

A New Fluorescent Sensor for Transition Metal Ions in Aqueous Solution

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Abstract: A new fluorescent sensor consisted of fluorenyl and dioxotetraaza unit, namely, 2,10-dimethyl-6-(9-fluorenyl)-1,4,8,11-tetraazaundecane-5,7-dione (L), was synthesized. It is a fluorescent sensor for transition metal ions in aqueous solution.

Keywords: Fluorenyl, dioxotetramine, fluorescence, sensor, transition metal.

Molecular systems which combine binding ability and photochemical and/or photophysical properties are of great interest for designing molecular devices displaying photoactivity features¹. During the last decade, a number of fluorescent sensors for cation detection have been developed²⁻¹². Most of them operates by a photoinduced electron transfer (PET) mechanism. In a classic example¹⁰, the uncomplexed sensor is not fluorescent as the photoexcited fluorophore is deactivated by the transfer of an electron from the highly reducing proximate tertiary amine group. Following metal incorporation, the metal-ligand interaction decreases the amine oxidation potential and prevents the electron transfer. As a consequence, fluorescence of fluorophore is largely restored. Most of the mentioned system were performed either in nonaqueous solution or in mixed solvent.

In view of the convenience in aqueous solution and high quantum yield and long fluorescent lifetime of fluorenyl, we linked it as fluorophore to a dioxotetramine receptor and obtained a new fluorescent sensor in aqueous solution, namely, 2,10-dimethyl-6-(9-fluorenyl)-1,4,8,11-tetraazaundecane-5,7-dione (L). The results of fluorimetric titration indicate that fluorescence of fluorenyl was quenched by transfer of electron from metal center to photoexcited state of fluorenyl during coordination of Cu (II) or Ni (II).

Experimental

Reagents and organic solvents are of reagent grade and purified prior to use. IR spectra were measured as KBr disc using a Nicolet 5DX-FT IR spectrophotometer. UV spectra were measured on a UV-3100 spectrophotometer. Emission spectra were recorded with AB-2 luminescence spectrometer (excitation wavelength 280 nm, maximum emission

intensity at 312 nm) and were all uncorrected instrument response. Cyclic voltammetry and pH titration were performed by literature method¹³.

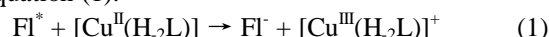
The mixture of diethyl 2-(9-fluorenyl) malonate (6.48 g, 0.02 mol) and freshly distilled propylene diamine (30 mL) was stirred at room temperature for two weeks. Excess propylene diamine was distilled off under reduced pressure. After cooling, the yellow residue was washed with alcohol and diethyl ether. Compound L was obtained. Yield: 76% (Found: C, 69.23; H, 7.28; N, 14.54. C₂₂H₂₈N₄O₂ requires C, 69.45; H, 7.42; N, 14.72%). IR/cm⁻¹ 3250 (m, NH) 3030 and 2930 (w, CH), 1660 (s, CO), 1540 (s, NH), 760 and 742 (m, C-C). UV/nm (MeOH) 266 (ϵ /dm³·mol⁻¹·cm⁻¹ 18700), 291 (4300) and 302 (4600).

Results and Discussion

The features of cyclic voltammetrical curves of the 4×10^{-4} mol·dm⁻³ complex [M(H₂L)] (M = Cu, Ni) solution are indicative of one-electron quasi-reversible electrode process. Their values of $E_{1/2}$ for M^{III}/M^{II} (M=Cu, Ni) are 0.699, 0.763 V, respectively. The result of the titration of L + 4HNO₃ shows that the pKa₁ and pKa₂ of the ligand are 8.3 and 9.1, respectively. This indicates that following three species are present in solution: H₂L²⁺ in which the two terminal amino groups are protonated, the predominant species at pH < 8, HL⁺ at pH values from 8 to 10, and L at pH >10. The titrations of L + 4HNO₃ plus M(NO₃)₂ (M=Cu, Ni) show that the stability sequences for both predominant species [M(H₂L)] and [ML]²⁺ are Cu(II) > Ni(II). The values of the stability constants are -4.12 and 7.80, -9.73 and 4.80, for Cu(II) and Ni(II) complexes [M(H₂L)] and [ML]²⁺, respectively.

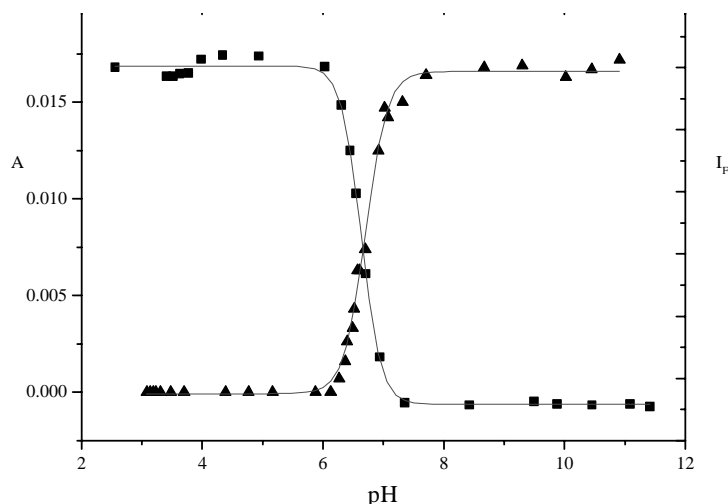
The compound L in aqueous solution ($c = 5.4 \times 10^{-5}$ mol·dm⁻³, pH = 9) displays the typical emission spectrum of fluorene; its maximum emission appears at 312nm, which corresponded to the excited potential E(FI*) 3.98 V. The fluorescence intensity of the ligand keeps constant over the pH range 3-6.5, and increases from pH = 6.5 to pH= 10.5 up to two times at pH = 10.5. However, if one equivalent of Cu(II) is added to an acidic solution of L, the fluorescence intensity steadily decreases on titration with NaOH. Complete fluorescence quenching is observed when the excess strong acid has been neutralized and two further equivalents of OH⁻ have been added. Inversely, when increment of acidity and resultant decrement of coordination of Cu (II) ions reach certain levels, revival of fluorescence of fluorenyl happens. The plot of fluorescence intensity (I_F) vs. pH (■ in **Figure 1**) display a typical on-off curve. An analogous titration experiment was performed in a spectrophotometric cuvette. On addition of base, the solution becomes pink-violet and an absorption band at 504 nm develops. The absorbance A reaches its maximum value after neutralization of the excess strong acid and addition of two further equivalents of base. The plot of A vs. pH (▲ in **Figure 1**) shows an on-off curve, which is symmetrical to the I_F /pH profile and centered at the same pH (≈ 6.4). The pink-violet color arises from a d-d band of the square-planar complex of copper (II) with the ligand. Deprotonation of the two amide groups yields the tetradentate ligand L²⁻, which chelates the metal ion. All these experimental facts demonstrate that the quenching of fluorescence of the fluorenyl is associated with

coordination of copper (II) ion by the dioxotetraaza unit of the ligand. The radiationless deactivation of excited state (Fl^*) of the fluorophore can take place by means of a Cu^{II} -to-fluorene electron transfer process ($Cu^{II} \rightarrow Fl^*$) which can be described by equation (1).



The variation of potential (ΔE_{ET}) of the process ($Cu^{II} \rightarrow Fl^*$) can be calculated by equation (2). Redox potential $E(Fl/Fl^*)$ of fluorenyl linked to dioxotetraaza moiety used in equation (2) is -2.65 V, which is the value of $E(Fl/Fl^*)$ of fluorene, because the substituents linked to fluorenyl hardly alter the redox potential of fluorenyl¹⁴, $E(Cu^{III}/Cu^{II})$ is $E_{1/2}$ (0.701 V) obtained from cyclic voltammetrical curve.

Figure 1. Dependence of the fluorescence intensity (I_F , $C=6.55 \times 10^{-5}$, $\lambda = 310$ nm, ■) and the absorbance (A , $C=2.62 \times 10^{-4}$, $\lambda = 504$ nm, ▲) on H for a solution of equimolar amounts of L and Cu^{II} in aqueous



$$\Delta E_{ET}(Cu^{II} \rightarrow Fl^*) = E(Fl^*) - E(Cu^{III}/Cu^{II}) + E(Fl/Fl^*) = 0.63 \text{ V} \quad (2)$$

For Ni (II) complex, the curves of I_F vs. pH and A vs. pH are similar to those of copper(II), but both curves shift to high pH regions centered at the same pH (≈ 7.8). Its value of ΔE_{ET} is 0.57 V.

In the view of thermodynamics, the electron transfer process from M (II) ($M = Cu, Ni$) center to fluorenyl is favored as indicated by the positive value of ΔE_{ET} . Furthermore, in fluorescence quenching process, positive values of ΔE_{ET} is more favored for copper (II) than for nickel (II). If the solution of the ligand (L) was adjusted to pH = 7.0 and Ni (II) is added, no substantial decrease in I_F was observed, even after the addition of one or more equivalents of metal ion. But when Cu (II) was

added to the same solution, I_F decreased linearly and reached zero on addition of one equivalent of the metal ion. Thus, Cu^{II} and Ni^{II} can be distinguished with the ligand L.

In conclusion, extent to which fluorescence was quenched, is influenced by stability constants of the complexes and ability of the ligand to stabilize high valent metal ions, that is, controlled by host-guest interaction. Fluorene has high chemical stability, higher quantum yield. Therefore, it can be used as light-emitting unit linked to receptors, and show a well-defined switch property in aqueous solution. Compound L is the prototype of a new family of pH-sensitive fluorescent sensors for transition metal ions in aqueous solution. Sensor selectivity towards transition metal ions can be modified by changing the structural features of the chelating unit, we are currently designing and testing new sensors consisted of fluorenyl and other chelating units.

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