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New Ferrocene COMplexes and Polymers for Nonlinear Optical Applications

by

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<p>Bis(functionalized) Ferrocene based NLO-phores were prepared. One cyclopentadienyl (Cp) ring was modified with a β-(α-cyanoacrylate) group and the other with a hydroxymethyl moiety. The ferrocene complex was placed in a poly(methyl methacrylate) matrix and subjected to corona onset poling. The polymer solutions exhibited SHG activity. The ferrocene complex was also melt cast polymerized to afford a polymer of unknown structure. The ferrocene system was modified with methacryloyl chloride and then successfully copolymerized with methyl methacrylate. A single-crystal X-ray diffraction study on a ferrocene NLO-phore is reported.</p>					
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NEW FERROCENE COMPLEXES & POLYMERS FOR NONLINEAR OPTICAL APPLICATIONS

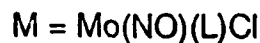
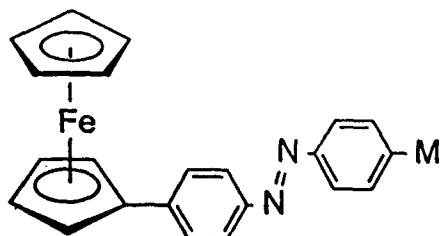
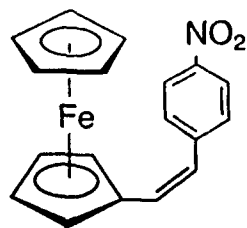
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INTRODUCTION

Ferrocene was the starting point for organometallic chemistry nearly four decades ago and is still today one of the most studied and versatile organometallic building blocks.¹ Ferrocene has been incorporated in polymeric systems to alter bulk properties of the material.² Ferrocene possesses excellent thermal and photochemical stability and can also protect polymeric systems from photodegradation.³ In addition, the ferrocene building block has been used in conducting polymers⁴ and in main chain liquid crystalline polyesters.⁵

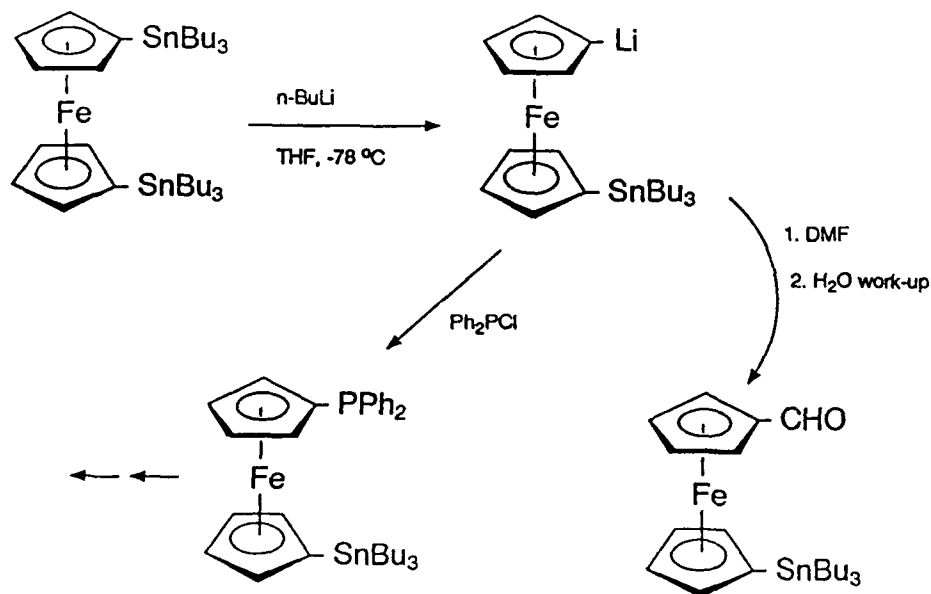
Nonlinear Optical (NLO) materials is a relatively new area of chemistry and has caught the attention of both the polymer and organometallic chemist.⁶ The use of ferrocene derivatives in NLO applications was first independently studied by two research groups.⁷ As anticipated, the metal center in ferrocene was found to serve as an excellent electron-donor.⁸ The crystalline compounds (see below) exhibited very high second harmonic generation (SHG) efficiencies relative to urea.⁷



Several key questions regarding the utilization of organometallic NLO systems remain unanswered. For instance, there is no example of an organometallic NLO system which has been poled and then shown to have SHG activity. Thus, it was not established that an organometallic NLO material would even survive the strong electric field (~5 KV) applied during the poling process. Other key questions have also not yet been addressed. For example, determining the ability (or lack) of polymeric-organometallic materials to retain alignment and can they survive the laser irradiation. The mission of our research effort is to answer these questions concerning polymeric organometallic NLO materials. This paper presents the initial stages of our research endeavor in polymeric-organometallic NLO materials.

Recent work from our laboratory developed new methodology for the preparation of novel *bis*-functionalized ferrocene complexes (Scheme I).⁹ The synthetic strategy gave us the ability to functionalize the cyclopentadienyl rings in a sequential manner. The strategy proved to be invaluable for ferrocene monomer synthesis and permits an array of novel complexes to be prepared.

Scheme I

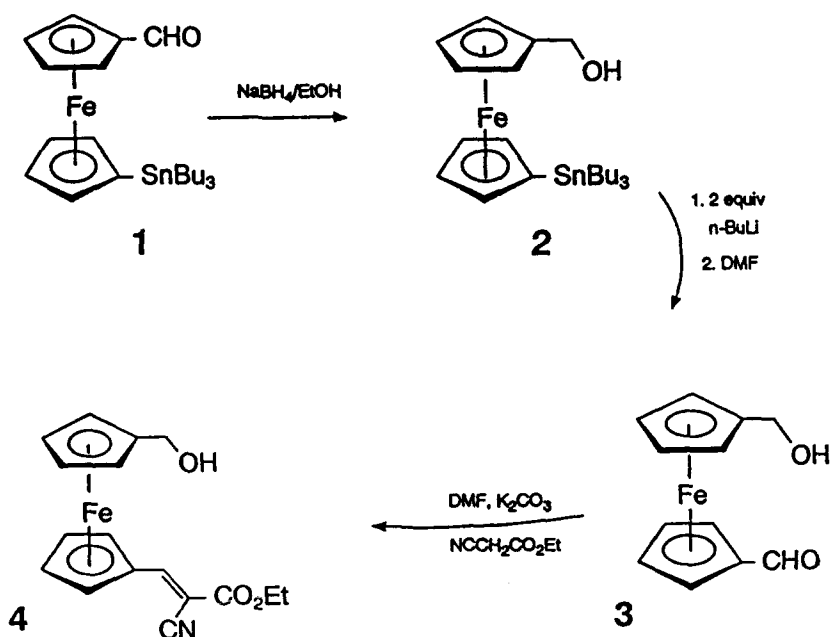


RESULTS & DISCUSSION

Complex 4 was prepared in good yield through a sequence involving selective transmetalation of the tri-*n*-butylstannyl groups combined with established condensation chemistry of ferrocene carboxaldehydes (Scheme II).¹⁰ Compound 4 crystallizes as long needles (some were 3 cm long!) but were unfortunately not suitable for a single-crystal X-ray diffraction study. The UV-Vis spectrum for compound 4 gave a λ_{max} of 515 nm ($\epsilon = 2.24 \times 10^3$). The compound forms beautiful purple solutions which are air-stable for hours. In the solid state the material is air-stable indefinitely.

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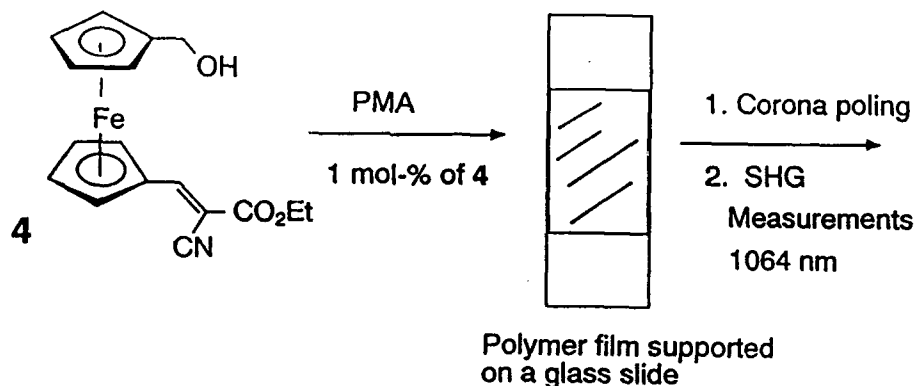
Scheme II



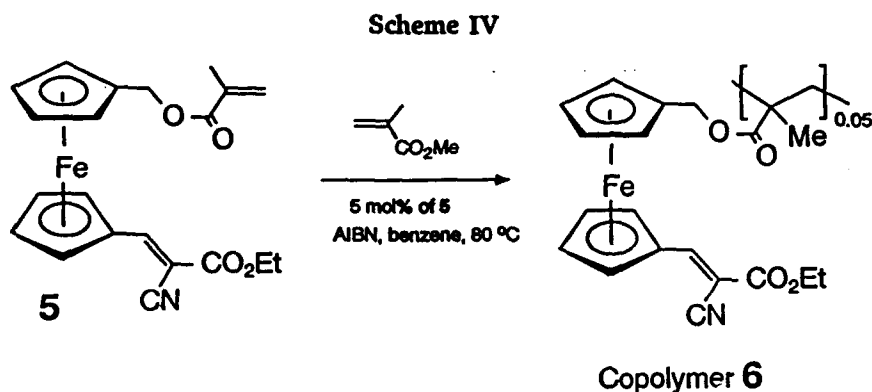
Compound 4 was suspended in poly(methyl methacrylate) (PMA) and then cast into a thin film. The "polymer solution" of 4 was then subjected to corona poling at elevated temperature.¹¹ The poling process afforded a polymer film which exhibited significant SHG (Scheme III). Using a primary frequency of 1064 nm the SHG band at 532 nm (*i.e.* green light) was visible to the naked eye. At this time there were no reference standards available for quantification of the data. After standing for several days the film showed little, if any SHG activity.

There are two very significant points which can be drawn from the results above. First, it was very clear that *the ferrocene "polymer solution" survived the poling process*. No apparent damage occurred to the polymer film (*e.g.* electrical arcing). Secondly, *the ferrocene systems responded to the poling process*. That is, the ferrocene compound has a significant permanent dipole to facilitate alignment.

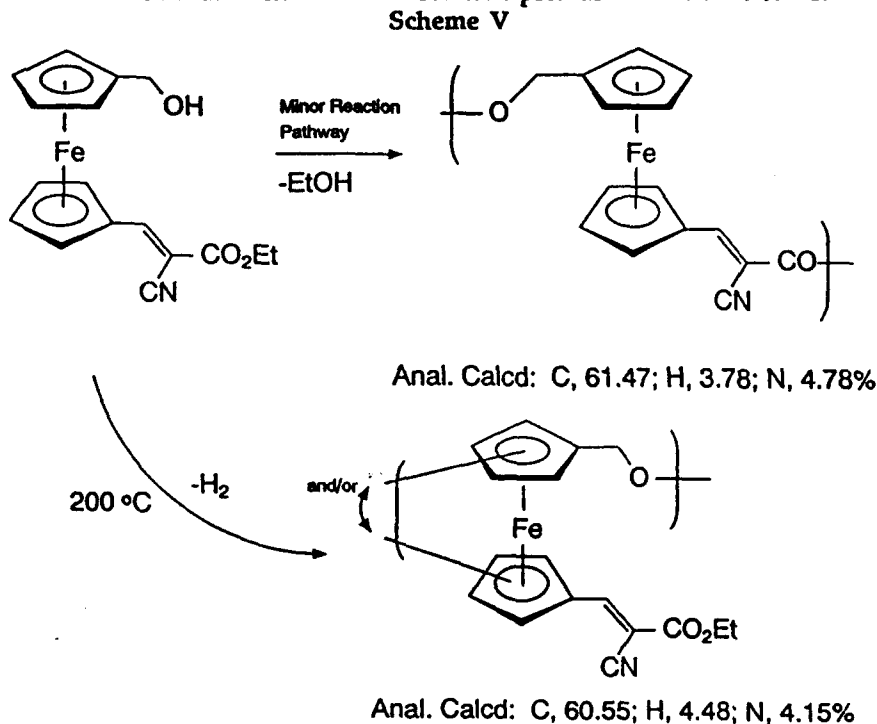
Scheme III



Modification of 4 with methacryloyl chloride afforded the new monomer 5 in excellent yield (Scheme IV). Monomer 5 was copolymerized with methyl methacrylate (5/95 molar ratio, respectively) using the free-radical initiator AIBN. Copolymer 6 was purified by multiple precipitations into pentane and methanol. At this point we know the copolymer will cast good films but do not have any results on poling and SHG measurements.



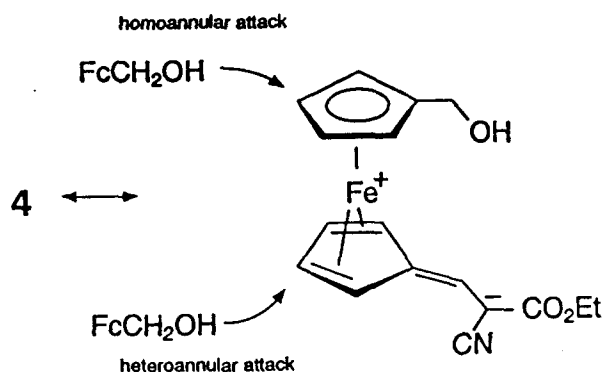
Another specific goal of our research program is to prepare homopolymers of NLO active ferrocene units. To accomplish this we carried out the homopolymerization of 4 (Scheme V). The polymerization was conducted under a nitrogen atmosphere as a melt at 200 °C. The polymer was isolated as a very tough and brittle glassy material. The polymeric material was collected and extracted with hot benzene for 24 h and then dried at reduced pressure for 24 h at 65 °C.



Polymer 7 was assigned the structure illustrated in Scheme V based on spectroscopic, analytical data, and additional experiments discussed below. Polymer 7 was also prepared using the Lewis acid catalyst $\text{Bu}_2\text{Sn}(\text{laurate})_2$ and found to afford a similar polymeric material. The latter conditions even though at $150\text{ }^\circ\text{C}$ did promote elimination of HCN from the polymer as evidenced by a carbon-carbon triple bond stretch ($\nu_{\text{C}\equiv\text{C}}$ 2357 & 2341 cm^{-1}) in the infrared spectrum and a lowering of the nitrogen content.

Thermal gravimetric analysis (N_2 , $10\text{ }^\circ\text{C}/\text{min}$ ramp) of 7 exhibited a weight loss of $\sim 8\%$ by $300\text{ }^\circ\text{C}$ which corresponds to ejection of HCN from the homopolymer. Continued heating of the sample to $700\text{ }^\circ\text{C}$ resulted in a total weight loss of 32% . Subjecting a sample to differential scanning calorimeter (N_2 , $10\text{ }^\circ\text{C}/\text{min}$ ramp) showed the loss of HCN and the final mode of decomposition were exothermic events.

Ferrocenylalkanol derivatives have been homopolymerized using Lewis acid catalysis.¹² The mode of polymerization has been explained through formation of the α -ferrocenyl carbocation,¹³ followed by a homo- or heteroannular Friedel-Crafts alkylation of a η^5 -cyclopentadienyl ring of another ferrocene unit. We believe complex 4 deviates from this type of reaction pathway because of the very electron-withdrawing β -(α -cyanoacrylate) group. Depicting a logical resonance contributor to the structure of 4 illustrates why nucleophilic attack of the η^5 -cyclopentadienyl ring is deemed reasonable (see below). Attack of the fulvene ring (*i.e.* heteroannular) represents conjugate addition of an alcohol to a very electron-poor olefin. The addition of alcohols to such olefins (*i.e.* good Michael acceptors) is in fact a well established organic reaction.¹⁴ We have been unable to model this reaction and thus at this point we cannot prove beyond a shadow of a doubt our mechanism is indeed correct.



We have initiated a systematic X-ray diffraction study on ferrocene systems having electron-poor olefins attached to the cyclopentadienyl ring. In particular we are looking for structural evidence to support the fulvene resonance contribution to the ground state. To date, we have completed the single-crystal X-ray structure of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{C}(\text{CN})\text{CO}_2\text{Et})\text{Fe}$ (8).¹⁰ A drawing of the structure is displayed in Figure I. The structure was refined to $R = 3.14\%$ with a GOF of 1.30. There are distinct bond length values which are consistent with a fulvene-like structure. However, at this point with only one structure in the series we are hesitant to put forth any strong conclusions. We are continuing to prepare analogues and accumulate more structural data.

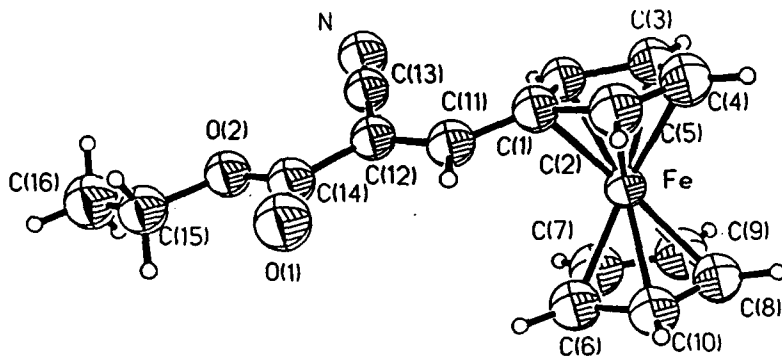


Figure 1. Drawing of the single-crystal molecular structure of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_3\text{H}_4\text{CH}=\text{C}(\text{CN})\text{CO}_2\text{Et})\text{Fe}$ (**8**) showing the labeling scheme employed. The atoms are drawn to include 30% of the electron density and hydrogen atoms have been given arbitrary isotropic thermal parameters.

Cyclic voltamograms of **4** and **8** show the reversible oxidation event to be shifted 0.30 V and 0.32 V, respectively, more positive than the ferrocene/ferrocenium redox couple. These data would suggest that the iron centers in **4** and **8** are much less capable of stabilizing a positive charge. It is logical to argue they would also form a much less stable α -ferrocenyl carbocation intermediate; hence, we tend to rule out such a species in the homopolymerization of complex **4**.

CONCLUDING REMARKS

In this study we have demonstrated that ferrocene complexes can be placed in a polymer solution and successfully aligned by the corona poling technique. In a qualitative terms the film showed significant SHG activity (*i.e.* a visible green beam emitted from the film) and as expected, lost this activity over time. In addition, the synthesis of a new copolymer was presented. This latter material has been submitted for poling and subsequent SHG activity evaluation.

EXPERIMENTAL

General. 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 $(\eta^5\text{-C}_5\text{H}_4\text{CHO})(\eta^5\text{-C}_3\text{H}_4\text{SnBu}_3)\text{Fe}$ was prepared by the literature method.⁹ Polymer analyses were performed using a duPont 9900 thermal analysis data station. Elemental analyses were performed at Atlantic Microlab Inc, Norcross, Georgia.

$(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{OH})(\eta^5\text{-C}_3\text{H}_4\text{SnBu}_3)\text{Fe}$ (**2**). ^1H NMR (CDCl_3) δ 4.33 (t, $J = 1.7$ Hz, 2 H), 4.32 (d, $J = 5.8$ Hz, 2 H), 4.18 (t, $J = 1.8$ Hz, 2 H), 4.09 (d, $J = 1.8$ Hz, 2 H), 4.03 (t, $J = 1.7$ Hz, 2 H), 1.56 (m, 7 H, OH & CH_2), 1.35 (m, 6 H, CH_2), 1.01 (apparent triplet, 6 H, CH_3), 0.91 (t, $J = 7.3$ Hz, 9 H, CH_3); ^{13}C NMR (CDCl_3) δ 88.0 (*ipso*-Cp),

74.7, 70.6 (Cp-SnBu₃), 69.5 (*ipso*-Cp), 68.4, 67.9 (Cp-CH₂OH), 60.9 (CH₂OH), 29.2 (CH₃), 27.4 (CH₃), 13.7 (CH₃), 10.2 (Sn-CH₃). Anal. Calcd for C₂₂H₂₃FeOSn: C, 54.69; H, 7.58%. Found: C, 54.78; H, 7.60%.

(η^5 -C₅H₅CH₂OH)(η^5 -C₅H₅CHO)Fe (3). ¹H NMR (CDCl₃) δ 9.98 (s, 1 H, CHO), 4.81 (t, *J* = 1.8 Hz, 2 H), 4.64 (t, *J* = 1.8 Hz, 2 H), 4.36 (t, *J* = 1.8 Hz, 2 H), 4.32 (d, *J* = 5.6 Hz, 2 H), 4.25 (t, *J* = 1.8 Hz, 2 H), 2.08 (br s, 1 H, OH); ¹³C NMR (CDCl₃) δ 194.3 (C=O), 90.3 (*ipso*-CpCHO), 79.4 (*ipso*-CpCH₂OH), 73.7 (Cp), 70.1 (Cp), 69.6 (Cp), 69.0 (Cp), 59.9 (CH₂OH); IR (CH₂Cl₂) $\nu_{C=O}$ 1702 cm⁻¹. Anal. Calcd for C₁₅H₁₂FeO₂: C, 59.05; H, 4.96%. Found: C, 58.78; H, 4.93%.

(η^5 -C₅H₅CH₂OH)(η^5 -C₅H₅CH=C(CN)CO₂Et)Fe (4). ¹H NMR (CDCl₃) δ 8.17 (s, 1 H, =CH(CN)CO₂Et), 5.03 (t, *J* = 1.8 Hz, 2 H), 4.74 (t, *J* = 1.8 Hz, 2 H), 4.33 (t, *J* = 7.1 Hz, 2 H), 4.32 (m, 4 H), 4.27 (t, *J* = 1.8 Hz, 2 H), 1.70 (br s, 1 H, OH), 1.39 (t, *J* = 7.1 Hz, 3 H); ¹³C NMR (CDCl₃) δ 163.2 (CO₂Et), 158.4 (C=CH), 116.8 (CN or =C(CN)CO₂Et carbon), 97.2 (*ipso*-Cp), 90.0 (*ipso*-Cp), 74.5 (Cp), 72.1 (Cp), 70.6 (Cp), 70.0 (Cp), 62.1 (OCH₂CH₃), 59.7 (CH₂OH); IR (film) $\nu_{C=N}$ 2220, $\nu_{C=O}$ 1718, and $\nu_{C=C}$ 1588 cm⁻¹; UV-Vis (CH₂Cl₂) 322 (ϵ = 1.37 x 10⁴) and 516 (ϵ = 2.23 x 10³) nm. Anal. Calcd for C₁₇H₁₇FeNO₂: C, 60.18; H, 5.06%. Found: C, 60.24; H, 5.06%.

Polymer 7. IR (film) 2200, 1718, 1588 cm⁻¹. A new IR band appeared at 1400 cm⁻¹. Direct side-by-side comparison of films showed no change in color (the human eye as the spectrophotometry) before and after polymerization. Anal. Found: C, 60.80; H, 4.22; N, 4.09%.

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