An Yttrium Ion-Selective Fluorescence Sensor Based on Metal Ion-Controlled Photoinduced Electron Transfer in Zinc Porphyrin−Quinone Dyad

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Yttrium is considered a relatively disperse element in nature. However, the availability of improved analytical techniques has revealed that yttrium is present throughout living matter, even though only a relatively limited number of species have so far been analyzed.[1] During the past two decades, there has been a significant increase of research into the biological significance and applications of yttrium ion.[1] However, the routine analysis of yttrium in biological samples certainly needs further improvement. In this context, fluorescence sensors for the selected metal ions have merit for obtaining quantitative information about the amount of those metal ions, where a fluorescence sensor with an appropriate size cavity is introduced for molecular recognition with a certain metal ion.[2−5] On the other hand, it has been shown that the driving force of electron transfer is finely controlled by complexation of radical anions, produced in the electron transfer, with metal ions which act as Lewis acids, in a variety of intermolecular and intramolecular electron-transfer systems.[6−8] Quantitative measures to determine the Lewis acidity of a variety of metal ions have now been established in relation with the promoting effects of metal ions on the electron-transfer reactions.[9] If a metal ion binds with a donor (D) or acceptor (A) in a D−A-linked dyad, including a fluorophore, the fluorescence intensity may vary, depending on the concentration of the metal ion. However, such a D−A-linked dyad has yet to be explored as a fluorescent metal ion sensor, in particular for yttrium ion (Y^{3+}).

We report herein a highly Y^{3+}-selective fluorescence sensor based on metal ion-controlled photoinduced electron transfer in zinc porphyrin−quinone-linked dyad (**ZnP−CONH−Q**, Chart 1). **ZnP−NHCO−Q**-linked dyad and the reference compound (**ZnP−CONH−ref**) are also employed for comparison (Chart 1).

Chart 1. Drawing of Fluorescence Sensors (**ZnP−CONH−Q**, **ZnP−NHCO−Q**) and Reference Compound (**ZnP−CONH−ref**) for **ZnP−CONH−Q**
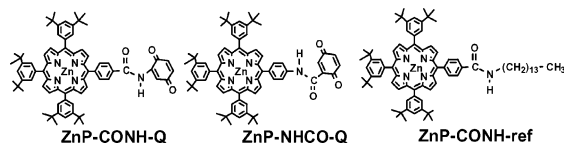
The preparation and characterization of **ZnP−CONH−Q**, **ZnP−NHCO−Q**, and **ZnP−CONH−ref** are described in the Supporting Information (S1−S5). The fluorescence spectrum of **ZnP−CONH−Q** as compared with that of reference compound (**ZnP−CONH−ref**) is shown in Figure 1a, where the ZnP moiety is excited at 560 nm. The fluorescence intensity of **ZnP−CONH−Q** is significantly quenched as compared with that of **ZnP−CONH−ref** in deaerated PhCN. The fluorescence intensity of **ZnP−NHCO−Q** was also significantly quenched as compared with that of **ZnP−CONH−ref** in deaerated PhCN. The driving force of
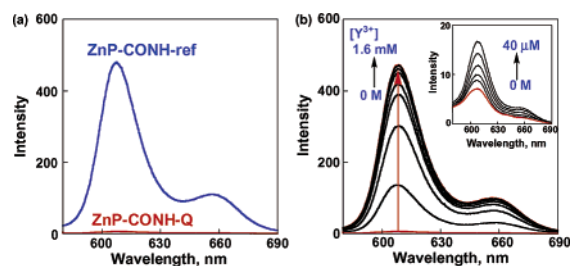

Figure 1. (a) Fluorescence spectra of **ZnP−CONH−Q** and **ZnP−CONH−ref** (3 µM) excited at 560 nm in deaerated PhCN. (b) Fluorescence spectra taken during the titration of **ZnP−CONH−Q** (3 µM) with $Y(OTf)_3$; $[Y(OTf)_3] = 0$, 200 µM, 400 µM, 600 µM, 800 µM, 1 mM, 1.2 mM, 1.4 mM, and 1.6 mM. Inset: $[Y(OTf)_3] = 0$, 5 µM, 10 µM, 20 µM, 30 µM, and 40 µM, excited at 560 nm in deaerated PhCN.

electron transfer ($-\Delta G_{ET}$) from the singlet excited state ($^1ZnP^*$) to Q in **ZnP−CONH−Q** was determined to be 0.91 eV in PhCN from the one-electron oxidation potential of the ZnP moiety ($E^0_{ox} = 0.78$ V vs SCE) and the one-electron reduction potential of the Q moiety ($E^0_{red} = -0.36$ V vs SCE), determined by the cyclic voltammetry measurements, and the $^1ZnP^*$ energy level (2.05 eV). The occurrence of the photoinduced electron transfer was confirmed by observation of the ESR spectrum of **ZnP•+−CONH−Q•−**, which was generated by photoirradiation of a deaerated PhCN solution of **ZnP−CONH−Q** at 173 K (see Supporting Information, S6). The ESR spectrum of **ZnP•+−CONH−Q•−** ($g = 2.0030$) consists of the superposition of the ESR signals of **ZnP•+−CONH−Q** ($g = 2.0023$) and **ZnP−CONH−Q•−** ($g = 2.0043$), produced by chemical oxidation and reduction, respectively (S6).

A remarkable enhancement of the ZnP fluorescence intensity is observed by adding a small concentration of yttrium triflate $[Y(OTf)_3]$ ($10^{-6}-10^{-3}$ M) to a deaerated PhCN solution of **ZnP−CONH−Q** without change of spectral features, as shown in Figure 1b. From the fluorescence titration of Y^{3+} in **ZnP−CONH−Q**, the binding constant (K) between Y^{3+} and **ZnP−CONH−Q** is estimated as 3900 M^{-1} in deaerated PhCN.

The fluorescence intensities of **ZnP−CONH−Q** (3 µM) and **ZnP−NHCO−Q** (3 µM) in the presence of a 400 µM concentration of various metal ions, with respect to those in the absence of metal ion, are determined in deaerated PhCN, as shown in Figure 2. A remarkable enhancement of the fluorescence intensity is observed exclusively in the case of **ZnP−CONH−Q** in the presence of Y^{3+}, whereas **ZnP−NHCO−Q** exhibits only moderate enhancement of the fluorescence intensity in the presence of metal ions. Such a significant difference in the fluorescence intensity between **ZnP−CONH−Q** and **ZnP−NHCO−Q** in the presence of Y^{3+} indicates that the binding sites of **ZnP−CONH−Q** to Y^{3+} are more suitable than those of **ZnP−NHCO−Q**. The optimized structure of the **Ph−CONH−Q/Y³⁺** complex is evaluated by ADF calculation with the II (large) basis set, as shown in the inset of Figure 2, which demonstrates the strong binding of Y^{3+} with two carbonyl oxygens
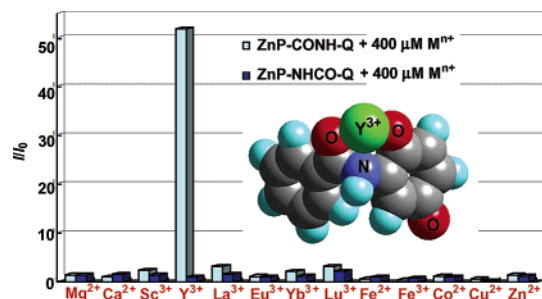
Figure 2. Fluorescence responses (I/I₀ at 610 nm) of **ZnP−CONH−Q** and **ZnP−NHCO−Q** (3 μM) in the presence of 400 μM metal ions excited at 560 nm with respect to those in the absence of metal ion in deaerated PhCN: $CF_3OSO_3^-$ salt (Ca^{2+}, Sc^{3+}, Y^{3+}, La^{3+}, Eu^{3+}, Yb^{3+}, Lu^{3+}, Zn^{2+}); ClO_4^- salt (Mg^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}). The optimized structure of the **Ph−CONH−Q/Y³⁺** complex is obtained by ADF calculation with the II (large) basis set.

of **ZnP−CONH−Q**. Metal ions with weaker Lewis acidity than Y^{3+} (Lu^{3+}, La^{3+}, Eu^{3+}, Yb^{3+}, Lu^{3+}, Zn^{2+}, Mg^{2+}, Ca^{2+})[9] may have weaker binding with the two carbonyl oxygens of **ZnP−CONH−Q**, leading to the smaller fluorescence intensity. Although Lewis acidities of Sc^{3+}, Fe^{3+}, Fe^{2+}, Co^{2+}, and Cu^2 are much stronger than that of Y^{3+},[9] the ionic radii of Sc^{3+} (0.87 Å), Fe^{2+} (0.92 Å), Fe^{3+} (0.78 Å), Co^{2+} (0.90 Å), and Cu^2 (0.73 Å) may be too small for the binding with two carbonyl oxygens of **ZnP−CONH−Q** as compared with that of Y^{3+} (1.02 Å).[10−12]

From the fluorescence quenching in Figure 1a, the rate constant (k_{ET}) of photoinduced electron transfer from the singlet excited state of the ZnP moiety to the Q moiety in **ZnP−CONH−Q** is determined to be 1.5×10^{10} s⁻¹ by comparison of the intensity of **ZnP−CONH−ref** ($\tau_S = 2.04$ ns determined from fluorescence decay).[13] Similarly, the k_{ET} value of **ZnP−NHCO−Q** is determined to be 6.3×10^8 s⁻¹ ($-\Delta G_{ET} = 1.11$ eV).

The k_{ET} values are evaluated using the Marcus equation for intramolecular electron transfer (eq 1),[14]

$$k_{ET} = \left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} V^2 \exp\left[-\frac{(\Delta G_{ET} + \lambda)^2}{4\lambda k_B T}\right] \quad (1)$$

where V is the electronic coupling matrix element, k_B is the Boltzmann constant, h is the Planck constant, and T is the absolute temperature. The λ and V values are evaluated from the k_{ET} and ΔG_{ET}, values using eq 1, as 0.57 eV and 17 cm⁻¹, respectively. The strong binding of the reduced quinone ($Q^{\bullet-}$) moiety of **ZnP−CONH−Q^{\bullet-}** with Y^{3+} results in a significant positive shift of the one-electron reduction potential of the Q moiety in the presence of 2 mM Y^{3+} (0.42 V vs SCE) in deaerated PhCN as compared with the value (−0.36 V) in its absence (see Supporting Information, S8).[15] In such a case, the driving force ($-\Delta G_{ET}$) of photoinduced electron transfer from the singlet excited state of the ZnP moiety to the Q/Y^{3+} complex moiety is 0.78 eV larger than the corresponding driving force in the absence of Y^{3+}. On the other hand, the strong binding of the $Q^{\bullet-}$ moiety of **ZnP^{\bullet+}−CONH−Q^{\bullet-}** with Y^{3+} is expected to result in a much larger λ value for the photoinduced electron transfer because of the large change in the binding strength associated with the electron transfer. In the case of the binding of the anthraquinone moiety with Y^{3+} in ferrocene−anthraquinone dyad, the λ value of electron transfer has previously been evaluated to be as large as 2.9 eV.[7a] When such a large λ value is applied to the **ZnP−CONH−Q/Y³⁺** system with $V = 17$ cm⁻¹, the k_{ET} value is evaluated as 3.2×10^8 s⁻¹ from the $-\Delta G_{ET}$ value (1.69 eV) in the presence of 2 mM Y^{3+} using eq 1. The estimated k_{ET} value in the presence of 2 mM Y^{3+} is 47 times smaller

than the value in the absence of Y^{3+} (1.5×10^{10} s⁻¹). Thus, the Y^{3+}-selective enhancement of the fluorescence of **ZnP−CONH−Q** results from the strong binding of Y^{3+} to the quinone moiety, which causes a significant increase in the λ value and, thus, retards the photoinduced electron transfer, despite the larger driving force of electron transfer. Since the k_{ET} value in the **ZnP−CONH−Q/Y³⁺** complex is much smaller than the intersystem crossing (ISC) rate constant (7.7×10^8 s⁻¹),[16] photoexcitation of the **ZnP−CONH−Q/Y³⁺** complex is expected to result in formation of the triplet excited state of the ZnP moiety (^{3}ZnP*). This is confirmed by the laser flash photolysis of the **ZnP−CONH−Q/Y³⁺** complex in which the triplet−triplet absorption was observed (see Supporting Information, S9).

In conclusion, the selective binding of Q with Y^{3+} results in drastic changes in the driving force and reorganization energy of photoinduced electron transfer in **ZnP−CONH−Q**, leading to a significant deceleration of the electron-transfer rate, and thereby a drastic enhancement in the fluorescence intensity, making it useful as a highly Y^{3+}-selective fluorescence sensor.

Supporting Information Available: Synthetic procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) In fact, the binding constant (3900 M⁻¹) of Y^{3+} with **ZnP−CONH−Q** determined from the fluorescence titration is larger than that (580 M⁻¹) of Sc^{3+} in deaerated PhCN (see Supporting Information, S7).
(12) The fluorescence of **ZnP−CONH−ref** has been quenched by redox-active metal ions such as Fe^{2+}, Fe^{3+}, and Cu^{2+}, which may also act as electron acceptors in the fluorescence quenching of **ZnP−CONH−Q**.
(13) The k_{ET} value is determined from the equation $k_{ET} = (\tau_{ZnP−CONH−ref})^{-1}([I_0/I] − 1)$.
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JA045374X