The Fluorescent 7-Aminodipyrido[3,2-a:2',3'-c] phenazine(7-amino-dppz) Functionalized as an Europium Ion (Eu^{3+}) Sensor

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ABSTRACT: The Fluorescent 7-aminodipyrido[3,2-a:2',3'-c]phenazine (7-amino-dppz, 1) is functionalized as an europium ion (Eu^{3+}) sensor, which showed the effective emission quenching when europium cation is chelated to the bpy site of 1 compound. The complexation ratio indicated that the 1 compound forms a 1 : 1 complex with Eu^{3+}.

Fluorescent artificial receptors are attracting considerable interest in sensory, biochemical, medical, photoelectronic and other applications.[1] These receptors are composed of a host unit (binding site) and a signaling unit (fluorescent site), and communication between the two units is essential for guest specific response. Though various molecular designs have been proposed in order to develop efficient fluorescent receptors,[2] most receptors are designed by introducing molecular recognition site(s) into known fluorophores. However, this approach alone is not sufficient to develop novel fluorescent receptors with high sensitivity or other useful properties, since connection of the host unit often attenuates the emission property of the parent fluorophore. In addressing this point, new design strategy, rendering fluorescence properties to a non-fluorescent functional unit, should be developed.

Polypyridyl compounds are useful molecular units as binding sites. They have multiple interaction sites, and the number of pyridine units is adjustable. 2,2-Bipyridine (bpy) is the most studied among such compounds owing to its excellent property as a bidentate ligand and as a hydrogen bond acceptor.[3] Moreover, rational receptor design using more than one bpy unit can lead to selective and strong interaction with guests.[4] However, bpy itself is non-fluorescent,[5] and only a limited number of fluorescent bpy based species have been known until now.[6] We previously reported[6c] that 6-amino substitution is an effective method to convert non-fluorescent bpy to a strongly fluorescent species, and have demonstrated that the resultant fluorescent bpy derivative served as a highly sensitive fluorescent receptor for phosphodiester guests.[3b] The essence of the molecular design is that a known fluorescent dye, 2-aminophenazine (2-aphz),[7] is integrated with a non-fluorescent bpy. Therefore, as reported previously,[8] the resultant 7-aminodipyrido[3,2-*a*:2,3-*c*] phenazine (7-amino-dppz, 1) was synthesized. The 1 compound and its derivatives were studied in order to examine the metal ion sensing ability through the spectroscopic method. These fluorescent materials have been almost utilized as a metal ion sensing study for monovalent or divalent metal cation. In this paper, the study on europium cation sensing ability of 1 compound is reported. In addition, the fluorescent site of 1 compound is investigated by using the ZINDO[9] (CI = 9) method after successive geometrical optimizations by MM2 and MOPAC/AM1[10] calculations in order to observe the fluorescence behavior of 1 compound after chelation of europium ion. All spectroscopic measurements were carried out with 1.95×10^{-5} mol dm^{-3} 1 compound in acetonitrile at room temperature. Thus the fluorescence titration experiment was carried out by adding up to europium ion 5 equivalent to 1.95×10^{-5} mol dm^{-3} 1 compound in acetonitrile at room temperature. As shown in Fig. 1, the molecular orbitals and the simulated absorption spectra of 1 compound and 2-aphz were investigated by using ZINDO method. The results of this calculation clearly demonstrate that the HOMO and LUMO orbitals are localized on the phenazine site and these orbitals are involved in the lowest energy absorption band.

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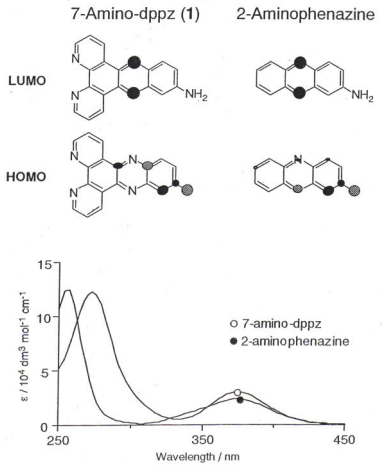

Figure 1. Calculated molecular orbitals and simulated absorption spectra of 1 compound and 2-aminophenazine by ZINDO

As shown in Fig. 2, the absorption peaks of 1 compound were found at 295 nm and 440 nm due to $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively, along with the absorption shoulder at 350 nm. The isosbestic points were observed at 320 nm, 390 nm and 450 nm. The two absorption peaks of 1 compound were red-shifted to 300 nm and 450 nm, respectively, upon addition of europium ion in the presence of 1.95×10^{-5} mol dm^{-3} 1 compound in acetonitrile at room temperature. Meanwhile, when 1 compound was excited at 365 nm, the fluorescence emission peak appeared at 550 nm. As shown in Fig. 2, when europium ion was added up to 5 equivalent in the presence of 1.95 x 10^{-5} mol dm^{-3} 1 compound in acetonitrile, the fluorescence emission peak was decreased and almost quenched at about 5equivalents. Also, as shown in the inset, this fluorescence behavior could be confirmed when the change of the fluorescence emission intensity was plotted as the complexation ratio related to $[Eu^{3+}]/[1]$ at the emission wavelength 550 nm.

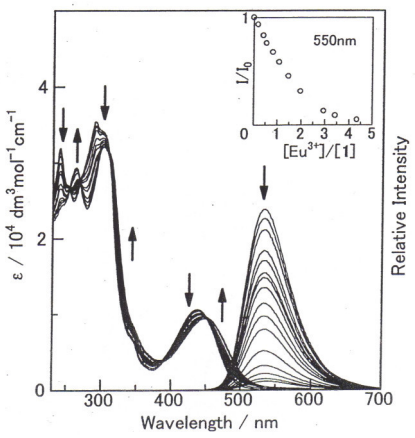

Figure 2. Absorption and fluorescence spectral titration of 1 compound (1.95 x 10^{-5} mol dm^{-3}) upon addition of Eu^{3+} (up to 5 equivalents) in acetonitrile at room temperature.

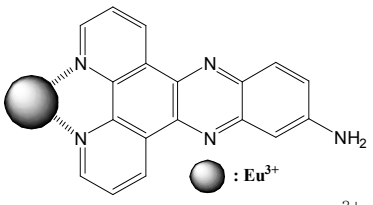

Figure 3. The complex structure of $[Eu^{3+}]:[1]$ = 1:1 appeared in 1 compound (1.95 x 10^{-5} mol dm^{-3}).

Association constant (M^1) between 1 compound and europium ion was estimated to be K_a = 2.9 x 10^4 M^1 by computational simulation. This association constant was almost consistent with the association constant (very smaller than K_a = 1 x 10^{10} M^1) obtained in the complexation ratio $[M^{2+}]:[1]$ = 1:1.[8]

We was known from this result that this complex structure is $[Eu^{3+}]:[1]$ = 1:1, not $[Eu^{3+}]:[1]$ = 1:2 due to having the value more than K_a = 1 x 10^{10} M^1 in the case of complexation ratio $[M^{2+}]:[1]$ = 1:2 as reported previously.[8]

In conclusion, we confirmed that the electronic communication between bpy chelating unit and fluorescent phenazine unit is existed and the europium chelating to 1 compound is induced to effective emission quenching occurred from phenazine unit. In particular, this results will be opened a new way for the application as an effective metal ion sensor in the near future.

KEYWORDS: europium ion sensor, absorption, fluorescence, complexation, fluorescence titration, phenazine

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