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Diironcarbonyl-coumarin complex: preparation, intramolecular electron transfer, and electro-generation of hydrogen

Research Article

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Abstract: A new organometallic complex coupling photoactive coumarin to a diironhexacarbonyl unit has been successfully prepared and its composition and electronic structure confirmed by elemental and spectroscopic analyses. Emission spectral analysis of the complex reveals photoinduced intramolecular electron transfer from coumarin to the iron-carbonyl moiety. The compound is electrochemically reduced at -1.24 V vs. Fc/Fc^+ . This reduction is irreversible, attesting to the instability of the complex. Electrochemical evolution of hydrogen in the presence of the complex has been studied and results are discussed.

Keywords: *Catalysis • Coumarin • Electron transfer • Hydrogenase model • Organometallic*
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1. Introduction

Photosynthesis is the process by which plants harness solar energy and convert it to chemical energy. To meet the need for clean and sustainable energy sources, there is renewed impetus to develop efficient catalytic systems that will mimic photosynthesis [1-6]. These artificial photosynthetic systems are generally composed of a photosensitizer, electron transport chain, and an electron acceptor (catalytic) unit. Many studies have examined such photocatalytic designs for the production of hydrogen (a clean alternative to fossil fuels) from water or acids (Scheme 1) [7-12]. Recent examples have employed photosensitizers such as ruthenium complexes and porphyrins coupled to models of the active site of [Fe-Fe] hydrogenase (1) [13-19].

This report presents studies on a new organometallic compound (2), Scheme 2, composing of a diironhexacarbonyl (catalytic) unit tethered to coumarin (photosensitizer). Coumarin chromophores have found wide industrial use as laser dyes. They have also been investigated as sensitizers for dye-sensitized solar cells with high solar to energy transfer efficiency [20-26]. One of our main objectives in designing

compound 2 is to investigate intramolecular electron transfer from coumarin to the iron-carbonyl moiety. The diiron-carbonyl unit, as a model for the active site of [Fe-Fe] hydrogenase enzyme (1, $X = \text{CH}_2, \text{NH}$; Scheme 2) [26], could potentially utilize the transferred electron to reduce protons to molecular hydrogen. Therefore, compound 2 could serve as a photocatalyst for the production of hydrogen. We present herein, the preparation, electrochemical, and spectroscopic characterization of 2. Fluorescence emission spectroscopy is used to study photoinduced intramolecular electron transfer in 2, and the result is discussed. Also discussed is the electrochemical reduction of acetic acid to produce hydrogen by compound 2.

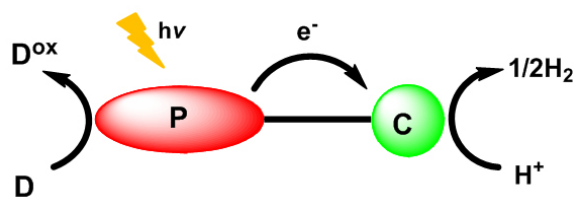
2. Experimental procedure

2.1. General

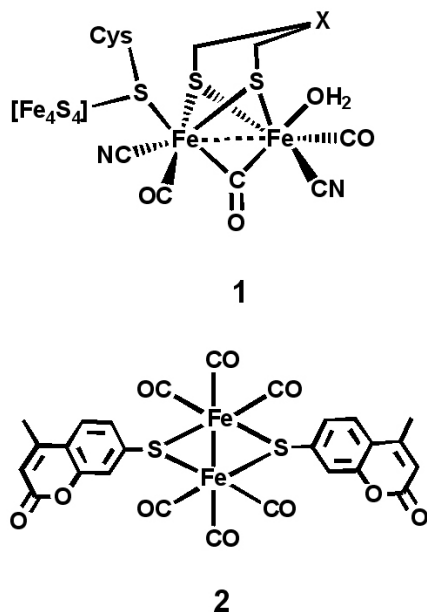
Electrochemical study was conducted using an Epsilon BAS potentiostat. Cyclic voltammograms were obtained using a three-electrode cell under nitrogen at room temperature. The electrodes used were a glassy carbon

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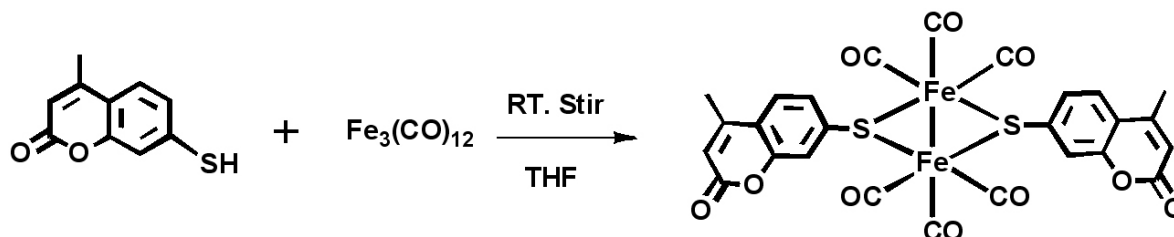
working electrode, a platinum auxiliary electrode, and a Ag/AgCl reference electrode. The platinum and glassy carbon electrodes were polished with aluminum paste and rinsed with water and acetone. A 0.1 M acetonitrile solution of Bu_4NPF_4 was used as a supporting electrolyte. The concentration of compound **2** was 0.2 mM, and the scan rate was 100 mV s^{-1} . UV/Visible spectrum of **2** was measured using a Shimadzu UV2501 PC spectrophotometer, and the infrared spectrum was recorded on a Nicolet FT/IR Magna spectrometer using an IR cell with a 0.20 mm spacer and NaCl windows. The fluorescence spectra



Scheme 1. Schematic representation of a photocatalytic design for hydrogen production (P; Photosensitizer, D; Sacrificial donor, C; Catalytic site).



Scheme 2. Structures of the active site of [Fe-Fe] hydrogenase (1) and complex **2**.



Scheme 3. Synthesis of compound **2**.

were obtained with a Perkin-Elmer LS 55 luminescence spectrometer. Nuclear Magnetic Resonance spectroscopy was performed on a Bruker 300 MHz spectrometer. Deuterated chloroform was used as solvent and reference for the measurements. The melting point was determined using an Electrothermal melting point apparatus. Elemental Analysis was performed by Columbia Analytical Services in Tucson Arizona, USA. All chemicals and solvents were purchased from commercial sources. Tetrahydrofuran (THF, DriSolv) was obtained from Aldrich and transferred to the reaction flask using a syringe.

2.2. Synthesis of compound **2**

A THF solution (100 mL) of $\text{Fe}_3(\text{CO})_{12}$ (1.58 g, 3.1 mmol) and 7-mercapto-4-methylcoumarin (1.21 g, 6.2 mmol) was stirred overnight until a color change from green to red was observed. The solvent was removed by rotary evaporation, and the product was isolated by column chromatography on silica gel using dichloromethane as eluent. Compound **2** was obtained as an orange solid (1.56 g, 77.5%). m.p 260°C . IR (DCM) ν 2080, 2044, 2000, 1720, 1650 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 6.9-7.4 (m, 6H, aromatic protons), 6.1 (s, 2H, $-\text{CH}=\text{C}=\text{O}$), 2.2 (s, 6H, 2 x CH_3). ^{13}C NMR (75 MHz, CDCl_3): 115.2, 119.5, 121.9, 124.2, 127.5, 129.5, 135.1, 144.6, 152.2, 159.8, and 208 ppm UV (DCM) λ_{max} (log ϵ) 288 (4.23) 338 nm (4.39). Anal Calcd for $\text{C}_{26}\text{H}_{14}\text{S}_2\text{Fe}_2\text{O}_{10}$: C 47.13, H 2.12, S 9.67. Found: C 47.60, H 2.26, S 9.74.

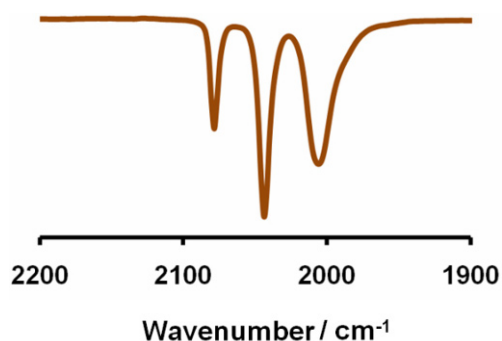
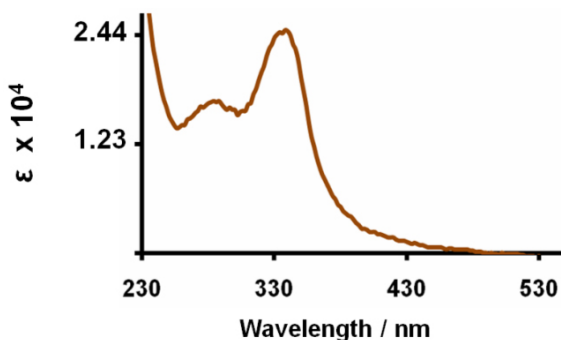
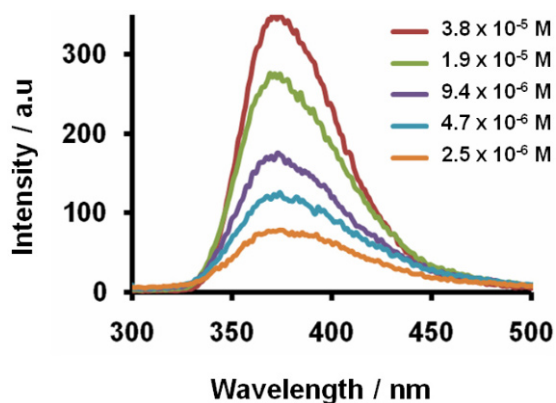
3. Results and discussion

3.1. Synthesis and spectroscopy

The synthesis of compound **2** is described in Scheme 3. It involves the reaction of 7-mercapto-4-methylcoumarin and $\text{Fe}_3(\text{CO})_{12}$ in tetrahydrofuran (THF) under nitrogen, using Schlenk-line techniques. The reaction mixture was stirred overnight and a color change from green to red was observed. The desired complex was isolated and purified using column chromatography on silica gel with dichloromethane as the solvent. Compound **2** was obtained as an orange solid in 77.5% yield.

Table 1. Spectroscopic and electrochemical data for compound **2**.

	IR ν / cm^{-1}	UV-Vis $\lambda_{\text{max}} / \text{nm}$ ($\log \epsilon$)	Fluorescence $\lambda_{\text{max}} / \text{nm}$	Cyclic voltammetry V vs.Fc/Fc ⁺
Compound 2	2080, 2044, 2000, 1720, 1650	288 (4.23) 338 (4.39)	370	$E_{\text{pa}} = +0.33$; $E_{\text{pc}} = -1.24$ $E_{\text{cat}} = -2.18$; OP = -0.72

**Figure 1.** IR spectrum of **2** recorded in dichloromethane.**Figure 2.** UV-visible of **2** (8.2×10^{-6} M) recorded in dichloromethane.**Figure 3.** Fluorescence emission spectra of **2** recorded in dichloromethane.

To ascertain the structure of **2**, elemental and spectroscopic analyses were conducted. Proton NMR spectrum of **2** shows a peak (singlet) at 2.2 ppm assigned to the methyl groups and a set of broad peaks between 6.0 to 7.6 ppm for the aromatic protons. Also, its carbon-13 NMR spectrum showed among other peaks,

a peak at 208 ppm ascribed to the CO ligands. Infrared spectroscopy is useful in probing the electronic structure of metal carbonyl complexes. For compound **2**, the IR spectrum was recorded in dichloromethane, and the result is contained in Fig. 1. The IR spectrum contains peaks at 2080, 2044, and 2000 cm^{-1} corresponding to the vibrational frequencies of terminal metal carbonyls. This is in agreement with IR data reported for similar diironcarbonyl complexes [28–37]. In addition to the Fe–CO peaks, a peak centered at 1720 cm^{-1} corresponding to the coumarin C=O (lactone) stretching vibration was observed. These spectroscopic data (Table 1) in combination with the elemental analysis results provide adequate evidence for the formation and structure of the desired compound, **2**.

The UV-visible spectrum of **2** is presented in Fig. 2 and shows bands at 288 nm ($\epsilon = 1.71 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 338 nm ($\epsilon = 2.44 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) assigned to $\pi \rightarrow \pi^*$ electronic transitions within the coumarin moieties of **2**. These assignments are based on previous studies [36] and supported by the high intensities (ϵ -values) of the absorption bands. Fluorescence emission spectra of **2** were collected at different concentrations and are contained in Fig. 3. The emission spectra were obtained upon excitation at 275 nm and the emission band was recorded at 370 nm. As expected, the intensity of the emission band decreases with decrease in concentration of the complex. A comparison of the emission spectra of 7-mercapto-4-methylcoumarin (ligand) and **2** recorded under the same conditions is presented in Fig. 4A. We observed that the intensity of the emission band of **2** is lower than that of 7-mercapto-4-methylcoumarin. This quenching or decrease in fluorescence intensity is attributed to intramolecular electron transfer from the photoexcited coumarin to the diironhexacarbonyl center Fig. 4B. The quenching efficiency for **2** is 88%. This quenching efficiency is close to the values reported for a diironhexacarbonyl system tethered to zinc porphyrin (78%) [15] and porphyrin macrocycle (86.4%) [16]. Electron transfer between excited coumarin and a number of organic electron acceptors have been studied. Low yields of net electron transfer were observed and attributed to either inefficient singlet quenching or low production of the more photoactive coumarin triplets. It is expected that acceptors with reduction potentials less negative than -1.5 vs. SCE (-1.9 vs. Fc/Fc⁺) can effectively

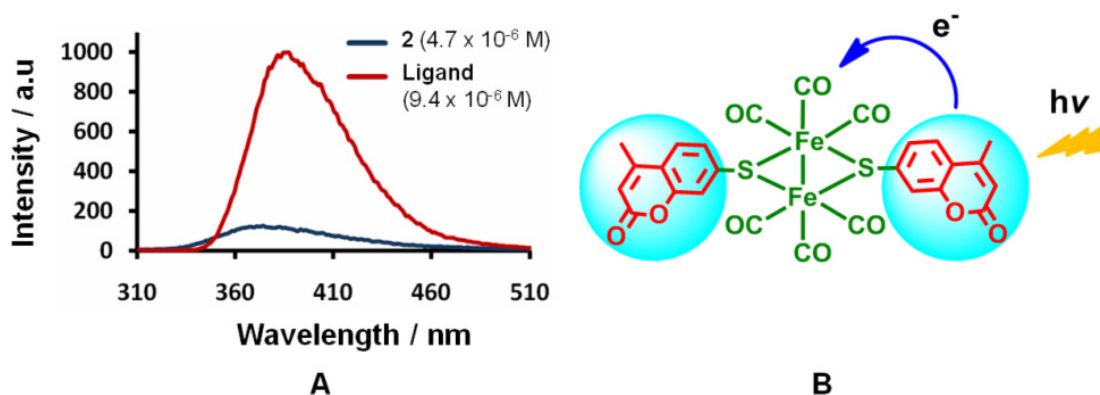


Figure 4. **A:** Fluorescence emission spectra of **2** and 7-mercapto-4-methylcoumarin (ligand) recorded under the same conditions (λ_{ex} : 275 nm, solvent; dichloromethane); **B:** Schematic representation of photoinduced electron transfer from coumarin to the diironhexacarbonyl unit in **2**.

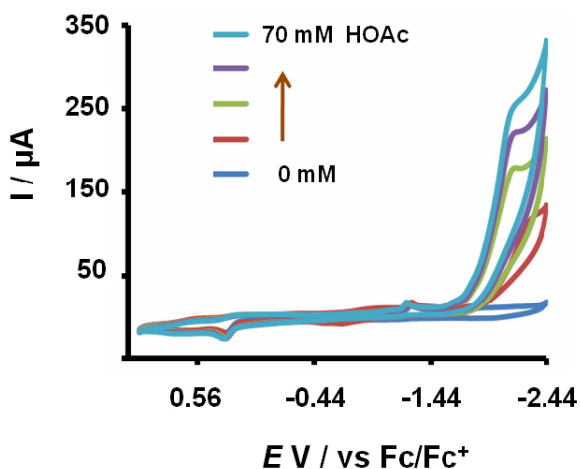


Figure 5. Cyclic voltammograms of **2** (0.2 mM, 10 mL) with acetic acid (0, 7, 35, 49, 70 mM) in 0.1 M $\text{Bu}_4\text{N}^+\text{PF}_6^-$ /acetonitrile at a scan rate of 100 mV/s.

accomplish diffusion limited quenching of coumarin singlet states [19]. Therefore, the diironhexacarbonyl unit of **2** with a reduction potential of -1.24 vs. Fc/Fc^+ (Table 1) has the right potential for oxidative quenching of the photoexcited coumarin moieties.

3.2. Electrochemistry

Compound **2** was subjected to cyclic voltammetric studies to probe its electrochemical and electrocatalytic properties (Table 1). The cyclic voltammogram of **2** was recorded in acetonitrile and shows one irreversible reduction event at -1.24 V vs. Fc/Fc^+ . Based on results of similar compounds [38], this can be tentatively ascribed to the $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{I}}\text{Fe}^0$ couple. The irreversibility of the electrochemical process attests to the instability of compound **2**. On the oxidation scan, one peak at $+0.33$ V Fc/Fc^+ was observed and assigned to the $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ couple.

The electro-generation of hydrogen by **2** from acetic acid (a weak acid; $\text{pK}_a = 22.3$ in acetonitrile) has been studied, and the results are contained in Fig. 5. It represents cyclic voltammograms of **2** with increasing amounts of acetic acid (0, 7, 35, 49, 70 mM). In the absence of acid, the two redox events described above were observed. On addition to the 7 mM of acetic acid, a new peak (E_{cat}) at -2.18 V vs. Fc/Fc^+ appears and its current intensity increases with sequential increments of acid concentration. These observations are indicative of reduction of protons to molecular hydrogen [37,38]. The overpotential (OP) was determined to be -0.72 V using the standard reduction (E_{HA}^0) of -1.46 V vs. Fc/Fc^+ for acetic acid [38]. This value is comparable to those reported for other diironcarbonyl models of the hydrogenase enzyme [37].

4. Conclusions

A diironhexacarbonyl cluster covalently linked to coumarin has been prepared and characterized by elemental and spectroscopic analyses. The complex is electrochemically unstable and exhibits photoinduced intramolecular electron transfer from coumarin to the iron-carbonyl unit. The electro-generation of hydrogen from acetic acid by compound **2** was observed at -2.18 V vs. Fc/Fc^+ .

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