

## Ferrocenyl Chalcones with 1- and 2-Naphthalenyl Group: Spectroscopic Characterizations and Electrochemical Properties

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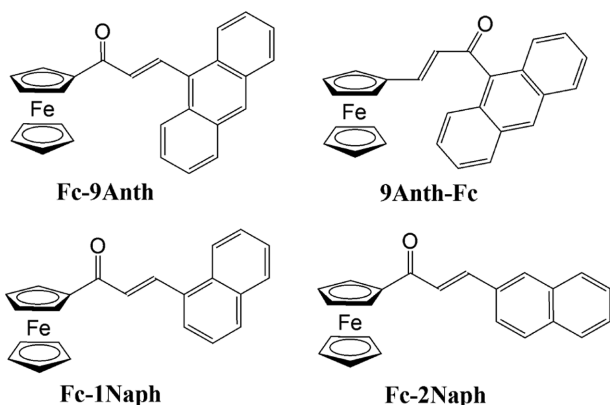
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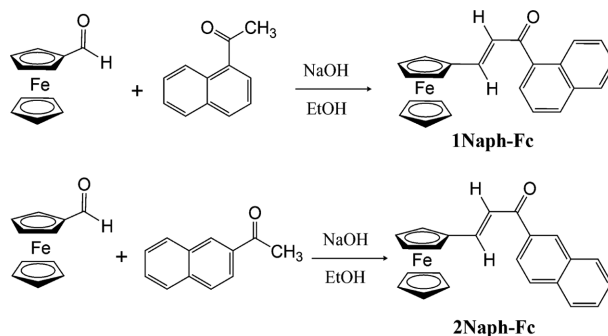
Chalcone is one class of the organic compounds with two aromatic groups linked by an enone moiety, showing diverse bioactivities.<sup>1-5</sup> In particular, the ferrocenyl chalcone, in which the ferrocenyl group is linked with an aromatic group by an enone moiety, exhibits wide spectrum of properties from antiplasmodial activity<sup>6,7</sup> to chemosensor for selective metal ions.<sup>8</sup> Recently, we developed a new class of ferrocenyl chalcones with fluorophore such as anthracene, naphthalene, pyrene, and carbazole,<sup>9-15</sup> as shown in *Scheme 1*, and investigated their structural, electrochemical, and fluorescent properties. In this study, we prepared and characterized **1Naph-Fc** (1Naph-C(O)CH=CH-Fc) and **2Naph-Fc** (2Naph-C(O)CH=CH-Fc) (*Scheme 2*) and investigated their electrochemical and fluorescent properties, compared to those of **Fc-Naph** (denoted for both **Fc-1Naph** and **Fc-2Naph**) and the reactants.

Two **Naph-Fc** (denoted for both **1Naph-Fc** and **2Naph-Fc**) compounds were prepared by the thermal reaction in organic solvent and spectroscopically characterized. The UV-Vis spectra of **Naph-Fc** compounds (*Fig. 1*) showed an absorption band for the enone linkage at 319 nm ( $\epsilon = 18.2 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and 323 nm ( $\epsilon = 3.80 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) for **1Naph-Fc** and

**2Naph-Fc**, respectively. The absorption band because of ferrocenyl group was observed at 508 nm ( $\epsilon = 2.60 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) for **1Naph-Fc**, and was more intense than that of **2Naph-Fc** at 517 nm ( $\epsilon = 0.68 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The EIMS spectrum of **2Naph-Fc** (*Fig. 2*) showed the most intense peak  $[M^+]$  at  $m/z = 366$ . The second intense peak was found at  $m/z = 301$ , corresponding to the loss of cyclopentadienyl ring, that is  $[M^+ - C_5H_5]$ . The similar pattern of spectrum was obtained for **1Naph-Fc**. The fragmentation mode was definitely different from that of **Fc-9Anth** and **9Anth-Fc**, where the C-C single bond intervening Fc and anthracenyl moiety was broken.<sup>11</sup> The conformation around the C-C bond can be assigned based on the <sup>1</sup>H NMR data: The ethylenic protons of enone moiety exhibit two doublets at 7.48 and 6.89 ppm ( $J = 15.6 \text{ Hz}$ ) for **1Naph-Fc** and at 7.83 and 7.36 ppm ( $J = 15.3 \text{ Hz}$ ) for **2Naph-Fc**, indicating that the ethylene moiety is in the *trans*-conformation<sup>16</sup> as shown in *Scheme 2*. Moreover, the two doublets in each compound are clearly split with no broadening, indicating that the protons are not interacting with the lone-pair electrons of carbonyl oxygen atom.<sup>11</sup> The possible interpretation is that the C=O and C=C bonds are in the *s-trans* conformation around C-C single bond, and the naphthalenic moiety is not coplanar with the enone moiety.



*Scheme 1.* Schematic structures of some ferrocenyl chalcones.



*Scheme 2.* Synthesis of **1Naph-Fc** and **2Naph-Fc**.

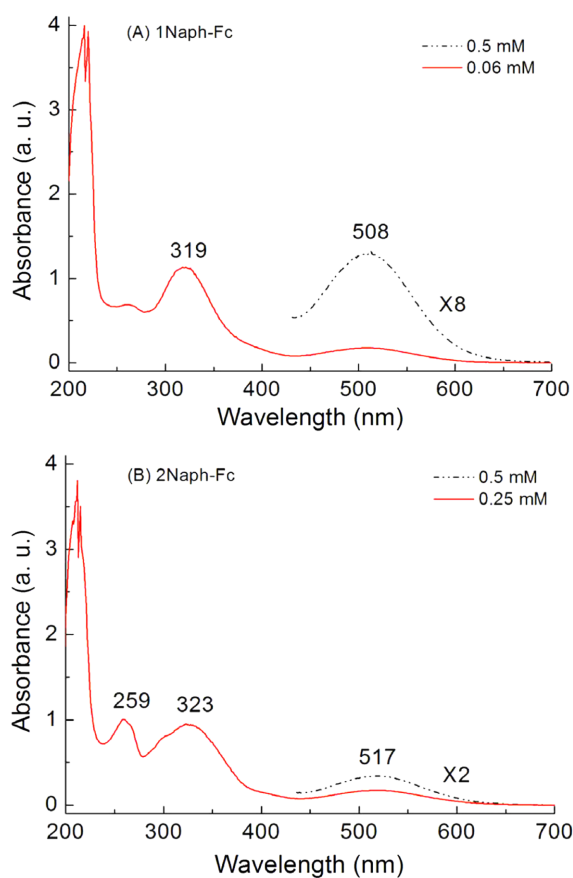


Figure 1. UV-Vis spectra of (A) **1Naph-Fc** and (B) **2Naph-Fc**.

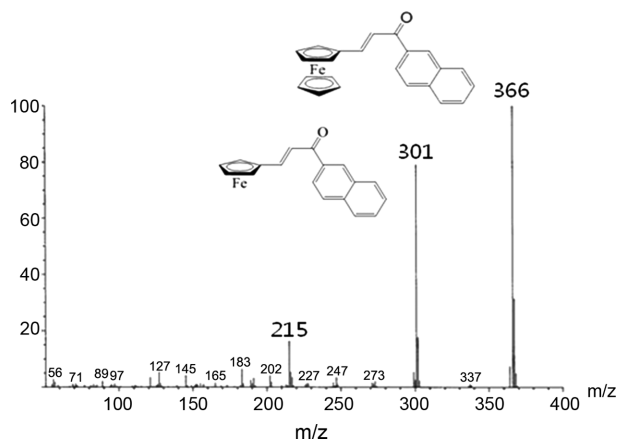


Figure 2. EI-MS spectrum of **2Naph-Fc**. Two intense peaks at  $m/z = 366$  and  $301$  are corresponding to  $M^+$  and  $[M-C_5H_5]^+$ , respectively.

The fluorescence properties of the two **Naph-Fc** compounds prepared in this study were investigated in several solvents with different dielectric constants, such as methanol, ethanol, and chloroform. The **Naph-Fc** compounds were non-fluorescent, irrespective of the solvent polarity,

even in the presence of the naphthalenyl fluorophore. In the previous fluorescence studies of the other ferrocenyl chalcones, **Fc-1Naph**<sup>15</sup> and **2Anth-Fc**<sup>10</sup> were fluorescent, whereas **Fc-2Naph**<sup>9</sup> and **9Anth-Fc**<sup>11</sup> were not, indicating that even though the ferrocenyl derivatives are effective quenchers of excited states,<sup>17</sup> a minor difference in molecular structure significantly affected their fluorescence properties.

The redox behaviors of **Naph-Fc** were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in  $CH_2Cl_2$  solvent in the scanning range between 0.0 and +2.0 V. Their cyclic voltammograms (Figs. 3 and 4) show one reversible cycle at  $E_{1/2} = 0.649$  and 0.650 V (Table 1), respectively, owing to the redox processes of the ferrocenyl group. The corresponding cycle in the CV of **Fc-1Naph** and **Fc-2Naph** was observed in more anodic region at  $E_{1/2} = 0.727$  and 0.719 V, respectively, even more anodic compared to the reactants such as acetylferrocene (ActFc;  $E_{1/2} = 0.805$  V) and ferrocenyl aldehyde (FcAlc;

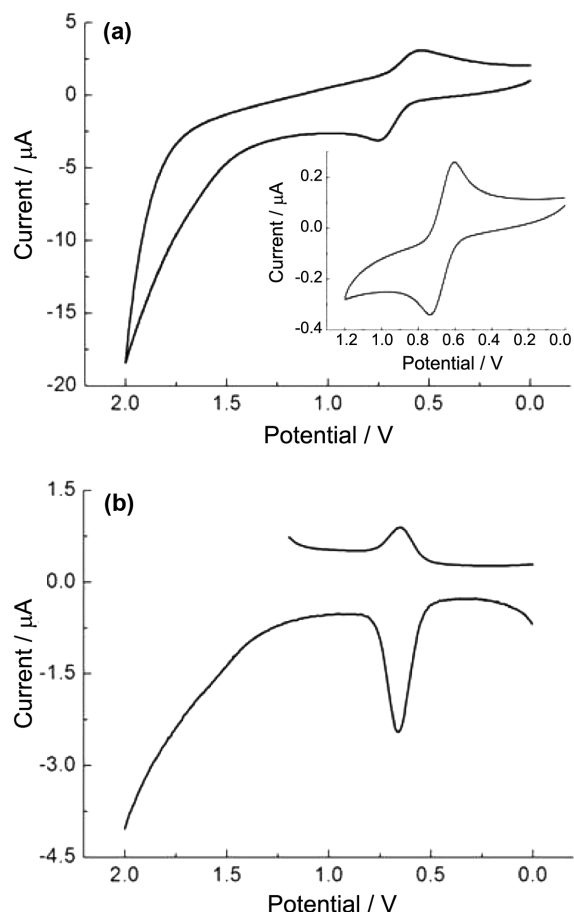
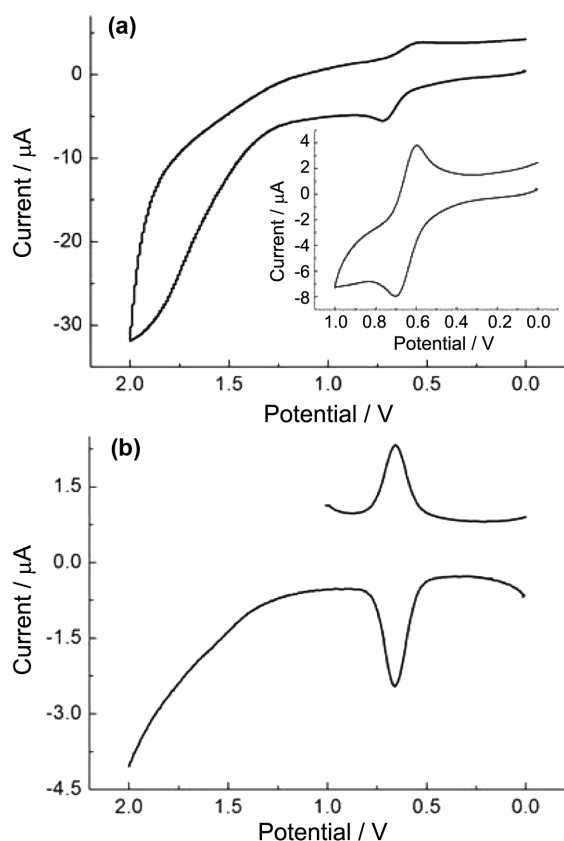


Figure 3. CV (a) and DPV (b) of **1Naph-Fc**. The inset shows a reversible redox cycle of the ferrocenyl group scanned between 0.0 and 1.2 V.



**Figure 4.** CV (a) and DPV (b) of **2Naph-Fc**. The inset shows a reversible redox cycle of the ferrocenyl group scanned between 0.0 and 1.2 V.

**Table 1.** CV parameters (in Volt) of **Naph-Fc**, **Fc-Naph**, and the reactants

Compound	$E_{pa}^1$	$E_{pa}^2$	$E_{pc}^1$	$E_{1/2}^{(2)}$	Ref.
Fc	0.387	–	0.722	0.554	This work
ActFc	0.841	–	0.769	0.805	15
FcAld	0.765	–	0.853	0.809	This work
Fc-1Naph	0.761	1.817	0.692	0.727	15
Fc-2Naph	0.755	1.878	0.682	0.719	9
1Naph-Fc	0.550	–	0.748	0.649	This work
2Naph-Fc	0.566	–	0.733	0.650	This work

$E_{1/2} = 0.809$  V) as shown in Table 1. These data indicated that the carbonyl moiety directly linked to ferrocenyl group pushes the half-wave potentials ( $E_{1/2}$ ) to the higher potential region. In other words, the vinyl moiety linked to the ferrocenyl group leads the electron delocalization over the vinylferrocene group in **Naph-Fc**, thereby decreasing the redox potential compared to the carbonyl-directed ferrocene group in **Fc-Naph**. It is also rationalized when the potentials were compared to that of molecular vinylferrocene ( $E_{1/2} = 0.589$  V vs. Ag/AgCl)<sup>18</sup> against reference

Fc/Fc<sup>+</sup> ( $E_{1/2} = 0.554$  V). The negatively increasing current in high potential region up to 2.0 V in Figs. 3 and 4 indicated the oxidation of naphthalenyl group as discussed in the electrochemical properties of **Fc-Naph**,<sup>9,15</sup> **Fc-Anth**,<sup>11</sup> and **Anth-Fc**.<sup>10,11</sup>

In conclusion, the central ethylene moieties of **Naph-Fc** preferred to be in *trans*-conformation based on the <sup>1</sup>H NMR data. The C=O and C=C bonds were in the *s-trans* conformation around the C–C single bond. The **Naph-Fc** showed one reversible cycle centered at  $E_{1/2} = 0.650$  V, attributed to the redox cycle of ferrocenyl group, more cathodic than those of **Fe-1Naph** (0.727 V), **Fe-2Naph** (0.719 V), ActFc (0.805 V) and FcAld (0.809 V). The fluorescence of naphthalenic group in **Naph-Fc** were quenched in several organic solvents with variable polarity possibly because of a minor difference in molecular structure as well as the presence of well-known ferrocenyl quencher.

## EXPERIMENTAL

Electron ionization-mass spectrometry (EI-MS) measurement was performed at the National Center for Inter-University Research Facilities (NCIRF). Infrared spectra were recorded by the KBr pellet method using a Perkin Elmer Spectrum 100 spectrometer between 4,000–400 cm<sup>-1</sup>. <sup>1</sup>H NMR measurements were performed at room temperature using an Avance 300 (Bruker) spectrometer using CDCl<sub>3</sub> as the solvent. UV-Vis spectra were measured using an HP 8452A diode array spectrophotometer. Fluorescence spectra of **1Naph-Fc** and **2Naph-Fc** were recorded at room temperature in several solvents such as CHCl<sub>3</sub>, CH<sub>3</sub>CN, EtOH and MeOH using a Cary Eclipse fluorescence spectrophotometer (Varian). Electrochemical properties of Naph-Fc compounds were investigated by cyclic voltammetry at room temperature using a CHI 620A electrochemical analyzer (CHI Instrument Inc.) under the following conditions: 0.5 mM sample and 0.1 M n-Bu<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> electrolyte dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>, using round-disk ( $r = 0.2$  cm) Pt working-electrode, Ag/AgCl reference electrode, and Pt-wire counter electrode ( $\varphi = 0.5$  mm) at a scan rate of 100 mV s<sup>-1</sup>. All the redox potentials were measured against reference Fc/Fc<sup>+</sup> redox couple ( $E_{1/2} = 0.554$  V).

### Preparation of 1Naph-Fc

An ethanol solution (40 mL) of ferrocenecarboxaldehyde (215 mg, 1 mmol), 1-acetonaph-thone (0.152 mL, 1 mmol), and NaOH (200 mg, 5 mmol) was stirred overnight at room temperature (Scheme 2). The red-colored reaction mixture was then dried under reduced pressure.

The product was extracted with  $\text{CH}_2\text{Cl}_2$  and dried with anhydrous  $\text{MgSO}_4$ . After filtration, the solution was evaporated. The solid product was then purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ). EI-MS ( $m/z$ , %) 366 ( $\text{M}^+$ , 100), 301 ( $\text{M}^+ - \text{C}_p$ , 90); FTIR (KBr,  $\text{cm}^{-1}$ ): 3093, 2926 (Ar C–H), 1655, 1628 (C=C), 1580 (C=O), 1508, 1460 (Ar C=C), 1284, 1247, 1133, 1104, 1044 (Ar C–H ip def), 806, 780 (Ar C–H oop def), 484, 497 (Fe-ring vib);  $^1\text{H}$  NMR (300 MHz, ppm,  $\text{CDCl}_3$ )  $\delta$  8.27 (1H, CH, d,  $J = 9.60$  Hz), 7.97 (2H, CH, m), 7.70 (1H, CH, d,  $J = 6.90$  Hz), 7.58 (3H, CH, m), 7.48 (1H, CO–CH=CH, d,  $J = 15.6$  Hz), 6.89 (1H, CO–CH=CH, d,  $J = 15.6$  Hz), 4.55 (2H,  $\text{C}_p$ , t,  $J = 1.80$  Hz), 4.50 (2H,  $\text{C}_p$ , t,  $J = 1.80$  Hz), 4.19 (5H,  $\text{C}_p$ , s).

### Preparation of 2Naph-Fc

An ethanol solution (40 mL) of ferrocenecarboxaldehyde (215 mg, 1 mmol), 2-acetonaph-thone (170 mg, 1 mmol), and NaOH (200 mg, 5 mmol) was stirred overnight at room temperature (Scheme 2). The red-colored reaction mixture was then dried under reduced pressure. The product was extracted with  $\text{CH}_2\text{Cl}_2$  and dried with  $\text{MgSO}_4$ . After filtration, the solution was evaporated. The solid product was then purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CHCl}_3:\text{CH}_2\text{Cl}_2 = 1:5$ ). EI-MS ( $m/z$ , %) 366 ( $\text{M}^+$ , 100), 301 ( $\text{M}^+ - \text{C}_p$ , 80); FTIR (KBr,  $\text{cm}^{-1}$ ) 3089, 3058, 2926 (Ar C–H), 1653, 1627 (C=C), 1586 (C=O), 1470 (Ar C=C), 1250, 1216, 1187, 1125, 1026 (Ar C–H ip def), 822, 757 (Ar C–H oop def), 497, 480 (Fe-ring vib);  $^1\text{H}$  NMR (300 MHz, ppm,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.55 (1H, CH, s), 8.08 (2H, CH, m), 7.97 (2H, CH, m), 7.83 (1H, CO–CH=CH, d,  $J = 15.3$  Hz), 7.64 (2H, CH, m), 7.36 (1H, CO–CH=CH, d,  $J = 15.3$  Hz), 4.71 (2H,  $\text{C}_p$ , t,  $J = 1.80$  Hz), 4.56 (2H,  $\text{C}_p$ , t,  $J = 1.80$  Hz), 4.24 (5H,  $\text{C}_p$ , s).

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