

Ferrocenyl Chalcone with 2-Anthracenyl Group (2-Anth-C(O)CH=CHFc): Electrochemical and Fluorescent Properties

Su-Kyung Lee, Chae-Mi Lim, Ji-Yeon Lee, and Dong-Youn Noh*

Department of Chemistry, Seoul Women's University, Seoul 139-774, Korea. *E-mail: dynoh@swu.ac.kr
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Ferrocenyl chalcones (**Fc-Ar**, Fc-C(O)CH=CHAr and **Ar-Fc**, Ar-C(O)CH=CHFc), in which ferrocenyl (Fc) and aromatic (Ar) groups are linked by an enone bridge (-CH=CHC(O)-), are versatile compounds exhibiting antiplasmodial¹ and antitumor activities,² fluorescent and electrochemical properties,^{3,4} and molecular chemosensor activity.^{5,6} Ferrocenyl chalcones bearing the fluorophores such as 2-naphthalene,^{3d} 9-anthracene,^{3a} 1-pyrene,^{5,6} and *N*-ethyl carbazole,^{3b} are regarded as good candidates for new fluorescent material (Scheme 1). However, ferrocenyl chalcones containing 9-anthracene and 2-naphthalene derivatives have been reported as being not fluorescent, while those containing 1-pyrene and *N*-ethyl carbazole derivatives are fluorescent. It means that the ferrocenyl group, known as an effective quencher of excited states,⁷ is therefore not the only reason why they are non-fluorescent. Some derivatization of fluorophores can also disable fluorescence, as demonstrated by 2-acetylanthracene being fluorescent⁸ while 9-acetylanthracene is not.⁹

In this study, a ferrocenyl chalcone with a 2-anthracenyl group (2-Anth-C(O)CH=CHFc, **2Anth-Fc**), an analogue of **9Anth-Fc**, was prepared. Unlike **9Anth-Fc**,^{3a} **2Anth-Fc** is fluo-

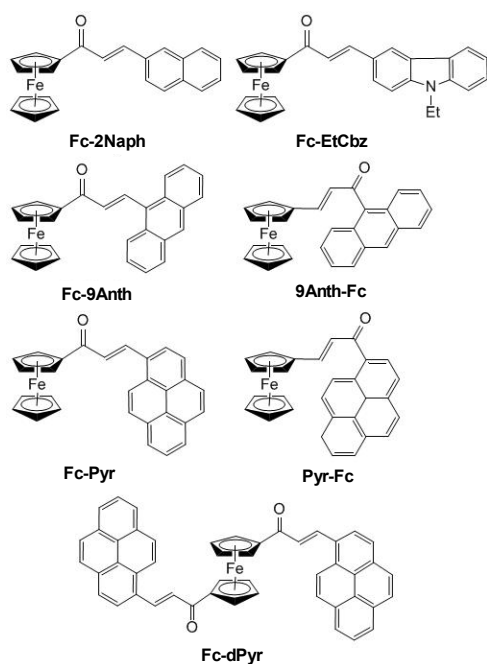
rescent and its fluorescence was investigated in relation to its solvent's polarity. Its electrochemical properties were also studied and the local geometry of **2Anth-Fc** is suggested from ¹H NMR results.

Experimental

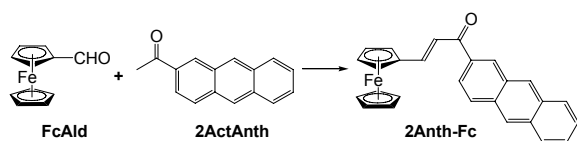
General Methods. Ferrocenecarboxaldehyde (FcAld), 2-acetylanthracene (**2ActAnth**) and first grade organic solvents were used as received. Melting points were determined using a Stuart SMP3 (Barloworld Scientific Ltd.). Measurement of Matrix-Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) masses was performed with a Voyager-DETM STR Biospectrometry Workstation (Applied Biosystems Inc.). Infrared spectra were recorded by the KBr pellet method on a Perkin Elmer Spectrum 100 between 4,000 - 400 cm⁻¹. ¹H NMR measurements were performed at room temperature using an Avance 500 (Bruker) with CDCl₃ solvent. UV-vis spectra were obtained on an HP 8452A diode array spectrophotometer. Fluorescence spectra of about 3 mL samples of **2Anth-Fc** and **2ActAnth** at concentration of 10⁻⁵ ~ 10⁻⁴ M in quartz cells were measured at room temperature by a Cary Eclipse fluorescence spectrophotometer (Varian) in CHCl₃, CH₃CN, EtOH and MeOH. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out at room temperature with a CHI 620A Electrochemical Analyzer (CHI Instrument Inc.) on 0.5 mM samples in 3.0 mL CH₃CN, with 0.1 M *n*-Bu₄N·BF₄ as supporting electrolyte, a Ag/AgCl reference electrode, a Pt button working electrode, a Pt wire counter electrode and a scan rate of 100 mV s⁻¹. All redox potentials were referenced against the Fc/Fc⁺ redox couple (*E*_{1/2} = 0.474 V).

Preparation of 2Anth-Fc. A mixture of **FcAld** (1.0 mmol, 0.215 g), **2ActAnth** (1.0 mmol, 0.220 g) and solid NaOH (5.0 mmol, 0.258 g) was ground homogeneously with a mortar and pestle. This mixture was allowed to stand in a 60 °C water bath overnight. The product was extracted with CH₂Cl₂ and dried with MgSO₄. After filtration, the red-orange solution was evaporated and separated by column chromatography. The dark red band was collected by CHCl₃ and recrystallized from CH₂Cl₂/*n*-hexane (Scheme 2).

Yield 55% (228 mg). mp 222 - 223 °C. MALDI-TOF-MS (*m/z*) 416.0328 (M⁺), 417.0365 (M⁺+1). FT-IR (KBr, cm⁻¹) 3088, 3053 (Ar C-H), 1660 (C=O), 1587 (C=C), 1287, 1198, 1176 (Ar C=C), 1043, 978 (Ar C-H ip def), 881, 815 (Ar C-H oop def), 531, 478, 465 (Fe-ring vib). ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.69 (1H, CH, s), 8.62 (1H, CH, s), 8.47 (1H, CH, s),



Scheme 1. Some ferrocenyl chalcones bearing polycyclic aromatic hydrocarbon fluorophores

Scheme 2. Synthesis of **2Anth-Fc**

8.09 (1H, CH, d, $J = 12.69$ Hz), 8.07 (2H, CH, d, $J = 10.69$ Hz), 8.05 (1H, CH, d, $J = 9.43$ Hz), 7.85 (1H, CH=CH-CO, d, $J = 15.3$ Hz), 7.53 (2H, CH, m, $J = 7.74$ Hz), 7.35 (1H, CH=CH-CO, d, $J = 15.3$ Hz), 4.68 (2H, Fc, s), 4.53 (2H, Fc, s), 4.23 (5H, Fc, s).

Results and Discussion

Synthesis and Characterization. The **2Anth-Fc** was synthesized by the base-catalyzed reaction of 2-acetylanthracene (**2ActAnth**) and ferrocenecarboxaldehyde (**FcAld**) through solid-phase aldol condensation (Scheme 2). The product was purified by column chromatography and characterized by MALDI-TOF mass, FT-IR, UV-vis and ^1H NMR spectroscopies. Single crystals were not obtained after many efforts using common solvent pairs, for example $\text{CH}_2\text{Cl}_2/n$ -hexane and $\text{CHCl}_3/\text{MeOH}$. The MALDI-TOF mass spectrum of **2Anth-Fc** ($m/z = 416.0864$) has two main peaks at $m/z = 416.0328$ (96.52%) for M^+ and 417.0365 (100.0%) for $(\text{M}^+ + 1)$, with almost equal intensities, indicating that mono-protonated form of **2Anth-Fc** is approximately as stable as the mother compound. The protonation site is possibly the carbonyl oxygen. The ^1H NMR spectrum of **2Anth-Fc** has two doublets at 7.85 and 7.35 ppm with $J = 15.3$ Hz for the ethylene protons, upfield of those of **9Anth-Fc** (7.03 and 6.89 ppm with $J = 16.0$ Hz). They are comparable to the corresponding two broad singlets of **Fc-9Anth**.^{3a} These data suggest that the ethylene moiety in the enone bridge is in the *trans*-conformation,¹⁰ and possibly in a *trans*-position to the carbonyl moiety around the C-C bond (*s-trans*), as shown in Scheme 2.

Electrochemical Properties. The cyclic voltammograms (CV) and differential pulse voltammograms (DPV) of **2Anth-Fc** scanned between 0.0 V and 1.6 V are shown in Fig. 1. The parameters are compared with those of its precursors and **9Anth-Fc** in Table 1. The CV's pattern is similar to those of **9Anth-Fc** and **Fc-9Anth**.^{3a} The reversible cycle at $E_{1/2} = 0.605$ V (Fig. 1(A) inset) is ascribed to the redox process of the ferrocenyl moiety in **2Anth-Fc** and is very close to that of **9Anth-Fc** ($E_{1/2} = 0.615$ V). It is more cathodic than those of **FcAld** ($E_{1/2} = 0.759$ V) and **Fc-9Anth** ($E_{1/2} = 0.740$ V). These observations arise from the ferrocenyl group's oxidation being aided by the vinyl moiety linked to it in the vinyl ferrocene system,^{3c} whereas oxidation is not aided by the carbonyl group. Moreover, the irreversible peak ($E_{\text{pa}}^2 = 1.487$ V) from the oxidation of the anthracenyl moiety is very close to that of **2ActAnth** ($E_{\text{pa}}^2 = 1.465$ V) in both form and value. It suggests that the electronic state of the 2-carbonyl anthracene moiety (Anth-2-C(O)-) was not significantly modified even though the methyl group was substituted with a vinylferrocene group. This result is reflected in the fluorescence properties of **2Anth-Fc**, as discussed below.

UV-vis Absorption and Fluorescence Properties. The UV-vis spectra of **2Anth-Fc** obtained in solvents of different polarities

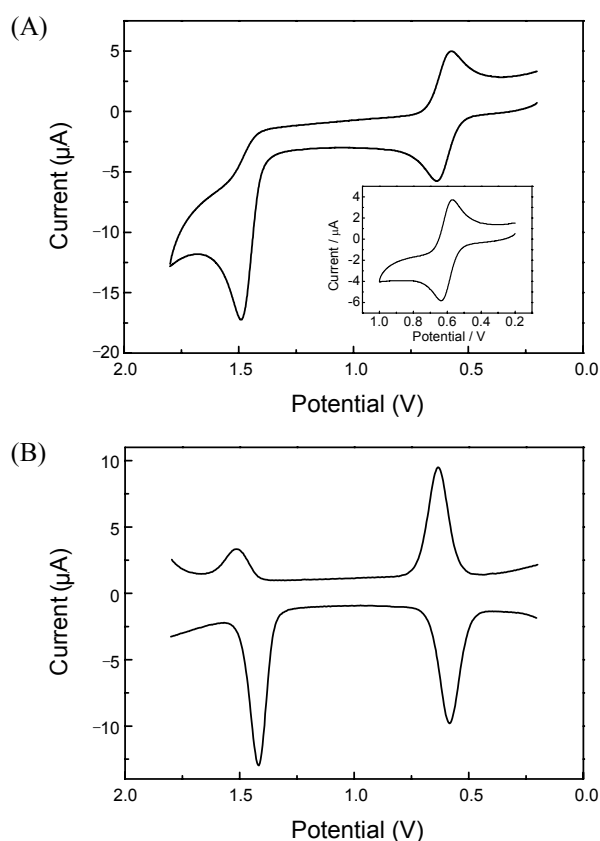


Figure 1. Cyclic voltammograms (A) and differential pulse voltammograms (B) of **2Anth-Fc**. The inset shows the reversible cycle of the ferrocenyl group in **2Anth-Fc**.

Table 1. Cyclic voltammetry parameters of **2Anth-Fc** and its reactants compared with **9Anth-Fc**^a

compound	E_{pa}^1/V	E_{pa}^2/V	E_{pc}^1/V	$E_{1/2}/\text{V}^b$
FcAld	0.790		0.727	0.759
2ActAnth		1.465		
2Anth-Fc	0.636	1.487	0.574	0.605
9Anth-Fc ^c	0.652	1.491	0.577	0.615

^aSupporting electrolyte: 0.1 M *n*-Bu₄NBF₄; Working electrode: Pt disk; Counter electrode: Pt wire; Ref. electrode: Ag/AgCl; 0.5 mM samples in 3.0 mL CH₃CN; 100 mV s⁻¹ scan rate; $E_{1/2} = 0.474$ V for Fc/Fc⁺. ^b $E_{1/2} = (E_{\text{pa}}^1 + E_{\text{pc}}^1)/2$. ^cValues reported in ref. 3(a) vs. Ag/Ag⁺ have been converted to the ones vs. Ag/AgCl by adding +0.338 V.

Table 2. UV-vis spectral data (nm) of **2Anth-Fc** dissolved in various solvents

Solvent	$\pi \rightarrow \pi^*$ (enone)	$n \rightarrow \pi^*$ (enone)	$\pi \rightarrow \pi^*$ (Fc)	d \rightarrow d (Fc)
Acetonitrile	244	322	390	510
Chloroform	248	326	400	518
Ethanol	244	326	402	520
Methanol	244	326	404	520

are compared in Table 2. The $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the enone bridge are identical, irrespective of solvent polarity, within an acceptable error range (226 ± 2 and 324 ± 2 nm, respectively).^{3,10} In contrast, the $\pi \rightarrow \pi^*$ (402 ± 2 nm) and d \rightarrow d (519 ± 1 nm) transitions of the ferrocenyl group^{3,7a} obtained in

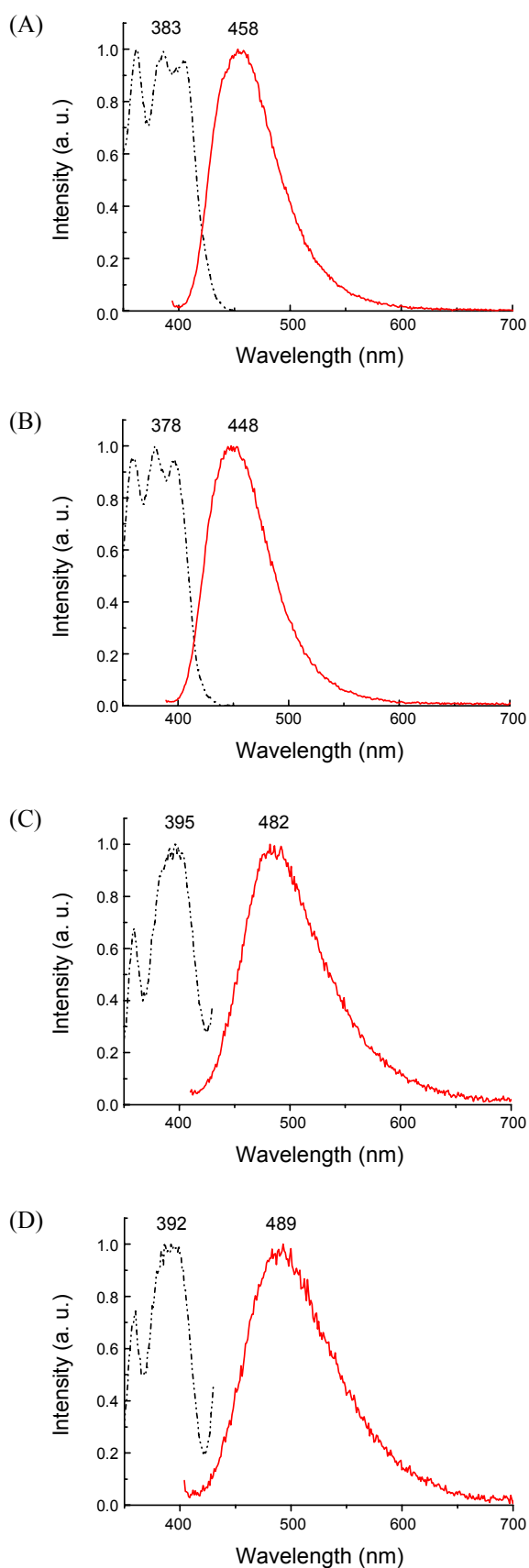


Figure 2. Optical absorption (broken line) and emission (solid line) spectra of **2Anth-Fc** measured in (A) CHCl_3 (3.1×10^{-5} M), (B) CH_3CN (3.1×10^{-5} M), (C) EtOH (1.2×10^{-4} M) and (D) MeOH (1.2×10^{-4} M).

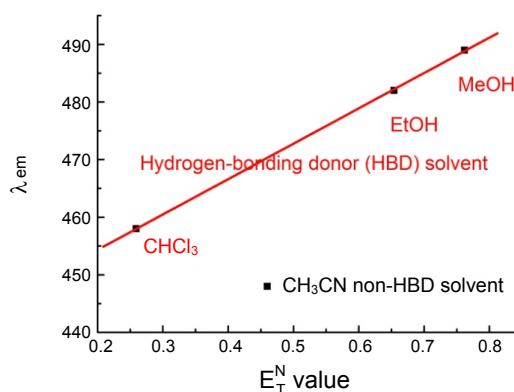


Figure 3. The dependence of λ_{em} on solvent polarity (E_T^N).

hydrogen-bonding donor (HBD) solvents¹¹ (CHCl_3 , EtOH and MeOH), red-shift to 390 nm and 510 nm, respectively, in the non-HBD solvent (CH_3CN).

Fluorescence spectra of **2Anth-Fc** measured at room temperature in the above solvents are shown in Fig. 2. The emission maxima (λ_{em}) observed at 458 nm (CHCl_3), 448 nm (CH_3CN), 482 nm (EtOH) and 489 nm (MeOH) are dependent on the solvent's polarity: emission colors range from blue in CH_3CN (448 nm) to greenish blue in MeOH (489 nm). These emission colors are identical, within an error range of ± 2 nm, to those of **2ActAnth**, according to measurements under the same conditions, indicating that the vinyl ferrocene group does not affect the fluorescence maxima of the anthracenyl moiety, while the solvent's polarity does. In order to investigate the dependency of the emission maxima (λ_{em}) on the solvent's polarity, emission maxima were plotted against normalized E_T^N values (a spectroscopic indicator of solvent polarity) of the solvents, CH_3Cl (0.259), CH_3CN (0.460), EtOH (0.654) and MeOH (0.762),¹¹ as shown in Fig. 3. Emission maxima are linearly correlated with the normalized E_T^N values of the three HBD solvents (CH_3Cl , EtOH and MeOH) whereas the non-HBD solvent (CH_3CN) deviates greatly from this relationship.

These results, integrated with the UV-vis and MALDI-TOF observations, indicate that the fluorescence properties of **2Anth-Fc** are greatly influenced by the solvent's hydrogen-bonding donor (HBD) ability, possibly through the interaction of the HBD solvent and the carbonyl moiety of **2Anth-Fc**.

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References

- (a) Wu, X.; Tiekink, E. R. T.; Kostetski, I.; Kocherginsky, N.; Tan, A. L. C.; Khoo, S. B.; Wilairat, P.; Go, M. L. *Eur. J. Pharm. Sci.* **2006**, *27*, 175. (b) Wu, X.; Wilairat, P.; Go, M. L. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2299.
- Zsoldos-Mady, V.; Csampai, A.; Szabo, R.; Meszaros-Alapi, E.; Pasztor, J.; Hudecz, F.; Sohar, P. *Chem. Med. Chem.* **2006**, *1*, 1119.
- (a) Jung, Y. J.; Son, K. I.; Oh, Y. E.; Noh, D. Y. *Polyhedron* **2008**, *27*, 861. (b) Son, K. I.; Kang, S. Y.; Noh, D. Y. *Bull. Korean Chem. Soc.* **2009**, *30*, 513. (c) Son, K. I.; Kang, S. Y.; Oh, Y. E.; Noh, D.

- Y. *J. Korean Chem. Soc.* **2009**, *53*, 79. (d) Son, K. I.; Noh, D. Y. *J. Korean Chem. Soc.* **2007**, *51*, 591.
4. (a) Belavaux-Nicot, B.; Maynadie, J.; Lavabre, D.; Lepetit, C.; Donnadiou, B. *Eur. J. Inorg. Chem.* **2005**, 2493. (b) Belavaux-Nicot, B.; Fery-Forgues, S. *Eur. J. Inorg. Chem.* **1999**, 1821.
5. Lee, S. K.; Noh, Y. S.; Son, K. I.; Noh, D. Y. *Inorg. Chem. Commun.* **2010**, *13*, 1343.
6. Son, K. I. *Ph.D thesis*, Seoul Women's University, Seoul, 2008.
7. (a) Fery-Forgues, S.; Delavaux-Nicot, B. *J. Photochem. Photobiol. A* **2000**, *132*, 137. (b) Rochford, J.; Rooney, A. D.; Pryce, M. T. *Inorg. Chem.* **2007**, *46*, 7247.
8. Meister, E. C.; Suter, G. W.; Wild, U. P. *J. Phys. Chem.* **1988**, *92*, 6537.
9. (a) Plummer, B. F.; Hamon, S.; Burke, J. A., III. *J. Phys. Chem.* **1987**, *91*, 2022. (b) Swayambunathan, V.; Lim, E. C. *J. Phys. Chem.* **1985**, *89*, 3960.
10. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 5th ed.; John Wiley: Singapore, 1991.
11. (a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley: Weinheim, Germany, 2003. (b) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.
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