Study on the Fluorescence of 1,8-Anthracenedicarboxylic Acid and 1,8-Anthracenediformamide

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Fluorimetric methods have been proven useful in the detection of metal ion in solution.[1] Sensitivity and selectivity of fluorescence make the assay of trace metal ions possible. Anthracene derivatives containing either crown or polyamine ligands have been extensively studied as photoinduced electron transfer (PET) sensors for metal ions[1] and also for neutral organic compounds.[2] Unlike most PET sensors in which ligands are linked *via* the methylene spacer, 1,8-anthracenedicarboxylic acid and 1,8-anthracenediformamide contain two carboxylic acid or amide groups which are directly attached at the 1,8 position of anthracene. Our study of the fluorescence of 1,8-anthracenedicarboxylic acid and 1,8-anthracenediformamide includes pH-fluorescence titration and fluorescence titration with metal ions and organic guests.

Hydrolysis of 1,8-anthracenedicarboxylic acid dimethyl ester **3** with potassium hydroxide in water at 90 °C produced 1,8-anthracenedicarboxylic acid **1** in a 92% yield (Scheme 1). After refluxing in thionyl chloride followed by treatment with ammonium hydroxide, 1,8-anthracenediformamide **2** was obtained in a 60% yield.[3]

It is reported[4] that 9-anthroic acid displays a typical emission spectrum with a vibrational structure. This result is attributed to steric hindrance between the 9-carboxylic acid group and *peri*-hydrogen atoms in the 1- and 8-positions of the anthracene ring, which minimizes the resonance interaction between the carboxyl group and the ring.

In our study, 1,8-anthracenedicarboxylic acid **1** shows structureless absorption spectra at acidic pH (pH 2-3). At pH 4, the absorption spectrum starts to show the characteristic vibronic pattern of anthracene, and at pH 5, this change becomes quite clear. A fluorescence emission of **1** in the aqueous solution is even more diffuse than its absorption spectrum (Figure 1). As pH of the solution increased, the fluorescence intensities of **1** also increased with a red-shift (16 nm) due to the first deprotonation. However, the second deprotonation caused a blue-shift (38 nm) in the fluorescence emission of **1**.

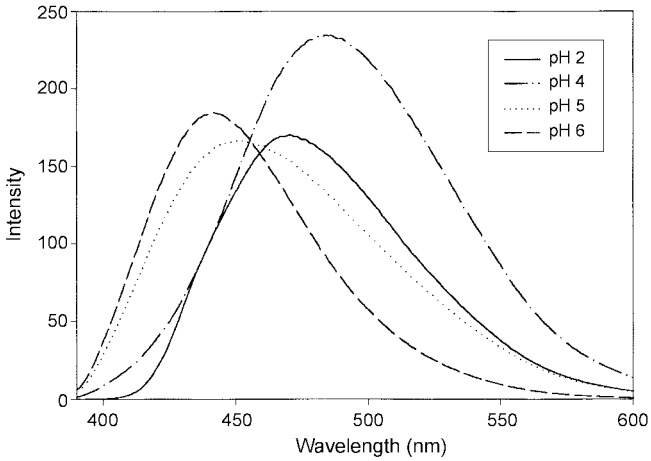
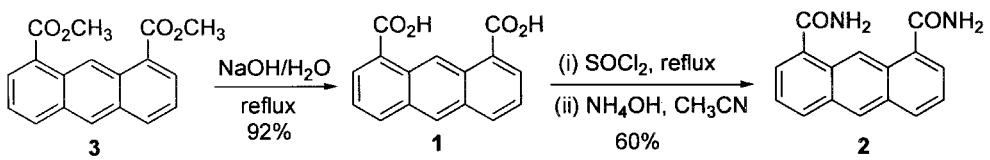


Figure 1. Fluorescent emission spectra of **1** (6 μM) in solutions of different pHs.

1-Anthroic acid is known[5] to display structureless absorption and fluorescence emission. When 1-anthroic acid is compared to 9-anthroic acid, there is a lessening of the steric hindrance. This allows a resonance overlap to occur between the carboxyl group and anthracene, which affects the fluorescence of the anthracene moiety. Resonance forms such as I, are less important for the ground state of 1-anthroate anion than forms like II for 1-anthroic acid. The carboxylate anion, already possessing a negative charge, will not readily accept the second negative charge necessary for resonance interaction (Figure 2). This explanation can be applied to our observation in which the absorption spectrum of **1** at pH 5 retains the characteristic vibronic pattern of anthracene. Furthermore, a blue shift (15 nm) of **1** between pH 5 and pH 2 was consistent with that of 1-anthroic acid[5] (λ_{max} = 373 nm for 1-anthroic acid in ethanol, and λ_{max} = 364 nm for sodium 1-anthroate in ethanol).

In the excited state of 1-anthroate anion, the carboxylate anion interaction with the aromatic nucleus is known to be sufficient to make the fluorescence spectrum more diffuse



Scheme 1. Syntheses of compound 1 and 2.

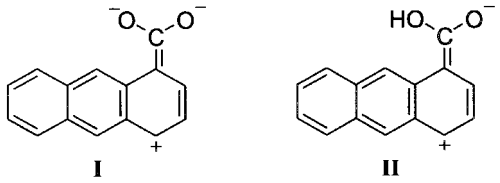


Figure 2. Proposed resonance forms of 1-anthroic acid.

than the absorption spectrum. However, the extent of the interaction is not sufficient to produce the large Stokes shifts observed in 1-anthroic acid. The blue shift (38 nm) observed in **1** at pH 5 or 6 may be due to this same reason. The reason for the relatively small red shift of **1** upon the first deprotonation is not clear at this moment. Unlike 1-anthroic acid, the carboxylate anion of **1** in the excited state can readily share a hydrogen in the next carboxylic acid group. This characteristic should make a difference in the emission change between the deprotonation of 1-anthroic acid and the first deprotonation of **1**.

9-Anthramide is also known to have electronic absorption and fluorescence spectra in water which are similar to those of anthracene.[7] On the other hand, 1,8-anthracenediformamide **2** shows a structureless fluorescence emission, and the fluorescence intensities of **2** continually increased as the pH of the solution was increased (up to pH 4). These observations closely compare to the reported results.[3]

Ca(II), Cd(II), Co(II), Cs(I), Cu(II), K(I), Li(I), Hg(II), Mg(II), Mn(II), Na(I), Ni(II), Rb(I), Sr(II), and Zn(II) ions were used to evaluate metal ion binding. All titration studies were conducted at pH 7 (0.1 M HEPES) using a 6 μM concentration of compound **1** and **2**. Using 200 equivalents of these metal ions, compound **1** displayed a large fluorescence quenching effect only with Cu(II), even though there was a relatively small fluorescence quenching effect with Hg(II) ion (Figure 3). Cu(II) and Hg(II) ions are known as effective quenching metals (*e.g.* open-shell, paramagnetic, large or easily reducible cation[8]). If a quenching metal ion binds tightly to the ligand, then intracomplex quenching takes place.

From the titration of **1** with Cu(II), dissociation constant (K_d) was calculated as 17 μM with overall emission change of 40-fold. On the other hand, among the metal ions examined, compound **2** displays a fluorescence quenching effect only with Hg(II). However, the binding was not strong and the dissociation constant was roughly in the millimolar range.

Fluorescence titration in ethanol is rather complicated. Diacid **1** also displays a structureless fluorescence emission in ethanol. Upon the addition of the metal ions (200 equivalents), there were huge changes in the emission spectra of **1**. The selected spectra are shown in Figure 4. Upon the addition of Co(II), Cu(II), Ni(II), and Pb(II) ions, fluorescence quenching effects were observed with a blue-shift (~30 nm). Furthermore, diacid **1** displays a typical anthracene-emission spectrum with a vibrational structure. The Binding of **1** with these metal ions probably perturbs the resonance between the carbonyl group and anthracene moiety, which results in a blue-shift due to the energy increase between S_0 and S_1 states and a typical emission spectra with a vibrational structure. Compound **1** shows fluorescence enhancement effects with Ca(II), Cd(II) and Mg(II) in ethanol with a small red-shift. The addition of 1,3-diaminopropane (10 eq.) to diacid **1** caused a blue-shift (60 nm). This is similar to the pH-titration shown in Figure 1. Obviously, amino group acts as a base to cause the deprotonation of the carboxylic acid.

Attempts to observe any change in the fluorescence intensity of **2** upon the addition of linear diamides, such as malonamide, succinamide and adipamide, failed in water, ethanol, or acetonitrile. Even though **2** can potentially form four hydrogen-bonds with linear diamides based on CPK model study, we could not observe any significant change in fluorescence intensity upon the addition of aliphatic amides (up to 300 eq.).

In conclusion, 1,8-anthracenedicarboxylic acid showed the characteristic emission changes upon the pH change. In

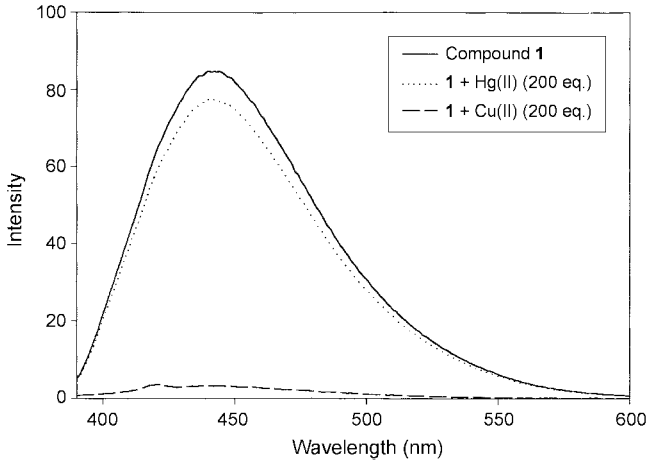


Figure 3. Changes in fluorescence emission spectra of compound 1 (6 μM) upon the addition of 200 eq. of Cu(II) and Hg(II) at pH 7 (0.1 M HEPES).

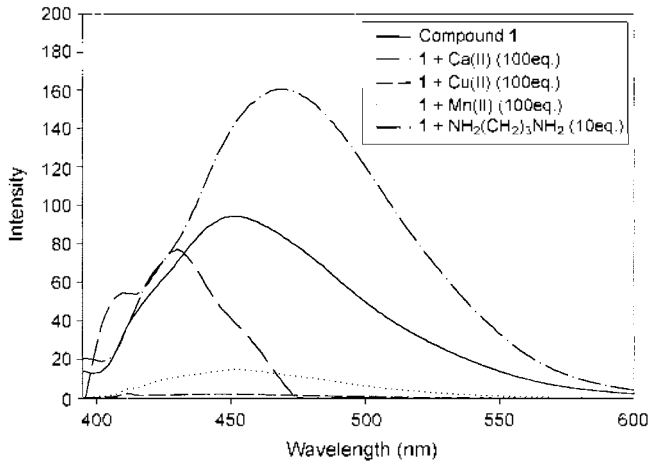


Figure 4. Fluorescence emission spectra of compound **1** (6 μM) upon the addition of metal ions and 1,3-diaminopropane in ethanol.

addition. compound **1** displayed a selective fluorescence quenching effect only with Cu(II) in 100% aqueous solution.

Experimental Section

^{1}H NMR spectra were recorded with a Varian Inova Nuity spectrometer at 500 MHz. Chemical shifts were given in ppm using TMS as internal standard. Melting points were determined in open capillaries and are uncorrected. Flash chromatography was carried out with Merck silica gel 60 (230-400 mesh). Thin layer chromatography was carried out with Merck 60 F_{254} plates with 0.25 mm thickness. $CHCl_3$, CH_2Cl_2, and MeOH were distilled from CaH_2, and THF was distilled from sodium-benzophenone ketyl. 1,8-anthracenedicarboxylic acid dimethyl ester **3** was purchased from TCI. Tokyo. Japan.

Preparation of 1,8-Anthracenedicarboxylic acid 1. A suspension of 1.8-dimethoxycarbonylanthracene (0.8 g. 2.72 mmol) in aqueous sodium hydroxide solution (150 mL) was refluxed for 24 hours. After filtering off the undissolved material. the filtrate was acidified with concentrated hydrochloric acid. The yellow precipitate was washed with water and taken up in hot isopropyl alcohol (50 mL). After cooling. a bright yellow power was collected and air dried (0.67 g, 92%): mp 340-343 °C dec. (lit.[9] 341-345 °C dec.): ^{1}H NMR (DMSO-d_6) δ 13.28-13.02 (br s, 2H). 10.48 (s. 1H), 8.74 (s. 1H), 8.30 (d, 2H, J = 8.3 Hz). 7.61 (dd, 2H. J = 7.7. 7.7 Hz).

Preparation of 1,8-Anthracenediformamide 2. A suspension of 1,8-anthracenedicarboxylic acid (0.6 g, 2.3 mmol) in thionyl chloride (10 mL) was refluxed overnight. The excess thionyl chloride was evaporated under reduced pressure to give 1,8-anthracenediformyl chloride as a brown solid. Ammonium hydroxide (15 mL) in acetonitrile (150 mL) was stirred on an ice-bath. 1,8-Anthracenediformyl chloride was added into the ice-cold solution. and stirred at the same temperature for 30 minutes. The pale yellow solid was collected by filtration and washed with water (3 × 50 mL) (0.36 g, 60%): mp 347-350 °C dec. (lit.[3] 349-352 °C dec.); ^{1}H NMR (DMSO-d_6) δ 9.94 (s. 1H), 8.68 (s, 1H). 8.05-8.23 (m. 4H), 7.5-7.7 (m. 6H).

Preparation of Fluorometric Metal Ion Titration Solutions. Stock solutions (1 mM) of the metal perchlorate salts (for Cd(II), chloride salt was used) were prepared using doubly distilled demineralized water or ethanol. Stock solutions of **1** and **2** were prepared either in ethanol (0.06 mM) or doubly distilled demineralized water (0.6 mM). The solutions were used on the day of preparation. Test solutions were prepared by placing 40 or 400 μL of the probe stock solution into a test tube, adding an appropriate aliquot of each metal stock, and diluting the solution to 4 mL with pH 7 0.1 M HEPES buffer or ethanol.

For all measurements, excitation was at 367 nm; Both excitation and emission slit widths were 5 nm.

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