the diacetyl mixture. Thus purified, **7** exhibited a single spot on analytical tlc (alumina or silica, rf of 0.8 on silica using $CHCl_3$): ir (KBr) 3080, 2940, 1670 (ν_{CO}), 1450, 1410, 1360, 1300, 1270, 1050, 1030, 850, 810 cm^{-1}; a parent ion at m/e 410; nmr ($CDCl_3$) τ 4.5 (7 H, multiplet, 3,4 ring H), 6.02 (8 H, multiplet, 2,5 ring H), 7.62 (3 H, singlet, acetyl H). *Anal.* Calcd for $C_{22}H_{18}Fe_2O$: C, 64.39; H, 4.39; Fe, 27.32. Found: C, 64.30; H, 4.60; Fe 27.06. The nmr assignments are based on those expected from the structure of **6** elucidated by Churchill.[22] The iron atoms are symmetrically located in the center of their ferrocenylene moieties at a Fe–Fe distance of 3.984 Å. Thus, the protons at the 2,5 positions should experience a greater diamagnetic anisotropy and be found upfield from the 3,4 protons. This assignment is the reverse of that suggested by Hedberg and Rosenberg[21] who postulated a distorted structure prior to Churchill's publication of the X-ray structure of **6**.

In order to purify enough of **7** for further synthetic efforts, a series of six acylations were run and the combined acetylated fractions, initially isolated by column chromatography, were combined and the mixture of mono- and diacetyl derivatives were separated by dry column chromatography (4.5 ft silica (7% H_2O) using $CHCl_3$). Clean separation of bands was not obtained, but tlc studies showed the first $^1/_4$ of the red-brown band contained no diacetylated product. Thus, by cutting the column at this point and by extracting with $CHCl_3$, **7** was isolated in 8–10% yield. This fraction exhibited the same spectral properties as did the fraction isolated by high pressure liquid chromatography (above). *Anal.* Calcd for $C_{22}H_{18}Fe_2O$: C, 64.39; H, 4.39; Fe, 27.32. Found: C, 64.30; H, 4.60; Fe 27.06.

Preparation of 3-Vinylbisfulvalenediiron (9). The reduction of **7** to 3-(1-hydroxyethyl)bisfulvalenediiron (8) was accomplished by dissolving **7** (2 g, 5.08 mmol) into a 10:10:1 (v/v) solution of $CH_2Cl_2:CH_3OH:H_2O$ (total 500 ml) at 22° containing excess $NaBH_4$ (5 g, 0.13 mol) and stirring for 4 hr. An aliquot of this solution was worked up, the product exhibited no carbonyl absorption in the ir, and tlc analysis was free of **7**. Dry column chromatography of the crude product isolated from the entire reaction gave **8** (1.56 g, 78% yield). The ir showed a broad OH band 3500–3300 cm^{-1}. *Anal.* Calcd for $C_{22}H_{20}Fe_2O$: C, 64.12; H, 4.89; O, 3.88; Fe, 27.11. Found: C, 64.31; H, 4.71; Fe, 26.82. This reaction sequence was repeated on a larger scale with essentially the same results.

The dehydration of **8** to give **9** was carried out by heating thoroughly ground samples of **8** and alumina (0.08 g of **8** per 1 g of alumina) in a vacuum sublimator.[18] Thus, **8** (0.32 g, 0.78 mmol) was heated to 210–215° at 0.7 Torr for several hours to give **9** on the cold surface (0.012 g, 0.031 mmol) in only a 4% yield. Thus, the pressure and temperature were lowered to 0.002 Torr and

190°, respectively, where **8** (0.41 g, 0.99 mmol) gave **9** (0.055 g, 0.14 mmol) in 14% yield. The yields of **9** varied from 10 to 20% using these conditions in several other runs. Extraction of the remaining alumina gave a mixture of decomposition products, undehydrated **8** and small amounts of **9**. Compound **9** was characterized by the following: ir (KBr) 3080, 1630 (sharp, m, C=C stretch), 1270, 1050, 1040, 1030, 890, 850, 810, 720 cm^{-1}; mass spectral, parent ion m/e 394; nmr (CDCl$_3$) τ 6.20–6.4 (8 H, m, hydrogens at 2,5 positions), 4.72–4.85 (7 H, m, hydrogens at 3,4 positions), 6.42 (1 H, m, -CH=CH$_2$), 5.31 (1 H, q, J_{trans} = 16 Hz, J_{gem} = 2 Hz, CH=CH_2), 4.97 (1 H, q, J_{cis} = 10 Hz, CH=CH_2). Anal. Calcd for C$_{22}$H$_{18}$Fe$_2$: C, 67.00; H, 4.57; Fe, 28.43. Found: C, 67.48; H, 4.75; Fe, 27.90.

Preparation of Poly(3-vinylbisfulvalenediiron) (10). The polymerization of **9** was carried out in dilute degassed benzene solutions. Compound **9** (40 mg, 0.102 mmol) and AIBN (1.7 mg, 10 mol % of **9**) were added to benzene (25 ml), and the solution was degassed by two freeze-thaw vacuum cycles each followed by a nitrogen purge. The solution was heated to 70° for 24 hr after which precipitation into methanol and drying gave polymer **10** (0.0017 g) in 18% yield. Gel permeation chromatography indicated the $\bar{M}_n$ was about 5000. Higher yields were obtained by successive additions of **9** and AIBN to the tube during the polymerization. A yield of 31% was obtained using three such successive additions at 4-hr intervals and gpc indicated the $\bar{M}_n$ had increased to about 8000. Polymer **10** was, like **6**, only slightly soluble in benzene and other solvents tested. Two successive precipitations of **10** (into petroleum ether and methanol) gave pure **10**. Anal. Calcd for C$_{22}$H$_{18}$Fe$_2$: C, 67.00; H, 4.57; Fe, 28.43. Found: C, 67.21; H, 4.46; Fe, 27.88.

Preparation of the (TCNQ)$_2$·$^-$ Polysalts of 10 (i.e., 12). Polymer **10** (0.50 g) was dissolved into benzonitrile (50 ml) and the solution was heated to 65°. Then excess TCNQ (0.95 g, 4.64 mmol) was added as a benzonitrile solution (20 ml) and the reaction mixture was heated at 65° overnight. The reaction mixture was then cooled to 0° and filtered cold to give a black powder (0.63 g). Analysis indicated that 71% of the BFD units of **10** had been oxidized if it is assumed that only (TCNQ)$_2$·$^-$ complexes had formed. This was further confirmed by Mössbauer analyses at 77°K which clearly showed two types of BFD units were present in a ratio of about 3:1. The more intense symmetrical doublet with a quadrupole splitting of 1.73 mm sec^{-1} was assigned to BFD$^+$ while the less intense symmetrical doublet of 2.4 mm sec^{-1} was assigned to BFD units. The close correspondence of the analytical and Mössbauer results suggests very few BFD$^+$TCNQ·$^-$ moieties exist in the polymer. Anal. Calcd and found for polysalt **10** where 71% of the BFD units were converted to BFD$^+$(TCNQ)$_2$·$^-$ derivatives: C, 68.55; H, 3.49; N, 11.59; Fe, 16.14.

Preparation of Copolymer 11 and Polysalt Complex 13. Styrene and **9** (4:1 mole ratio, 5 g total) were dissolved in benzene (100 ml) under nitrogen at 70°. AIBN (0.1 g) was added. The mixture was degassed, thoroughly, and heated at 70° for 24 hr. After precipita-

tion into 500 ml of petroleum ether, a 36% yield (1.80 g) of polymer was obtained which exhibited a $\bar{M}_n$ = 7500 via gpc. Analysis indicated that polymer **11** contained 28 mol % BFD units. Anal. Calcd for **11**, with 28 mol % **9**, and found: C, 74.70; H, 4.38; N, 10.47; Fe, 10.44.

The complexation of this copolymer was carried out in the manner described for the preparation of **12**. Analysis of the resulting complex showed that at least 88% of the BFD units were oxidized to (TCNQ)$_2$·$^-$ complexes. Anal. Calcd for 88% BFD$^+$(TCNQ)$_2$$^-$ in **13** and found: Fe/N = 0.882.

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