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Synthesis, Characterization, and Polymerization of New
Ferrocene-Fluorene Complexes. A Novel High-Molecular
Weight Conjugated Polymer with Pendant Ferrocene Groups.

Michael E. Wright* & Brooks B. Cochran

Department of Chemistry & Biochemistry, Utah State University,
Logan, Utah 84322-0300

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Abstract. Ferrocenecarboxaldehyde was successfully condensed with fluorene derivatives to afford a series of new complexes, $\{\eta^5\text{-C}_5\text{H}_5\}\text{Fe}\{\eta^5\text{-C}_6\text{H}_4\text{CH}=(9\text{-fluorenyl})\}$ [where fluorenyl = **1a**, 2-bromo; **2a**, 2,7-dibromo; **3**, 2-nitro]. The ferrocene-fluorenyl derivatives **1a** and **2a** were converted to the monocarboxaldehyde, tributylstannyl, bis(carboxaldehyde), and bis(tributylstannyl) complexes (**1b**, **1c**, **2b**, and **2c**, respectively). Complexes **1b** and **2b** were characterized by single-crystal x-ray molecular structures. The fluorenyl ring systems were tilted out of the $\eta^5\text{-C}_6\text{H}_4$ plane by 33 deg. Treatment of **1c** and **2c** with I_2 afforded the *mono*- and *bis*(iodo)fluorenyl complexes **1d** and **2d**, respectively. The reactivity of complexes **2a-d** was explored. The alkynylation (alkyne, L_2PdCl_2 , CuI , PPh_3) of **2a** was an extremely poor reaction giving little or no cross-coupling. Complex **2b** did not undergo the Knoevenagel polycondensation with bis(cyanoacetate) comonomers. Treatment of **2c** with acid chlorides under Stille cross-coupling conditions afforded ketone product and iodobenzene showed no cross-coupling. Complex **2d** did copolymerize very cleanly with 2,5-(diethynyl)-1,4-(deoxy)benzene using palladium catalysis to afford a soluble, high-molecular weight conjugated polymer, **4**. A model compound, **5**, was prepared from cross-coupling **1d** with 2,5-(diethynyl)-1,4-(deoxy)benzene. For compound **5** we observed

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two oxidation events, one at +0.11 V and the other at +0.71 V (relative to the ferrocene/ferrocenium couple). Cyclic voltammetry of polymer 4 showed one, very reversible oxidation event at +0.13 V.

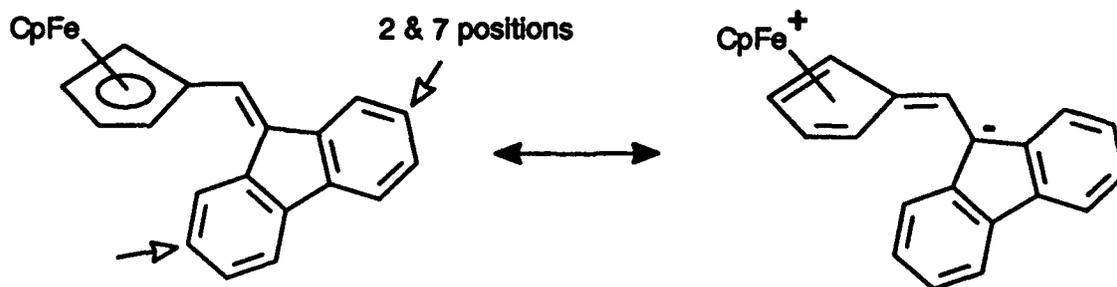
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Introduction

Transition metal containing polymeric materials represents an important and active area of materials chemistry.¹ Ferrocene containing polymers have been utilized in a broad range of applications, ranging from batteries² to nonlinear optical (NLO) materials.³ Ferrocene has long been recognized to stabilize alpha-carbocations⁴ and can serve as an excellent electron-donor for an NLO-phore.⁵ With this in mind, we envisioned that fluorenyl ferrocenes, as depicted below, would be an interesting new class of NLO-phores. With the placement of electron-withdrawing groups at the 2 and 7-positions the complexes would model the λ -organic NLO-phores designed by Watanabe and coworkers.⁶ Subsequent incorporation into a polymer backbone would give rise to an "accordion" NLO polymeric material with alternating apexes fixed.⁷ In principle, this should facilitate the alignment process by predisposing part of the polymer backbone into the desired orientation.



In the cartoon above the resonance structure on the right sacrifices one "cyclopentadienyl anion" to generate the fluorenyl carbanion; hence, there should be little net loss in aromaticity. This "no net loss of aromaticity" has recently been exploited by Marder and coworkers in designing NLO-phores with large hyperpolarizabilities.⁸

This paper presents details concerning the preparation and characterization of several new ferrocene-fluorenyl complexes, a study of their chemistry, and incorporation of this new monomeric unit in the backbone of a conjugated organic polymer.

Results & Discussion

Monomer Synthesis & Structural Analysis

To initiate the development of ferrocene-fluorenyl based polymeric materials we have prepared a series of mono- and bis(substituted) fluorenyl complexes by condensing 2-bromo-, 2,7-dibromofluorene, and 2-nitrofluorene with ferrocene carboxaldehyde to afford **1a**, **2a**, and **3**, respectively, all in reasonable yield.⁹ In the case of 2-nitrofluorene the base used is potassium *tert*-butoxide and for the bromofluorenes, lithium diisopropylamide (LDA). Complexes **1a** and **2a** undergo clean halogen-metal exchange by treatment with *n*-BuLi in tetrahydrofuran (THF) at -78 °C and are then converted to their respective carboxaldehyde¹⁰ and tributylstannyl¹¹ derivatives by treatment with DMF and Bu₃SnCl, respectively, in moderate yield (Scheme I). Oxidative cleavage of the aryl-tin bond with I₂ affords the *mono*- and *bis*(iodo) complexes in good yield (Scheme I).

distorted from planarity by 7-9 degrees (defined by C13-C12-C11-C1). The two structures do not show significant differences in their C1-C11 and C11-C12 bond distances [**1b**, 1.450(6), 1.354(6); **2b**, 1.458(3), 1.340(3); respectively]. We would anticipate that contribution of a dipolar structure to the ground-state configuration would lead to a shorting of the C(1)-C(11) bond and lengthening of the C(11)-C(12) bond.¹⁵

Table I. Summary of crystallographic data for Single-Crystal X-ray Structures of Complexes **1b** and **2b**.

Parameter	Complex 1b	Complex 2b
Formula	C ₂₅ H ₁₈ FeO	C ₂₆ H ₁₈ FeO ₂
Color; Habit	red plates cut to size	red plates cut to size
Crystal size (mm)	0.4 x 0.3 x 0.5	0.3 x 0.4 x 0.3
Crystal System	Monoclinic	Monoclinic
Space Group	P2 ₁ /c	P2 ₁ /c
Unit Cell Dimensions	<i>a</i> = 9.488(5) Å <i>b</i> = 7.592(2) Å <i>c</i> = 25.168(5) Å β = 90.84(3)°	<i>a</i> = 7.402(2) Å <i>b</i> = 9.929(2) Å <i>c</i> = 25.168(5) Å β = 93.84(2)°
Cell Volume	1812.8(10) Å ³	1901.6(7) Å ³
Z	4	4
Formula weight	390.2	418.2
D _{calcd}	1.43 g/cm ³	1.46 g/cm ³
Absorption Coefficient	8.43 cm ⁻¹	8.13 cm ⁻¹
Diffractometer Used	Siemens P3	Siemens P3
Radiation	MoK α (λ = 0.71073 Å)	MoK α (λ = 0.71073 Å)
Temperature (K)	ambient	ambient
2 θ Range	3.0 to 50.0°	3.0 to 50.0°
Scan Type	2 θ - θ	omega
Scan Speed	Variable; 3.0 to 14.6°/min	Variable; 3.0 to 14.6°/min
Independent Reflections	3211 (<i>R</i> _{int} = 0.76%)	3356 (<i>R</i> _{int} = 1.26%)
Observed Reflections	2287 (<i>F</i> > 3.5 σ (<i>F</i>))	2657 (<i>F</i> > 3.0 σ (<i>F</i>))
Refinement Method	Full-Matrix Least-Squares	Full-Matrix Least-Squares
Weighting Scheme	<i>w</i> ⁻¹ = σ^2 (<i>F</i>) + 0.0004 <i>F</i> ³	<i>w</i> ⁻¹ = σ^2 (<i>F</i>) + 0.0010 <i>F</i> ³
Number of Parameters Refined	245	280
Final R Indices (obs. data)	<i>R</i> = 5.01%, <i>R</i> _w = 5.47%	<i>R</i> = 3.11%, <i>R</i> _w = 4.18%
Goodness-of-Fit	1.64	0.97
Largest Difference Peak	0.49 eÅ ⁻³	0.23 eÅ ⁻³

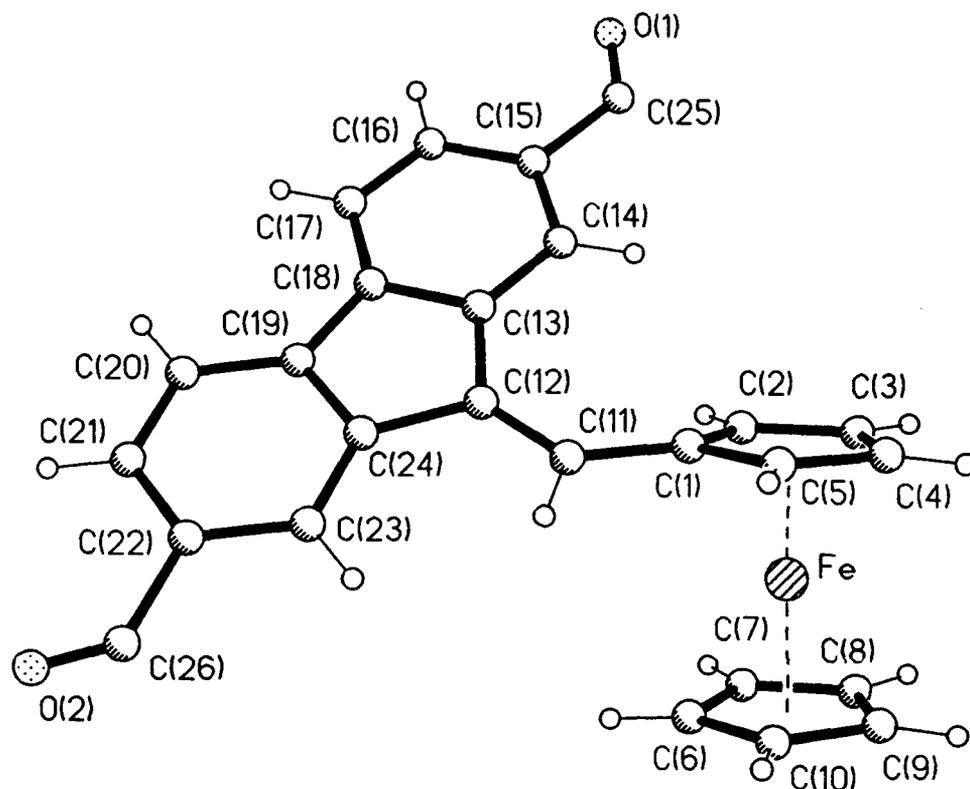


Figure I. Drawing of Complex **2b** with Labeling Scheme. The Aldehyde Groups Were Disordered in the Structure and Modeled with Partial Occupancy. One of the Two Possible Structures is Displayed.

Table II. Summary of UV-Vis Data.

Compound	Solvent	λ_{max} (nm) [$\epsilon \times 10^3$]
1a	CH ₂ Cl ₂	494 [2.93]
1b	CH ₂ Cl ₂	498 [6.36]
2a	CH ₂ Cl ₂	502 [3.01]
2b	CH ₂ Cl ₂	522 [6.50]
3	CH ₂ Cl ₂	512 [6.76]
	EtOH	506
	Hexanes	492

From the data presented in Table II is quite evident that the electron-withdrawing groups have an effect on the metal to ligand charge transfer (MLCT) band.¹⁶ These data

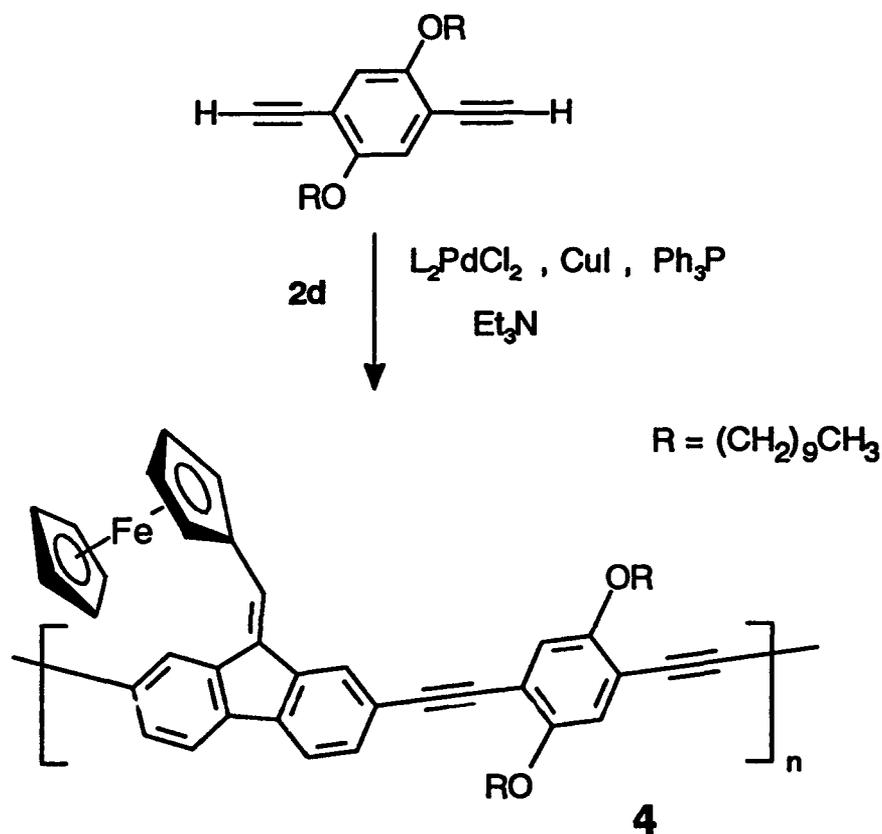
imply that there is indeed a meaningful interaction between the iron center and the fluorenyl-ring system. The observation of a solvatochromic effect for **3** (hexane => CH₂Cl₂, red-shift of 20 nm) is consistent with a dipolar excited state. It is worth noting that the change in dipole moment ($\mu_{\text{ground-state}} - \mu_{\text{excited state}}$), which is often indicated by a solvatochromic shift, can be used to estimate the hyperpolarizability of a given material.¹⁷

Monomer Reactivity and Polymer Synthesis

By analogy with our recent success in preparing ferrocenyl polymers via a Knoevenagel polycondensation¹⁸ we treated **2b** with a *bis*(cyanoacetate) comonomer. Regardless of the base employed, the reaction afforded a complicated mixture of products, none of which displayed the expected and distinctive cyanocinnamate vinyl proton resonance.¹⁹ A model study using **1b** and ethyl cyanoacetate again gave a complicated mixture of products. The product-mixture is yellow and this is suggestive that some type of reaction is occurring which isolates the fluorenyl ring from the ferrocene. Michael-addition at the C(11) vinyl carbon would represent such an event.

The palladium catalyzed cross-coupling of **2a** with phenylacetylene was found to lead to decomposition of the acetylene and recovery of **2a**.²⁰ In another model study we employed **2c** in the Stille cross-coupling reaction with acid chlorides.²¹ This reaction leads to the formation of the ketone, but also several additional by-products. With so many side-reactions we deemed the reaction unsuitable as a polymerization technique.

Scheme II



We did find that the iodo derivatives undergo facile palladium/copper catalyzed alkynylation (Scheme II).²² Copolymer 4 is produced in high yield and purity [$M_n = 67,000$, polydispersity 3.8]. In some polymerization runs the alkyne comonomer underwent slight decomposition, producing imbalanced stoichiometry, which in turn produces a low molecular weight polymer with fluorenyl-iodide end-caps [$M_n = 7000$, average degree of polymerization = 10]. Copolymer 4 is soluble in common organic solvents and casts very tough, free-standing films.

The thermal behavior and stability of copolymer 4 was measured using TGA and DSC (Figure II). In the DSC scan we observe a small endothermic transition (possibly a melting-point), then an exothermic event, and finally an endothermic event. The middle event is likely some type of organizational process (*e.g.* crystallization).²³ Stopping the DSC scan at 250 °C, cooling the sample, and then reheating the sample to 250 °C showed no exo- or endothermic events. A film of 4 was heated under nitrogen and viewed using a polarizing microscope. We did not observe any apparent phase transitions from 40 to 200 °C. An endothermic event, which begins at ~350 °C, is concomitant with a significant weight loss in the TGA (Figure II). The loss in mass corresponds to removal of two decyl groups per repeating unit. A film of 4 was cast on a sodium chloride plate and infrared spectra were obtained before and after heating the sample to 400 °C for 30 min. The infrared spectrum after heating does not indicate quinone formation (*i.e.* C=O stretch), but is supportive of the ferrocene-fluorenyl remaining intact.

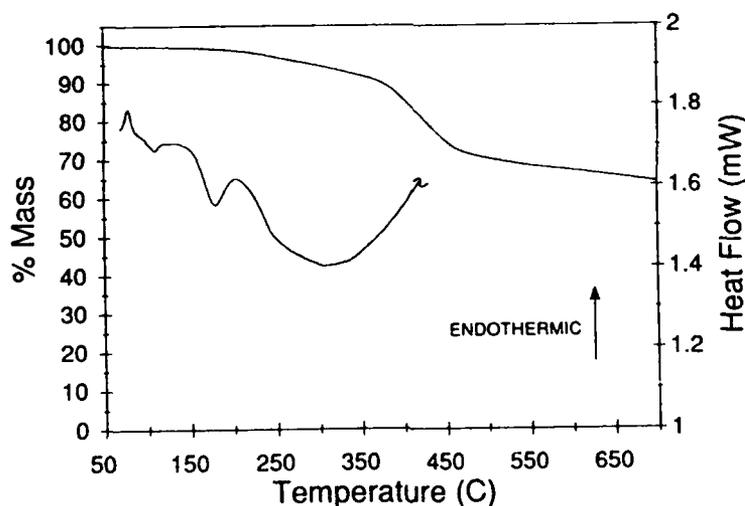
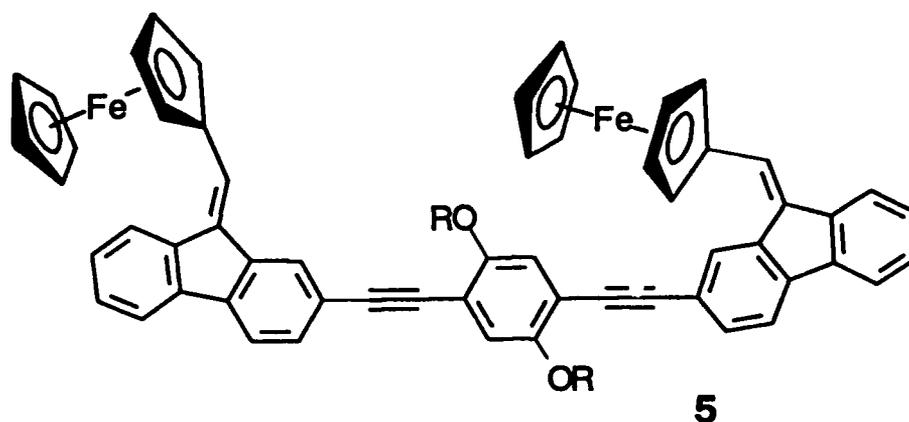


Figure II. TGA and DSC plots for Copolymer 4. In both analyses the samples were heated at 10 °C/min under an atmosphere of nitrogen.



We prepared model compound **5** by cross-coupling **1d** with 1,4-bis(ethynyl)-2,5-bis(deoxy)benzene. Complex **5** is isolated as an orange oil and displays spectroscopic data very similar to copolymer **4**. Cyclic voltametry of complex **5** shows two reversible oxidation events, one at +0.11 V (two-electron event) and another at +0.71 V (one-electron, peaks relative to the ferrocene/ferrocenium couple). We interpret this to be oxidation of the ferrocenyl²⁴ units (uncoupled events) followed by a more difficult oxidation of the hydroquinone moiety. Surprisingly, copolymer **4** (low molecular sample, $M_n = \sim 7,000$) shows *only a single* and very reversible oxidation event at +0.13 V. Could an extended array of ferrocenium ions be oriented in such manner as to "protect" the hydroquinone polymer backbone from further oxidation? This is an intriguing result and deserves further investigation.

Concluding Remarks

Our work has demonstrated the feasibility of preparing ferrocene-fluorenyl systems and that functionalization in the 2- and 7-positions can be carried out with reasonable efficiency. The 2,7-*bis*(carboxaldehyde) complex did not undergo the expected Knoevenagel condensation and led to unidentified by-products. Synthesis of the 2,7-*bis*(iodo)fluorenyl derivative and copolymerization afforded a novel conjugated polymer. The polymer was processable and displayed interesting thermal and cyclic voltammetry behavior. To our knowledge, this is the first conjugated organic polymer backbone to possess pendant ferrocene moieties.

Experimental Section

Methods. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ versus Me_4Si in ^1H NMR and assigning the CDCl_3 resonance at 77.00 ppm in ^{13}C spectra. The ferrocenecarboxaldehyde, *n*-butyllithium, 2-nitrofluorene, 2-bromofluorene, 2,7-dibromofluorene, tributyltin chloride, iodine, triphenylphosphine, and copper iodide were purchased from Aldrich Chemical Co. and used as received. The K_2CO_3 (granular, AR grade, Mallinckrodt) and Na_2SO_3 were purchased from Baxter. The $(\text{PPh}_3)_2\text{PdCl}_2$ was prepared by the literature method.²⁵

Polymer analyses were performed using a Perkin Elmer TGA7 and DSC7 thermal analysis data station. Elemental analyses were performed at Atlantic Microlab Inc, Norcross, Georgia.

Preparation of $\{\eta^5\text{-C}_6\text{H}_5\}\text{Fe}\{\eta^5\text{-C}_6\text{H}_4\text{CH}=[9\text{-}(2\text{-bromofluorenyl})]\}$ (1a). A chilled (-78 °C) THF (30 mL) solution containing freshly distilled diisopropyl amine (0.24 g, 2.3 mmol) was treated with *n*-BuLi (1.1 mL, 2.8 mmol) and warmed to 0 °C over a period of 30 min. The mixture was cooled to -78 °C and the 2-bromofluorene (0.57 g, 2.3 mmol) was added. After 5 min ferrocenecarboxaldehyde (0.50 g, 2.3 mmol) was added in one portion and the cooling bath removed. The mixture was stirred for an additional 2 h and then diluted with ether (100 mL). The organic layer was washed with water (2 x 100 mL), brine (100 mL), and then dried over potassium carbonate. The solvents were removed under reduced pressure. The crude product was subjected to column chromatography (4 x 30 cm) on deactivated alumina. Elution with hexanes/ethyl acetate (9/1, v/v) produced 2 major bands. The first band was a reddish-purple color and found to be pure 1a (0.77 g, 76%, mp > 300 °C) and the second orange band was unreacted ferrocenecarboxaldehyde. ^1H NMR (CDCl_3) δ 8.39 (s, 1 H, Ar CH), 8.19, 8.17 (2s, 1 H, Ar CH), 7.90 (s, 1 H, Ar CH), 7.77-7.70, 7.69-7.68 (2m, 1 H, Ar CH), 7.59 (dd, $J = 8.1, 4.6$ Hz, 2 H, Ar CH), 7.51 (s, 1 H, vinyl CH), 7.48-7.43 (m, 2 H, Ar CH), 7.37-7.33 (m, 2 H, Ar CH), 4.73-4.71 (m, 2 H, Cp CH), 4.53 (t, $J = 1.8$ Hz, 2 H, Cp CH's), 4.50 (t, $J = 1.8$ Hz, 2 H, Cp CH's), 4.23 (s, 5 H, Cp CH); ^{13}C NMR (CDCl_3) δ 141.8, 139.7, 139.5, 139.2, 138.6, 137.1, 136.9, 136.6, 132.3 (aromatic C), 130.3, 129.9, 128.0, 127.9, 127.8, 127.4,

127.1, 126.8, 124.1, 122.8, 20.8, 119.6 (aromatic or vinyl CH), 80.7, 80.6 (*ipso*-Cp), 70.8, 70.3, 70.1 (Cp CH's), 69.6 (Cp CH's); UV-Vis (CH₂Cl₂) λ_{\max} = 494 nm (ϵ = 2.93 x 10³).

Preparation of $\{\eta^5\text{-C}_6\text{H}_5\}\text{Fe}\{\eta^5\text{-C}_6\text{H}_4\text{CH}=[9\text{-}(2,7\text{-dibromofluorenyl})]\}$ (2a). A chilled (-78 °C) THF (30 mL) solution containing diisopropyl amine (0.24 g, 2.3 mmol) was treated with *n*-BuLi (1.1 mL, 2.8 mmol) and then allowed to warm to 0 °C over a period of 30 min. The reaction mixture was cooled to -78 °C and the 2,7-dibromofluorene (0.76 g, 2.3 mmol) was added in one portion. The mixture was stirred for 5 min and then ferrocenecarboxaldehyde (0.50 g, 2.3 mmol) was added. The cooling bath was removed and stirring was continued for 2 h. The mixture was diluted with ether (100 mL), then washed with water (2 x 100 mL), and finally with brine (100 mL). The organic layer was dried over potassium carbonate and the solvents removed under reduced pressure. The crude product was crystallized from chloroform (reflux => -25 °C) to give 0.93 g of pure 2a (77%, mp > 300 °C). ¹H NMR (CDCl₃) δ 8.40 (s, 1 H, Ar CH), 7.88 (s, 1 H, Ar CH), 7.57, 7.55 (2d, J = 4.0 Hz, 2 H, Ar CH), 7.48-7.44 (m, 3 H, Ar and vinyl CH), 4.72 (t, J = 0.6 Hz, 2 H, Cp CH's), 4.56 (t, J = 0.5 Hz, 2 H, Cp CH's), 4.24 (s, 5 H, Cp CH's); ¹³C NMR (CDCl₃) δ 141.6, 138.4, 138.3, 135.9 (Ar C), 131.1, 130.5, 130.1, 129.7, 127.1, 122.8, 120.9, 120.6 (Ar or vinyl CH's), 80.1 (*ipso*-Cp), 71.0, 70.6 (Cp CH's), 69.7 (Cp CH's); UV-Vis (CH₂Cl₂) λ_{\max} = 504 nm (ϵ = 3.01 x 10³); Anal. Calcd for C₂₄H₁₆Br₂Fe: C, 55.42; H, 3.10%. Found: C, 55.52; H, 3.16%.

Preparation of $\{\eta^5\text{-C}_5\text{H}_5\}\text{Fe}\{\eta^5\text{-C}_6\text{H}_4\text{CH}=[9\text{-}(2\text{-nitrofluorenyl})]\}$ (3). One equivalent of 2-nitrofluorene (0.99 g, 4.7 mmol) was added to a solution of ferrocenecarboxaldehyde (1.0 g, 4.7 mmol) in THF (100 mL) at room temperature. Two mol-equiv of potassium t-butoxide (1.1 g, 9.4 mmol) were added and the mixture was stirred for 15 min. The mixture was then diluted with ether (100 mL) and run through a flash column (deactivated Al_2O_3 , 1 cm) to remove a heavy black precipitate. The resulting solution was further diluted with ether (50 mL), washed with water (2 x 100 mL), then brine (100 mL), and dried over K_2CO_3 . The crude product was subjected to column chromatography (2 x 15 cm) on deactivated alumina. Elution with EtOAc/hexanes (1/20, v/v) gave two major bands, the first was a dark purple band and this was found to be pure **3** (0.38 g, 20%, mp > 300°C). ^1H NMR (CDCl_3) δ 9.16 (s, 1 H, Ar CH), 8.64 (s, 1 H, Ar CH), 8.31-8.22 (m, 2 H, Ar CH), 7.88-7.81 (m, 2 H, Ar or vinyl CH), 7.65-7.63 (m, 1 H, Ar or vinyl CH), 7.46-7.33 (m, 2 H, Ar CH), 4.78-4.76 (m, 2 H, Cp CH's), 4.61 (t, $J = 1.8$ Hz, 1 H, Cp CH's), 4.56 (t, $J = 1.8$ Hz, 1 H, Cp CH's), 4.25 (s, 5 H, Cp CH's); ^{13}C NMR (CDCl_3) δ 146.9, 146.6, 145.8, 143.3, 141.5, 140.5, 138.4, 138.2, 137.1, 135.8 (aromatic C), 131.3, 130.4, 130.1, 128.7, 128.5, 128.1, 127.6, 124.3, 122.9, 122.5, 121.0, 120.9, 119.8, 119.5, 115.1 (aromatic or vinyl CH's), 80.2, 79.9 (*ipso*-Cp) 71.1, 71.0, 70.6 (Cp CH's), 69.7 (Cp CH's). UV-Vis (CH_2Cl_2) $\lambda_{\text{max}} = 512$ nm ($\epsilon = 6.76 \times 10^3$).

Preparation of $\{\eta^5\text{-C}_5\text{H}_5\}\text{Fe}\{\eta^5\text{-C}_6\text{H}_4\text{CH}=[9\text{-}(2\text{-carboxaldehydefluorenyl})]\}$ (1b).

A chilled (-78 °C) THF solution of **1a** (0.50 g, 1.1 mmol) was treated with *n*-BuLi (0.54 mL, 1.4 mmol). After 10 min an excess of dry DMF (0.26 mL, 3.4 mmol) was added and

the cooling bath removed. The mixture was brought to room temperature and hydrolyzed with water (5 mL). It was then diluted with ether (100 mL), washed with water (2 x 100 mL), then brine (100 mL), and dried over potassium carbonate. The crude product was subjected to column chromatography (2 x 15 cm) on deactivated alumina. Elution with EtOAc/hexanes (1/3, v/v) gave two major bands, the first deep red band being pure **1b** (0.17 g, 39%, mp>300°C). ¹H NMR (CDCl₃) δ 10.1, 9.97 (2s, 1 H, CHO), 8.75 (s, 1 H, Ar CH), 8.33 (s, 1 H, Ar CH), 8.28, 8.26 (2 s, 1 H, Ar CH), 7.88-7.83 (m, 3 H, Ar or vinyl CH), 7.64, 7.60 (2 s, 1 H, Ar or vinyl CH), 7.44-7.37 (m, 2 H, Ar CH), 4.76 (s, 2 H, Cp CH's), 4.56-4.52 (m, 2 H, Cp CH's), 4.24 (s, 5 H, Cp CH's); ¹³C NMR (CDCl₃) δ 192.2, 192.0 (CHO), 145.8, 143.4, 141.2, 140.3, 138.9, 138.1, 137.0, 136.6, 134.9, 134.8, 132.0 (aromatic C), 130.0, 129.2, 128.8, 128.7, 128.2, 128.0, 127.9, 127.4, 125.8, 124.2, 120.8, 120.6, 120.0, 119.8, 119.7 (aromatic or vinyl CH), 80.5, 80.4 (*ipso*-Cp), 70.9, 70.8, 70.5, 70.2, 69.6 (Cp CH's); UV-Vis (CH₂Cl₂) λ_{max} = 498 nm (ε=6.36 x 10³); IR (CH₂Cl₂) 1684 cm⁻¹.

Preparation of {η⁵-C₉H₇}Fe{η⁵-C₉H₇CH=[9-(2,7-bis(carboxaldehyde)-fluorenyl)]} (2b). A chilled (-78 °C) THF (100 mL) solution of **2a** (0.50 g, 0.96 mmol) was treated with *n*-BuLi (1.0 mL, 2.6 mmol). After 10 minutes an excess of dry DMF (0.45 mL, 5.8 mmol) was added and the cooling bath removed. The mixture was brought to room temperature and hydrolyzed with water (10 mL). It was then diluted with ether (150 mL), washed with water (2 x 150 mL), then brine (150 mL), and dried over potassium carbonate. The crude product was subjected to column chromatography (2 x

15 cm) on deactivated alumina. Elution with EtOAc/hexanes (1/3, v/v) gave three bands. The first orange band was the the monoaldehyde-monobromo complex and the second, major purple band was the desired dialdehyde (0.16 g, 40%, mp > 300 °C). ^1H NMR (CDCl_3) δ 10.2 (s, 1 H, CHO), 10.0 (s, 1 H, CHO), 8.83 (s, 1 H, Ar CH), 8.38 (s, 1H, Ar CH), 8.01-7.92 (m, 4 H, Ar CH), 7.76 (s, 1 H, vinyl CH), 4.80 (t, $J = 1.8$ Hz, 2 H, Cp CH), 4.63 (t, $J = 1.8$ Hz, 2 H, Cp CH), 4.27 (s, 5 H, Cp CH); ^{13}C NMR (CDCl_3) δ 192.2, 192.0 (CHO), 144.0, 141.7, 138.4, 136.0 (Ar C), 131.3, 130.7, 129.7, 129.1, 126.0, 121.2, 121.0, 120.3 (Ar C, Ar and vinyl CH), 79.9 (ipso Cp), 71.2, 71.1 (Cp CH's), 69.8 (Cp CH's); UV-Vis (CH_2Cl_2) $\lambda_{\text{max}} = 522$ nm ($\epsilon = 6.50 \times 10^3$); IR (CH_2Cl_2) $\nu_{\text{C=O}}$ 1693 cm^{-1} . Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{FeO}_2$: C, 74.66; H, 4.33%. Found: C, 74.32; H, 4.39%.

Preparation of $\{\eta^6\text{-C}_6\text{H}_6\}\text{Fe}\{\eta^6\text{-C}_6\text{H}_4\text{CH}=[9\text{-}(2\text{-tributylstannylfluorenyl})\}$ (1c) .

A chilled (-78 °C) THF (100 mL) solution containing **1a** (1.0 g, 2.3 mmol) was treated with *n*-BuLi (1.3 mL, 3.3 mmol) and stirred at -78 °C for 1h. Tributyltinchloride (0.88 mL, 3.3 mmol) was then added and the cooling bath removed. The mixture was allowed to reach room temperature and was stirred an additional 1 h. The mixture was diluted with ether (100 mL), washed with water (2 x 100 mL), brine (100 mL), and then dried over K_2CO_3 . The crude product was subjected to column chromatography on deactivated alumina. Elution with EtOAc/hexanes (1/20, v/v) gave one major band (orange) which was found to be **1c** (1.0 g, 68%) contaminated with SnBu_4 . ^1H NMR (CDCl_3) δ 8.28 (s, 1 H, Ar CH), 8.16, 8.13 (2s, 1 H, Ar CH), 7.88 (s, 1 H, Ar CH), 7.75-7.61 (m, 2 H, Ar CH), 7.47-7.39 (m, 2 H, Ar or vinyl CH), 7.32-7.24 (m, 2 H, Ar or vinyl CH), 4.69 (t, $J = 1.4$

Hz, 2 H, Cp CH), 4.41 (t, $J = 1.6$ Hz, 2 H, Cp CH), 4.18 (s, 5 H, Cp CH), 1.62-1.21 (m, 12 H, CH₂'s), 1.20-0.98 (m, 6 H, SnCH₂'s), 0.9 (t, $J = 7$ Hz, 9 H, CH₃).

Preparation of $\{\eta^5\text{-C}_6\text{H}_5\}\text{Fe}\{\eta^5\text{-C}_6\text{H}_4\text{CH}=[9\text{-}(2\text{-iodofluorenyl})]\}$ (1d). A solution of $\{\eta^5\text{-C}_6\text{H}_5\}\text{Fe}\{\eta^5\text{-C}_6\text{H}_4\text{CH}=[9\text{-}(2\text{-tributylstannylfluorenyl})]\}$ (1.0 g, 1.5 mmol) in THF (40 mL) was cooled to 0 °C in an ice bath and I₂ (0.39 g, 1.5 mmol) was added. The solution was stirred at 0 °C for 30 minutes and then diluted with ether (40 mL), washed with 10% Na₂SO₃ (2 x 40 mL), brine (40 mL), and dried over K₂CO₃. The solvent was removed under reduced pressure and the crude product was crystallized from ether/hexanes to give pure 1d (0.30 g, 40%). ¹H NMR (CDCl₃) δ 8.60 (s, 1 H, Ar CH), 8.19, 8.17 (2s, 1 H, Ar CH), 8.10 (s, 1 H, Ar CH), 7.72-7.65 (m, 2 H, Ar CH), 7.50-7.43 (m, 3 H, Ar or vinyl CH), 7.37-7.31 (m, 2 H, Ar CH), 4.72 (t, $J = 1.7$ Hz, 2 H, Cp CH's), 4.53 (t, $J = 1.8$ Hz, 1 H, Cp CH's) 4.49 (t, $J = 1.8$ Hz, 1 H, Cp CH's), 4.23 (s, 5 H, Cp CH's); ¹³C NMR (CDCl₃) δ 142.0, 139.8, 139.6, 139.5, 138.9, 137.5, 137.2, 136.4, 136.2, 135.8, 133.0, 132.3, 132.2 (Ar C), 128.7, 128.0, 127.8, 127.4, 127.3, 127.0, 124.1, 121.2, 119.7, 119.6, 119.5 (Ar CH or vinyl CH), 91.9, 91.5 (*ipso*-Cp), 80.8, 80.6, 70.8, 70.3, 70.0, 69.6 (Cp CH's); UV-Vis (CH₂Cl₂) λ_{max} = 494 nm (ε=4.01 x 10³). Anal. Calcd for C₂₄H₁₇FeI: C, 59.05; H, 3.51%. Found: C, 58.81; H, 3.54%.

Preparation of $\{\eta^5\text{-C}_6\text{H}_5\}\text{Fe}\{\eta^5\text{-C}_6\text{H}_4\text{CH}=[9\text{-}(2,7\text{-}(bis)\text{tributylstannyl-fluorenyl})]\}$ (2c). A chilled (-78 °C) THF (100 mL) solution containing 2a (1.0 g, 2.3 mmol) was treated with *n*-butyllithium (1.1 mL, 2.7 mmol) and stirred at -78 °C for 1 h.

Tributyltinchloride (0.74 mL, 2.7 mmol) was then added and the cooling bath removed. The mixture was allowed to reach ambient temperature and was stirred an additional 1 h. It was then diluted with ether, washed with water, brine, and dried over K_2CO_3 . The crude product was subjected to column chromatography on deactivated alumina. Elution with EtOAc/hexanes (1/20, v/v) gave one major band (orange) afforded **2c** (1.3 g, 70%) also contaminated with some $SnBu_4$. 1H NMR ($CDCl_3$) δ 8.24 (s, 1 H, Ar CH), 7.87 (s, 1 H, Ar CH), 7.68-7.65 (m, 2 H, Ar CH), 7.45-7.37 (m, 3 H, Ar and vinyl CH's), 4.71 (t, $J = 1.7$ Hz, 2 H, Cp CH), 4.43 (t, $J = 1.7$ Hz, 2 H, Cp CH), 4.20 (s, 5 H, Cp CH) 1.65-0.78 (m, 54 H, tributyltin CH_2 and CH_3 's).

*Preparation of $\{\eta^5-C_9H_8\}Fe\{\eta^5-C_9H_7CH=[9-(2,7-bis(iodo)fluorenyl)]\}$ (**2d**).* A chilled (0 °C) THF (40 mL) solution of **2c** (1.0 g, 1.1 mmol) was treated with I_2 (0.54 g, 2.1 mmol). The solution was allowed to react at 0 °C for 30 min and then diluted with ether (40 mL). The organic layer was washed with 10% Na_2SO_3 (2 x 40 mL), brine (40 mL), and then dried over K_2CO_3 . The solvents were removed under reduced pressure and the crude product was crystallized from ether/hexanes to give pure **2d** (0.31 g, 48%); 1H NMR ($CDCl_3$) δ 8.60 (s, 1 H, Ar CH), 8.08 (s, 1 H, Ar CH), 7.69-7.64 (m, 2 H, Ar CH), 7.47-7.43 (m, 3 H, Ar and vinyl CH's), 4.71 (t, $J = 1.9$ Hz, 2 H, Cp CH), 4.56 (t, $J = 1.8$ Hz, 2 H, Cp CH), 4.25 (s, 5 H, Cp CH); ^{13}C NMR ($CDCl_3$) δ 141.5, 138.8, 138.4 (Ar C), 136.5, 136.3, 135.9, 132.9, 130.8, 129.6, 128.7, 121.3 (vinyl and Ar CH's), 80.1 (*ipso*-Cp), 71.0, 70.6 (Cp CH's), 69.7 (Cp CH's); UV-Vis (CH_2Cl_2) $\lambda_{max} = 502$ nm ($\epsilon = 3.29 \times 10^3$).
Anal. Calcd for $C_{24}H_{16}FeI_2$: C, 46.94; H, 2.63%. Found: C, 47.50; H, 2.72%.

Preparation of Polymer 4. A 25 mL Schlenk tube was charged with **2d** (70 mg, 0.11 mmol), 1,4-bis(decoxy)-2,5-diethynylbenzene (53 mg, 0.12 mmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (2 mg, 3 mol-%), CuI (1 mg, 6 mol-%), PPh_3 (2 mg, 6 mol-%), and triethylamine (5 mL) under nitrogen. The mixture was warmed to 50 °C with stirring for 2 h and then diluted with dichloromethane (100 mL). The organic layer was washed with 10% NaCN (100 mL), water (2 x 100 mL), brine (100 mL), and then dried over K_2CO_3 . The solvents were removed and the polymer washed with ether (5 mL) and then dried under reduced pressure at 65 °C for 24 h (53 mg, 61%). $^1\text{H NMR}$ (CDCl_3) δ 8.49-8.46 (br s, 1 H, Ar CH), 8.01-7.97 (br s, 1 H, Ar CH), 7.76-7.72 (m, 2 H, Ar CH), 7.61- 7.54 (m, 3 H, Ar CH), 7.12, 7.09, 7.06, 7.02 (4 br s, 2 H, Ar CH), 4.80-4.78 (m, 2 H, Cp CH), 4.59-4.55 (m, 2 H, Cp CH), 4.26 (br s, 5 H, Cp CH), 4.14-4.03 (m, 4 H, CH_2O -), 1.95-1.84 (m, 4 H, CH_2 's), 1.61-1.51 and 1.31-1.23 (2 m's, 28 H, CH_2 's), 0.85-0.83 (m, 6 H, CH_3 's). IR (CH_2Cl_2) (alkyne) ν 2206 cm^{-1} ; UV-Vis (CH_2Cl_2) $\lambda_{\text{max}} = 514 \text{ nm}$ ($\epsilon = 5.39 \times 10^3$). Anal. Calcd for $[\text{C}_{68}\text{H}_{64}\text{FeO}_2]_n$: C, 81.39; H, 7.59%. Found: C, 79.42; H, 7.72%.

Preparation of model Complex 5. A 25 mL Schlenk tube was charged with **1d** (70 mg, 0.14 mmol), 1,4-bis(decoxy)-2,5-diethynylbenzene (61 mg, 0.14 mmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (3 mg, 3 mol-%), CuI (2 mg, 6 mol-%), PPh_3 (2 mg, 6 mol-%), and triethylamine (10 mL) under nitrogen. The mixture was warmed to 50 °C with stirring for 2 h and then diluted with dichloromethane (100 mL). The organic layer was washed with 10% NaCN (100 mL), water (2 x 100 mL), brine (100 mL), and then dried over K_2CO_3 . The residue was subjected to column chromatography, eluting with

EtOAc/hexanes (1/4, v/v) to afford spectroscopically pure **5** as an orange oil (0.14 g, 87 %). ^1H NMR (CDCl_3) δ 8.60 (s, 1 H, Ar CH), 8.45 (s, 1 H, Ar CH), 8.21, 8.18 (2 s's, 1 H, Ar CH), 7.97 (s, 1 H, Ar CH), 7.82-7.69 (m, 4 H, Ar CH), 7.57-7.52 (m, 4 H, Ar and possible vinyl CH), 7.37-7.32 (m, 4 H, Ar and possible vinyl CH), 7.12, 7.08, 7.05, 7.01 (4s, 2 H, Ar CH), 4.78, 4.73 (2 m, 4 H, Cp CH), 4.53-4.52 (m, 2 H, Cp CH), 4.50-4.48 (m, 2 H, Cp CH), 4.23 (s, 10 H, Cp CH), 4.13-4.02 (m, 4 H, CH_2O -), 1.61-1.40, 1.35-1.18 (2 m, 34 H, aliphatic CH_2 's), 0.90-0.81 (m, 6 H, aliphatic CH_3 's); ^{13}C NMR (CDCl_3) δ 153.6 (Ar-oxy carbon), 140.4, 140.0, 138.0, 137.5, 137.3, 136.8, 132.8, 132.6, 131.2, 130.7, 127.8, 127.6, 127.3, 127.2, 124.2, 122.8, 121.4, 121.3, 119.9, 119.5, 117.0, 114.1 (Ar C, Ar and vinyl CH), 96.0, 86.0, 81.0 (Cp CH), 70.9, 70.7, 70.1, 69.9, 69.7, 69.5 (Cp CH and OCH_2), 31.9, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7 (CH_2 's), 14.1 (CH_3).

X-ray Diffraction Studies. Crystals suitable for x-ray analysis were grown by slow evaporation of benzene solutions containing **1b** and **2b**. Pertinent data for the x-ray studies, including crystal, collection, final solution data are summarized in Table I. Crystals were mounted on the tip of a glass fiber and secured by epoxy cement. Intensity data were collected at ambient temperature on a Siemens P3 diffractometer and data were processed on MICROVAX 3100 computer using SHELXTL PLUSTM (version 4.0) software. The intensities of two check reflections were measured for every 100 reflections of data collected. No decay was observed ($100 \pm 4\%$). The structures were initially solved using direct methods and remaining atoms were located using difference Fourier maps. Neutral atomic scattering factors internal to SHELXTL

PLUSTM were used. Final refinement was by full-matrix least-squares minimization of $\sum[w(F_o - kF_c)]^2$ with weights, $w = 1/[\sigma^2(F) + 0.0004 * F^2]$ (for **2b** the weighting factor was fixed at $0.001 * F^2$). All nonhydrogen atoms were refined anisotropically; the hydrogen atoms were refined with constrained geometrical {"riding" on the carbons to which they are attached} and isotropic thermal parameters. For **2b**, the C=O was disordered and the was refined using two models. The occupancy factors for O1 and O1' were 0.75 and 0.25, respectively, and for O2 and O2' they were both 0.50. The structures were refined to final R values given in Table I.

Acknowledgment. This work was supported by the Office of Naval Research and the donors to the Petroleum Research Fund, administered by the American Chemical Society. We also wish express our gratitude to the NSF (CHE-9002379) and Utah State University Research Office for funding the purchase of the single-crystal x-ray diffractometer. A special thanks to Prof. Vernon Parker for helpful discussions and Dr. Kishan Handoo for obtaining the cyclic voltammetry data for compounds **4** and **5**.

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Figure I

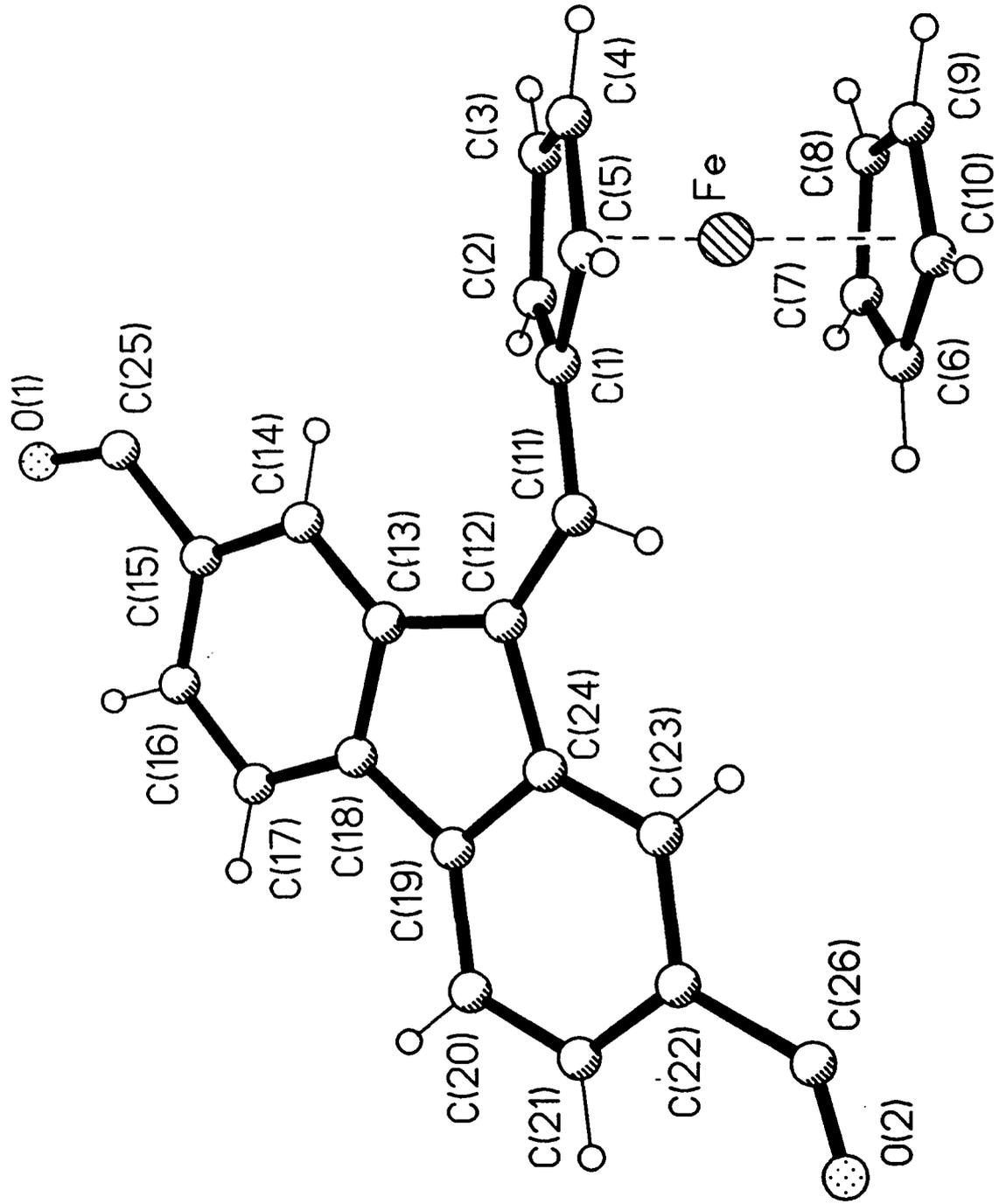


Figure II

