Electrochemical and Fluorescent Properties of Ferrocenyl Chalcone with *N*-Ethyl Carbazole Group

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Chalcone ($C_{15}H_{12}O$: 1,3-diphenyl-2-propene-1-one) is an aromatic ketone in which two phenyl groups are linked by an enone bridge.[1] It is a collective name, as well, for compounds with an enone moiety bridging two aromatic groups. They are reported to exhibit an important array of biological activities,[2] as well as optical properties[3] and sensing activities.[4] Among them, ferrocene-substituted chalcones are known as 'ferrocenyl chalcones'. Recently, we investigated a series of ferrocenyl chalcones linked with aromatic and polycyclic compounds such as ferrocene,[5] naphthalene[6] and anthracene.[7] These systems were designed in order to modulate the electrochemical and optical properties of the polycyclic moieties by the electron-donating ferrocenyl group through the enone linkage. However, the intrinsic optical properties of the naphthalene and anthracene moieties were quenched by the ferrocenyl moiety which acts as a quencher.

In an attempt to achieve a breakthrough with this system, we adopted a carbazole derivative as the polycyclic group in ferrocenyl chalcones. Carbazole ($C_{12}H_9N$) is a heterocyclic compound with a tricyclic structure, whose derivatives are used because of the optical phenomena they exhibit, such as fluorescence.[8,9] Therefore, its derivatives have been widely investigated as candidate optical materials such as light-emitting polymers,[8c] molecular fluorescence markers of cancer cells and fluorescent multi-carbazole molecules.[8a,9] Moreover, their optical properties can be tuned by linking an auxochrome to a carbazole molecule. In this paper, a ferrocenyl chalcone with an N-ethyl carbazole moiety (abbreviated as **Fc-EtCbz**) was synthesized and characterized by the spectroscopic methods such as high-resolution FAB-MS, ^{1}H NMR, FT-IR and UV-Vis spectroscopies. It's electrochemical and fluorescence properties were investigated and compared with those of 9-ethyl-3-carbazolecarboxaldehyde (**EtCbzAld**).

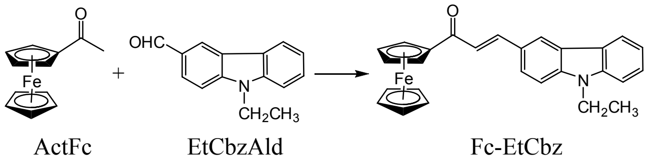
Experimental

General Methods. Acetylferrocene (**ActFc**) and **EtCbzAld** were commercially purchased (Aldrich) and used as received. HPLC-grade organic solvents (Aldrich) were used for the column chromatography, electrochemical study and fluorescence measurements without further purification.

The FT-IR spectra were recorded using the KBr pellet method on a MIDAC FT-IR spectrometer within the range of 4000 ~ 400 cm^{-1}. The electronic absorption spectra were obtained in several solvents, viz. CH_3CN, CH_2Cl_2, EtOH and MeOH, on an HP 8452A diode array spectrophotometer. The ^{1}H-NMR spectra were obtained on a Bruker Avance 500 using $CDCl_3$ as a solvent. The mass spectra were obtained on a JMS-700 Mstation by fast atom bombardment (FAB). The electrochemical studies were carried out at room temperature with a CHI 620A Electrochemical Analyzer (CHI Instrument Inc.) in an acetonitrile solution containing 0.5 mM of the sample and 0.1 M n-$Bu_4N \cdot BF_4$ supporting electrolyte, using a Pt-button (r = 1 mm) working electrode, Ag/AgCl reference electrode and Pt-wire (ϕ = 1 mm) counter electrode at a scan rate of 100 mV s^{-1}. All redox potentials were referenced against the standard Fc/Fc$^+$ redox couple ($E_{1/2} = +0.464$ V *vs.* Ag/AgCl). The fluorescence spectra were measured at room temperature by a Cary Eclipse fluorescence spectrophotometer (Varian) in CH_3CN, CH_2Cl_2, EtOH and MeOH. Approximately 3 mL of solutions of the samples at a concentration of $10^{-4} \sim 10^{-5}$ M in a quartz cell were used to obtain their spectra.

Preparation of Fc-EtCbz. A mixture of **ActFc** (1 mmol, 228 mg), **EtCbzAld** (1 mmol, 223 mg) and NaOH (5 mmol, 200 mg) was ground with an agate mortar and pestle. This mixture was allowed to stand in a water bath (85 °C) for 30 min. The product was extracted with CH_2Cl_2 and the organic solution was dried with $MgSO_4$. After filtration, the solvent was removed at reduced pressure and the final product was separated from the residue by column chromatography (SiO_2, CH_2Cl_2). (Scheme 1)

Yield: < 20%. Red colored powder. Mp: 190 ~ 191°C. FAB-MS (*m/z*, %): 433 (M^+, 100), 419 ($[M\text{-}CH_2]^+$, 21), 368 ($[M\text{-}C_5H_5]^+$, 7), 248 ($[M\text{-}(C_5H_5)Fe(C_5H_4)]^+$, 22). HR-FABMS Calc. for $C_{27}H_{23}FeNO$ 433.1129 Found 433.1143 (M^+). FT-IR (KBr, cm^{-1}): 2981(Cp C-H), 1642(C=O), 1106(Ar C=C), 988(=C-H), 919(Ar C-H), 816(Ar C-H), 801(Cp C-H), 485(Cp-Fe). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 1.47(3H, CH_3, t, J = 14.5 Hz), 4.24(5H, CH, s), 4.40(2H, CH_2, q, J = 21.7 Hz), 4.59(2H, CH, s), 4.98(2H, CH, s), 7.20(1H, CH, d, J = 15.3 Hz), 7.30(1H, CH, t, J = 14.8 Hz), 7.44(2H, CH, d, J = 9.8 Hz), 7.51(1H, CH, t, J = 15.2 Hz), 7.80(1H, CH, dd, J = 9.4 Hz), 8.04(1H, CH, d, J = 15.3 Hz), 8.17(1H, CH, d, J = 7.7 Hz), 8.38(1H, CH, s).

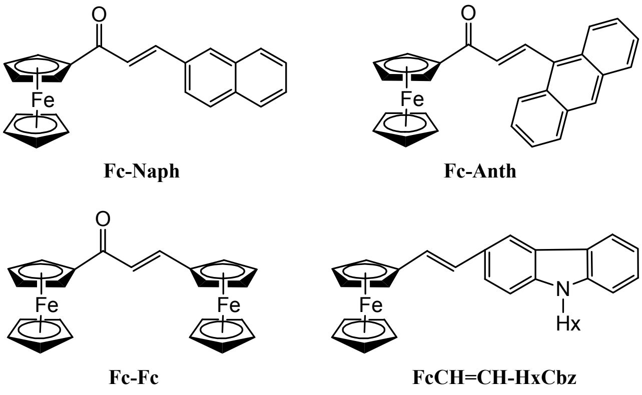


Scheme 1. Synthesis of **Fc-EtCbz**.

Results and Discussion

Synthesis and Characterization. **Fc-EtCbz** was synthesized by the solvent-free aldol condensation method using **ActFc** and **EtCbzAld**. The reactants were ground thoroughly to a homogeneous mixture in order to obtain the maximum yield. The purification of **Fc-EtCbz** was not easily achieved by column chromatography when eluting with CH_2Cl_2, as compared to the other ferrocenyl chalcones that we have prepared before, such as **Fc-Fc**,[5] **Fc-Naph**[6] and **Fc-Anth**[7] (Scheme 2). The crude product of **Fc-EtCbz** loaded on the chromatography column was first eluted with CH_2Cl_2/*n*-hexane (1 : 1) in order to separate the possible side products and unreacted compounds, and then eluted with CH_2Cl_2 to collect **Fc-EtCbz**. Nevertheless, the pure product was recovered in a yield of less than 20%, which is much lower than those obtained for **Fc-Fc** (63%),[5] **Fc-Naph** (73%)[6] and **Fc-Anth** (57%).[7] In this reaction, the use of stoichiometric amounts of the reactants is important to reduce the amount of side product. For example, the product (**Fc-EtCbz**) involving the enone moiety can react further with an excess of acetyl reactant to produce the 1,5-pentadione derivative.[9,10]

The purified product was characterized by the FAB-mass, FT-IR, ^{1}H-NMR and UV-Vis spectroscopic methods. The FAB-MS data of **Fc-EtCbz** shows the mother peak (M^+) at m/z = 433 with 100% intensity and the successive losses of the cyclopentadienyl (Cp) and Fc moieties at m/z = 368 and 248, respectively, are observed. HR-FAB mass spectroscopy detected the mass peak (m/z = 433.1143) for the exact mass of **Fc-EtCbz** (m/z = 433.1129) within an error range of +3.1 ppm. The ν(C=O) peak of **ActFc** observed at 1663 cm^{-1} shifts to a lower frequency of 1642 cm^{-1} for **Fc-EtCbz**. This is due to the conjugation of the π-electrons on the carbonyl moiety with those on the ethylene moiety in the enon linkage. The NMR spectra measured at room temperature show two doublets at 7.20 ppm (J = 15.3 Hz) and 8.04 ppm (J = 15.3 Hz), indicating that the ethylene moiety in the enon linkage is in the *trans*-conformation.[11] The UV-Vis spectra of **Fc-EtCbz** were measured in several solvents with different polarities in order to investigate the solvatochromic shift (Table 1). The π → π* (240 ~ 244 nm) and n → π* (316 ~ 320 nm) transitions of the enone linkage were virtually unaffected by the solvent polarity. However, the d–d transition of the ferrocenyl group varied from 480 nm in CH_3CN to 498 nm in MeOH. The extent of the solvatochromic shift of **Fc-EtCbz** (18 nm) is very close to those of **Fc–Anth** (16 nm)[7] and **Fc-Naph** (20 nm),[6] but much less than that of **Anth-Fc** (44 nm).[7] In spite of the many attempts we made to grow single crystals of **Fc-EtCbz** using different solvent pairs such as CH_2Cl_2/*n*-hexane, CH_2Cl_2/ether and CH_2Cl_2/MeOH, etc., no single crystals suitable for X-ray structure analysis were obtained. However, based on the above analytical results, we can confirm that the final product is the compound shown in Scheme 1.



Scheme 2. The reported ferrocenyl compounds.

Electrochemical Study. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements of **Fc–EtCbz** were performed in acetonitrile, as shown in Fig. 1. Its CV parameters are summarized and compared with those of the reactants (**ActFc** and **EtCbzAld**) in Table 2. The CV curve of **Fc-EtCbz** shows two groups of redox cycles in the potential range of 0.4 V ~ 2.0 V. The first one, which is observed in the lower potential region, consists of one reversible cycle, as shown in the inset with $E_{1/2}$ = 0.706 V. This half-wave potential value ($E_{1/2}$) is very close to that of **ActFc** ($E_{1/2}$ = 0.712 V), indicating that it is surely due to the redox process of the ferrocenyl group. However, it is quite different from that of 3-(E)-ferrocenyl-vinyl-N-hexyl carbazole (**FcCH=CH-HxCbz**; $E_{1/2}$ = 0.418 V)[12] in which ferrocenyl and carbazole groups are directly connected through a vinyl moiety (Scheme 2). This means that the half-wave potential of the ferrocenyl moiety of **Fc-EtCbz** is more anodic than that of **FcCH=CH-HxCbz**, possibly due to the carbonyl moiety in **Fc-EtCbz**. This was also evidenced in other ferrocenyl chalcone systems such as **Fc-Fc**,[5] **Fc–Naph**,[6] and **Fc-Anth**.[7] Moreover, the N-ethyl carbazole group in **Fc-EtCbz** is more electron donating than the methyl group, if the $E_{1/2}$ values of **Fc-EtCbz** (0.706 V) and **ActFc** (0.712 V) are compared. Therefore, **Fc-EtCbz** can be described as a D^1-π-D^2 system where two different donors (D^1 and D^2) are connected through a π-bridge, and the N-ethyl carbazole moiety lowers the HOMO level of **Fc-EtCbz**, possibly by electron-delocalization over the molecule. The second group of redox cycles consists of reversible multi-step processes, which can be roughly represented by two redox processes, based on the DPV cycle (Fig. 1B), of the carbazole moiety,

Table 1. UV-Vis data of **Fc-EtCbz** measured in various solvents (nm).

Solvent (polarity)	π → π*(enone)	π → π*(Cbz)	n → π*(enone)	π → π*(Fc)	d → d(Fc)
CH_3CN(5.8)	242s	288m	316m	356sh, 376m	480w
EtOH(5.2)	242s, 252sh	290m	320m	358sh, 388m	496w
MeOH(5.1)	240s, 250sh	290m	320m	358sh, 388s	498w
CH_2Cl_2(3.1)	244s	290s	318m	358sh, 378m	486w

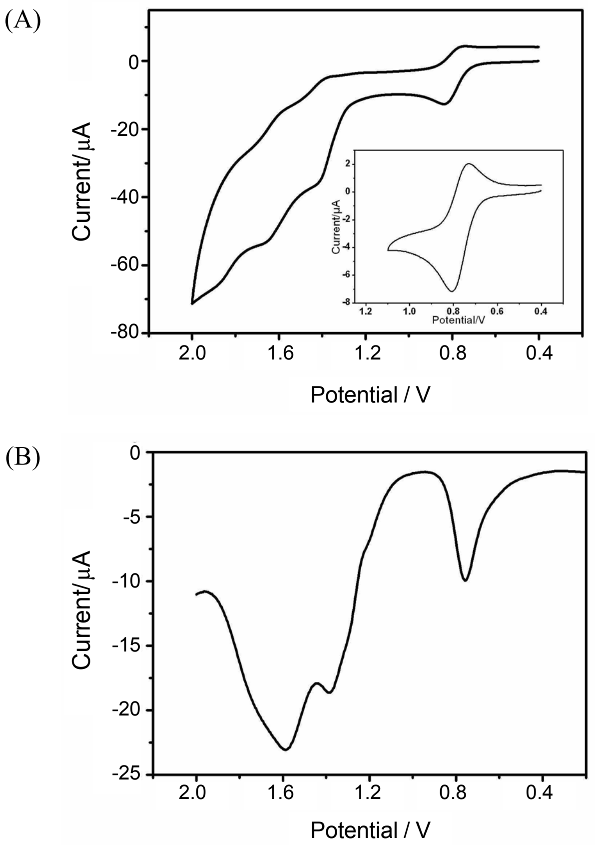


Figure 1. The cyclic voltammogram (A) and its differential pulse voltammogram (B) of **Fc-EtCbz** (*vs.* Ag/AgCl). The inset shows the reversible cycle for the redox process of the ferrocenyl group.

because its redox potentials are very similar to those of **EtCbzAld**. (Table 2).

Fluorescent Properties. The fluorescence spectra of **Fc-EtCbz** were measured at room temperature in several organic solvents, viz. CH_3CN, CH_2Cl_2, EtOH and MeOH, but no solvent-dependency of the fluorescence properties was observed. Among them, the fluorescence excitation (λ_{ex} = 408 nm) and emission (λ_{em} = 567 nm) spectra measured in MeOH are shown in Fig. 2, in comparison with those of **EtCbzAld** (λ_{ex} = 230 nm and λ_{em} = 476 nm). These spectra show that the fluorescence spectrum of **EtCbzAld** observed at 476 nm undergoes a large bathochromic shift to 567 nm in **Fc-EtCbz**, which no doubt originates from the carbazole moiety. Therefore, it is suggested that the ferrocenyl moiety in **Fc-EtCbz** essentially acts as an efficient auxochrome, resulting in an increase of the fluorescence λ_{em} value by 91 nm. This suggests that the ferrocenyl moiety lowers the first excited state (S_1) of the N-ethyl carbazole moiety in **Fc-EtCbz**. This result is in stark contrast with the observation that the fluorescence of the naphthalene and anthracene moieties in **Fc-Naph** and **Fc-Anth**, respectively, was quenched at room temperature and that no fluorescence spectra were obtained for these compounds.[6,7] In other words, the ferrocenyl moiety behaves as a fluorescence quencher in **Fc-Naph** and **Fc-Anth**, but as an auxochrome in **Fc-EtCbz**.

Table 2. The cyclic voltammetry parameters for **Fc-EtCbz** and its reactants.[a]

Compound	Anodic		Cathodic		$E_{1/2}$[b]
	E_{pa}^1	E_{pa}^2	E_{pc}^1	E_{pc}^2	
ActFc	0.745		0.679		0.712
EtCbzAld		1.56	1.36		1.46
Fc-EtCbz	0.756			0.655	0.706
		1.43	1.38		1.41
		1.66	1.59		1.63

[a] The samples (0.5 mM) are dissolved in MeCN containing 0.1 M n-$Bu_4N{\cdot}BF_4$ electrolyte, and the potentials (in volt) are referenced to Fc/Fc^+ ($E_{1/2}$ = +0. 464 V *vs.* Ag/AgCl) with a scan rate of 100 mV/s. [b] $E_{1/2} = (E_{pa} + E_{pc})/2$.

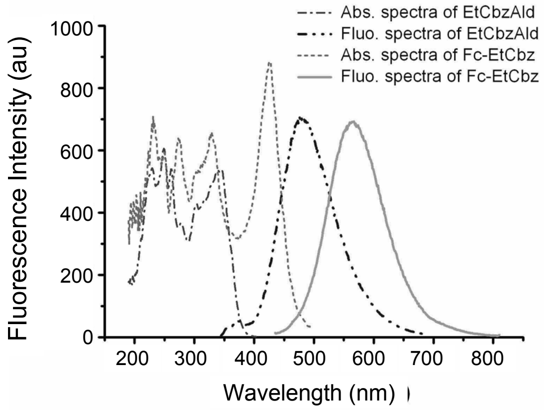


Figure 2. The absorption and fluorescence spectra of **EtCbzAld** (λ_{ex} = 230 nm and λ_{em} = 476 nm) and **Fc-EtCbz** (λ_{ex} = 425 nm and λ_{em} = 567 nm) measured in MeOH at room temperature.

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