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
Received November 1, 2010, Accepted November 7, 2010

Key Words: Ferrocenyl chalcone, Anthracene, Electrochemistry, Fluorescence

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,9 and N-ethyl carbazole,8 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,3a was prepared. Unlike 9Anth-Fc,3a 2Anth-Fc is fluorescent 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 (Barrloworld Scientific Ltd.). Measurement of Matrix-Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) masses was performed with a Voyager-DE STR Bio-spectrometry 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 Fe/Fc⁺ redox couple (E½ = 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 2. Synthesis of 2Anth-Fc

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. The resulting compound was obtained as yellow crystals in 60% yield. 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 (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 = 7.74 Hz), 7.35 (1H, C=C, 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).

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 2ActAnth and 9Anth-Fc. The reversible cycle at E1/2 = 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 (E1/2 = 0.615 V). It is more cathodic than those of FcAld (E1/2 = 0.759 V) and Fc-9Anth (E1/2 = 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, whereas oxidation is not aided by the carbonyl group. Moreover, the irreversible peak (Epa = 1.487 V) from the oxidation of the anthracenyl moiety is very close to that of 2ActAnth (Epa = 1.465 V) in both form and value. It suggests that the electronic state of the 2-carboxyl 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 are compared in Table 2. The π→π⁺ transitions of the enone bridge are identical, irrespective of solvent polarity, within an acceptable error range (226 ± 2 and 324 ± 2 nm, respectively). In contrast, the π→π⁺(Fc) (402 ± 2 nm) and d→d (519 ± 1 nm) transitions of the ferrocenyl group 5,76 obtained in...
Figure 2. Optical absorption (broken line) and emission (solid line) spectra of 2Anth-Fc measured in (A) CHCl₃ (3.1 × 10⁻⁵ M), (B) CH₃CN (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 (Eₕ).

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 (CHCl₃), 448 nm (CH₃CN), 482 nm (EtOH) and 489 nm (MeOH) are dependent on the solvent’s polarity: emission colors range from blue in CH₃CN (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 Eₕ values (a spectroscopic indicator of solvent polarity) of the solvents, CHCl₃ (0.259), CH₃CN (0.460), EtOH (0.654) and MeOH (0.762), as shown in Fig. 3. Emission maxima are linearly correlated with the normalized Eₕ values of the three HBD solvents (CH₃Cl, EtOH and MeOH) whereas the non-HBD solvent (CH₃CN) 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.

Acknowledgments. This work was supported by a Special Research Grant from Seoul Women’s University (2010).

References