Photochemical and complexation studies for new fluorescent and colored chelator

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Abstract

The photo-induced intramolecular proton (or hydrogen atom) transfer (ESIPT) and metal binding properties of Oxa-ester were studied in methanol solution. The dissociation constant between Oxa-ester and the metal ion was highly dependent with the metal ion and was determined by Hill plots or iterative least squares fitting to be 447 mM, 14.9 $\mu$M, and 290 nM for Ca$^{2+}$, Zn$^{2+}$, and Cu$^{2+}$, respectively, in methanol. The fluorescence intensity of Oxa-ester greatly increased with increasing concentration of Zn$^{2+}$, while the fluorescence intensity decreased with the addition of Ca$^{2+}$ and Cu$^{2+}$. Transient absorption spectroscopy revealed that Oxa-ester underwent ESIPT to give Z-NH isomer in the excited state in benzene, while Oxa did not undergo ESIPT probably due to the hydrogen bonding with solvent water.

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1. Introduction

Fluorescent probes for measuring biologically important ions such as Ca$^{2+}$, Mg$^{2+}$, and Zn$^{2+}$ have been developed in many research groups [1–16]. The fluorescence intensity of these metal probes changes mainly based on the differences of fluorescent properties between free form of the probe molecule and its metal complex. We have prepared several types of new chelators responded by light. For example, we have already reported azobenzene chelators where trans-isomer has usual binding affinities for Ca$^{2+}$ and Mg$^{2+}$, while the cis-isomer does not bind with these cations [17]. Another approach of the development of a new fluorescent sensor for biologically important ions, such as Zn$^{2+}$, is based on the idea that the fluorescent probes, which have two metal binding sites with two distinctive dissociation constants ($K_d^1$ and $K_d^2$), may be applicable for measuring Zn$^{2+}$ in wide concentration range depending upon the dissociation constants of each binding site. In this context, Oxa has been designed and synthesized (Scheme 1) [18].

Now, we can suppose that the affinity of probe molecules for metals may be controlled by light if the change in the electronic environment at the metal binding site can be induced by photoirradiation. When the affinity constant for a metal decreases by photoirradiation, the metal should be released and consequently, the concentration of the metal in the solution should immediately increase. With this idea caged compounds have been developed for the studies on the rapid biological processes (Fig. 1).

On photoirradiation, caged compounds undergo photodecomposition and can release not only metal ions but also many physiologically active molecules, such as ATP [19], cAMP [20–23], l-glutamic acid [24–27], and so on, depending on its structure. Development of the fluorescent metal probes and their photochemical control of the binding affinity between chelators and these cations with novel mechanism are of interest. Unlike to other caged compounds, our idea is to use the photosensitive molecules, which does not undergo photodecomposition reaction. For this purpose, we have been interested in using the photoinduced
intramolecular hydrogen atom transfer, which may induce the considerable change of the electronic structure in the chelating part. In this respect, Oxa [18] and its precursor Oxa-ester can be good candidates (Scheme 2).

Oxa and Oxa-ester have metal binding moieties and photoresponsive 2-(2'-hydroxyphenyl)benzoxazole (HBO) skeleton in its structure. HBO is well known as a typical molecule, which undergoes excited state intramolecular proton-transfer (ESIPT) [28–41]. Thus, the produced tautomer has different electronic structure and may have a considerably different binding constant with cations. By improving these properties we could prepare chelator regulated by light or caged chelator.

In order to prove the idea for the metal releasing by photoirradiation using HBO derivatives, the ESIPT of Oxa in aqueous solution and of Oxa-ester in organic solvents was explored. We wish to report here the concept and the preliminary results of some photochemical properties of metal ion chelators Oxa-ester having hydrogen bonding part. Especially, we report here the ESIPT of Oxa-ester as well as its fluorescence and color change depending upon the concentration of metal cations.

2. Background

Our approach for development of the photoresponsive chelator is based on our recent investigations of the photochemical isomerization and photo-induced intramolecular proton (hydrogen atom) transfer of the intramolecular hydrogen bonded molecules [42–57]. We have shown that olefin with a pyrrole ring and an indole or a phenanthroline ring (Scheme 3a and b) exhibited trans-to-cis one-way photochemical isomerization and the obtained cis-isomer underwent intramolecular hydrogen atom transfer in the excited singlet state [42–44]. When the phenanthroline moiety make a complex with Ni²⁺, the mode of the isomerization is changed to give a higher composition of the trans form at the photostationary state [44]. Another example of the one-way trans-to-cis photochemical isomerization caused by the intramolecular hydrogen bonding is shown in Scheme 3c. In this case, the introduction of formyl group in the pyrrole ring changed the isomerization behavior to give mutual isomerization in the triplet state through the quantum chain process after intersystem crossing [45]. A new photochromic compounds with the absorption at visible region can be prepared by using intramolecular hydrogen bonding. Thus, a hemiindigo derivative (Scheme 3d) exhibited almost one-way Z-to-E isomerization on irradiation at 366 nm, while on irradiation at 546 nm higher composition of Z-isomer was obtained [49]. Not only N–H:N hydrogen bonding, but also O–H:N or O–H:O hydrogen bonding induced ultrafast intramolecular hydrogen atom transfer in the excited state (Scheme 3e–g) [51,54]. Hydroxychalcones underwent intramolecular hydrogen atom transfer in the excited state followed by the one-way cis–trans isomerization or cyclization reaction. The mechanism and their intermediates of ESIPT and photosomerization of chalcone derivatives [55–57] have been investigated using nanosecond transient absorption spectroscopy and time-resolved infrared spectroscopy (Scheme 3g) [57]. Development of new photoresponsive chelator in this paper is originated from the change in the electronic structure of the hydrogen bonded compounds at the excited state produced by ESIPT.

![Scheme 1. Structures of Oxa and Oxa-ester.](image)

![Scheme 2. Schematic drawing of M²⁺ release on photoirradiation to Oxa-metal complex.](image)

![Fig. 1. Photolysis of caged compounds to release the biologically active species (uncaging).](image)
3. Experimental

3.1. Materials

The synthesis of Oxa and its precursor Oxa-ester and the data for all compounds have been reported in the previous paper [18].

3.2. Measurements

Absorption spectra were measured on a Shimazu UV-1600. Fluorescence spectra were measured on a Hitachi F-4500. Laser flash photolysis was performed by using an excimer laser (Lambda Physik LPX-100, 308 nm 20 ns fwhm) as an excitation light source and a pulsed xenon arc (Ushio UXL-159) as a monitoring light source. A photomultiplier (Hamamatsu R-928) and a storage oscilloscope (Iwatsu TS-8123) were used for the detection.

3.3. Determination of dissociation constants

All dissociation constants $K_d$ reported herein, were measured in methanol for Oxa-ester and are apparent dissociation constants. The effect of metal ions was investigated by adding the methanol solution of metal chloride to $2.5 \times 10^{-6}$ M solution of Oxa-ester. The concentration of metal chloride in the solution was 1.0, 0.1, or 0.01 M. The changes in the absorbance and the fluorescence spectra were measured with the addition of a solution of calcium, zinc, or cupper chloride. The values of dissociation constant $K_d$ for each metal ion were determined from an iterative least-squares fitting for a 1:1 binding model as described below:

$$ A_{\text{obs}} - A_0 = \frac{b(\varepsilon_{\text{ML}} - \varepsilon_0)}{2K} [1 + K[H]_0 + K[G]_0 - (1 + K[H]_0 + K[G]_0)^2 - 4K^2[H]_0[G]_0^{0.5}] $$

Scheme 3. Example of hydrogen bonded compounds.
4. Results and discussion

4.1. Absorption, fluorescence and fluorescence excitation spectra of Oxa-ester in organic solvents

Fig. 2a shows the absorption spectra of Oxa-ester in methanol and in benzene. The absorption maxima appeared at 352 and 357 nm in methanol and benzene, respectively. In benzene, the absorption clearly ended at 400 nm, while the absorption tail appeared down to 420 nm in methanol. These spectral properties are expectable for benzoxazole derivatives. Actually, fluorinated HBO derivatives exhibited very similar absorption tail in methanol due to the formation of its phenolate anion, while no absorption tails are observed in non-protic solvents [58]. In addition, the formation of the anion in polar solvents has also been reported for 2-(2'-hydroxyphenyl)benzothiazole (HBT) [59,60].

Fig. 2b and c shows the fluorescence and fluorescence excitation spectra of Oxa-ester in benzene and in MeOH, respectively. On excitation of Oxa-ester in benzene two emission maxima appeared at 404 and 500 nm (Fig. 2b). The Stokes shifts between the absorption maximum and the fluorescence maxima were calculated to be 3000 and 7800 cm\(^{-1}\) for the fluorescence of 404 and 500 nm, respectively. Thus, the former and the latter fluorescence spectra were reasonably assigned to the normal form (E-OH form) and the tautomer form (E-NH form) produced by photoinduced intramolecular hydrogen atom transfer (Scheme 4a). In methanol, Oxa-ester exhibited different fluorescence and fluorescence excitation spectra from those in benzene. Fluorescence spectra in methanol depended on the excitation wavelength and the monitoring wavelength (Fig. 2c). On excitation at 350 nm Oxa-ester gave fluorescence with maxima at 410 and 450 nm in methanol. When Oxa-ester is excited at 390 nm, the fluorescence maximum shifted to the longer wavelength and the fluorescence at shorter wavelength disappeared. The fluorescence excitation spectra in methanol also depended on the monitoring wavelength. With monitoring at 390 nm, the peak of the excitation spectrum was observed at 352 nm, indicating the existence of the E-OH form in methanol. When the fluorescence was monitored at 450 nm, the peak of the excitation spectrum was appeared at 386 nm, which can be ascribed to the anionic form. Thus, Oxa-ester gave fluorescence spectra from E-OH form (410 nm) and anionic form (450 nm) in methanol (Scheme 4b).

4.2. Absorption spectra of Oxa-ester in the presence or absence of metal ions in methanol

Fig. 3 shows the change in the absorption spectra of Oxa-ester in methanol (2.5×10\(^{-6}\) M) on addition of metal ions under air at room temperature. The spectra were changed by the addition of Ca\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) with the isosbestic points, indicating a simple 1:1 complexation equilibrium between Oxa-ester and [Oxa-ester+Ca–H]\(^{+}\) (Scheme 5). The absorption maximum shifted to the longer wavelength from 352 nm in methanol in the absence of the metal ions to 368, 376, and 368 nm in the presence of Ca\(^{2+}\), Cu\(^{2+}\), or Zn\(^{2+}\),
respectively. In the case of Oxa, the added Zn$^{2+}$, Ca$^{2+}$, or Mg$^{2+}$ precedently bind to the APTRA group [18]. However, the APTRA group in Oxa-ester should not play a role for complex formation due to the lack of the carboxylate anions. In fact, these spectral changes of Oxa-ester upon the addition of metals in Fig. 3 a–c are similar to those of the other HBO derivatives in organic solvents. Therefore, the results suggest that the added metals bind to HBO moiety, not to APTRA group in Oxa-ester, as shown in Scheme 5. The added Mg$^{2+}$ did not change the absorption spectra indicating no binding with Oxa-ester in methanol. The dissociation constant was determined by Hill plot or iterative least-squares fitting to be 447 mM, 14.9 μM, and 290 nM for Ca$^{2+}$, Zn$^{2+}$, and Cu$^{2+}$, respectively (Table 1). Thus, the binding constant ($K_d$) considerably depended on the metal ions.

4.3. Fluorescence spectra of Oxa-ester in the presence or absence of metal ions in methanol

The addition of metals also caused fluorescence change in methanol (Fig. 4). Upon the addition of

Scheme 5. Equilibrium between Oxa-ester and [Oxa-ester+M-H]$^+$ (M: Ca, Zn, Cu, or Mg).
Ca\(^{2+}\), decrease of the fluorescence intensity without isoemissive point was observed (Fig. 4a). The titration with Zn\(^{2+}\) gave the fluorescence increase at 448 nm, where the isoemissive point was observed at 406 nm (Fig. 4b). The similar fluorescence increase was observed in other HBO derivatives during the titration with Zn\(^{2+}\) [28]. The added Cu\(^{2+}\) caused fluorescence decrease (Fig. 4c). In the case of Oxa in aqueous solution, the fluorescence intensity was increased during the titration with Mg\(^{2+}\).

Table 1
Dissociation constant of Oxa-ester in methanol and Oxa in buffer at pH 7.2 for cations

| Metals  | \(K_d\) (Oxa-ester in MeOH) | \(K_d\) (Oxa in buffer (pH 7.2)) |
|---------|-----------------------------|---------------------------------|
| Ca\(^{2+}\) | 447 mM | 250 \(\mu\)M | 275 mM |
| Zn\(^{2+}\) | 14.9 \(\mu\)M | 1.50 \(\mu\)M | 140 \(\mu\)M |
| Cu\(^{2+}\) | 290 nM | – | – |
| Mg\(^{2+}\) | – | 943 \(\mu\)M | – |

\(^a\) Ref. [18].
of Ca$^{2+}$, Zn$^{2+}$, and Mg$^{2+}$. However, the fluorescence intensity of Oxa-ester in methanol was increased only by the addition of Zn$^{2+}$. These results indicate that the fluorescence properties of HBO-metal complex in organic solvents may be different from those in aqueous solution.

4.4. Laser flash photolysis

On excitation with 308 nm excimer laser in benzene, Oxa-ester gave the transient absorption spectra with intense band at 390–480 nm ($\tau = 5 \mu$s) and a broad band at 490–680 nm ($\tau = 1.8 \mu$s) under argon atmosphere (Fig. 5a). The latter band was quenched by oxygen and was assigned to the triplet state (Fig. 5b), while the former band was not quenched by oxygen and was assigned to the Z-NH tautomer in the ground state.

In methanol, Oxa-ester gave the similar transient absorption to that in benzene. The transient absorption at 420 nm was assigned to either the tautomer form or anionic form and the transient absorption band at 580 nm was assigned to the triplet state.

Fig. 5c shows the transient absorption spectra of Oxa in buffer solution at pH 7.2. Unlike the transient absorption spectra of Oxa-ester in organic solvents, Oxa did not show the absorption signal of Z-NH tautomer at 440 nm. The signal around 400 nm is ascribed to the anion form. Actually, the peak of the anion form of Oxa in 1 N KOH aqueous solution appeared at 350–430 nm. ESIPT of Oxa was not observed in aqueous solution probably because the O–H:N intramolecular hydrogen bonding was broken by water.

4.5. Mechanism of photochemical processes and some properties of metal complexes

The energy diagrams of the photochemical processes of Oxa-ester in benzene and in methanol are summarized in Fig. 6. In benzene Oxa-ester exists as a normal form with the OH:N intramolecular hydrogen bonding and undergoes either fluorescence emission or intramolecular hydrogen atom transfer in the excited singlet state to give the tautomer form giving the specific emission at longer wavelength region (Fig. 6a). In methanol Oxa-ester must exist as a mixture of normal form and the anionic form and gives fluorescence emission from both normal and the anionic form. Intramolecular hydrogen atom transfer to give the tautomer (E-NH form) did not takes place in methanol. In the case of Oxa in aqueous solution,

![Fig. 6. Potential energy diagram of Oxa-ester in organic solvents (a) and Oxa in aqueous buffer (40 mM HEPES, 100 mM KCl, pH 7.2) at room temperature (b).](image-url)
the OH:N intramolecular hydrogen bonding presented in non-polar solvent was broken by forming the hydrogen bonding with water [18]. Therefore, ESIPT could not observed in Oxa in aqueous solution (Fig. 6b).

5. Future prospect

We have started to prepare Oxa to induce the photochemical control of the dissociation constant of the metal binding to the chelator. We have found that Oxa exhibited two distinctive dissociation constants for Zn$^{2+}$ and Ca$^{2+}$ [18]. The first dissociation constant ($K_1$) is ca. 100 times lower than that of the second dissociation constant ($K_2$). For example, the $K_1$ and $K_2$ between Oxa and Zn$^{2+}$ are 1.50 μM and 140 μM, respectively (Table 1). We have also tried the photo-irradiation control of the metal binding. However, in aqueous solution the OH:N intramolecular hydrogen bonding was broken by solvent water. In this respect, we are now preparing the compound where the OH:N intramolecular hydrogen bonding part is protected by dendrimer type substituent with hydrophobic interior and water soluble outer peripheral (Fig. 7). Water-soluble dendrimers with photosensitive core have already been studied [61–66]. It was found that the poly aryl(ether) dendron with carboxylate anion at the periphery can produce a hydrophobic interior in aqueous solution (Fig. 8). The photoinduced hydrogen atom transfer was observed in Oxa-ester. In addition, the binding constant with cations are higher at APTRA than that at OH:N in Oxa. Thus, one can construct a caged chelator capable to

![Fig. 7. Photoresponsive chelator Oxa with water-soluble poly aryl(ether) dendron.](image)

![Fig. 8. Water-soluble dendrimers with poly aryl(ether) dendrons.](image)
release metal ions with the signal of photon by the introduction of the dendron substituents on the photocromic core with intramolecular hydrogen bonded chromophore (Fig. 7).

6. Conclusions

Novel photoresponsive chelators Oxa-ester and Oxa for divalent cations were designed and synthesized. The idea of the development of new chelating reagents was based on the photoinduced proton (or hydrogen atom) transfer (ESIPT) followed by the affinity change to release the biological important ions in buffer solution. Aminophenol triacetic acid (APTRA) structure was chosen for the chelating part. The absorption spectra of Oxa greatly increased with increasing the concentration of cations, indicating that the chelators showed the affinity for metal ions in solutions. The dissociation constants of Oxa-ester for cations were highly dependent with the metal ion and were determined by Hill plot or iterative least-squares fitting. The fluorescence intensity of Oxa-ester changed with increasing the concentration of cations, which were determined by Hill plot or iterative least-squares fitting. The fluorescence spectra of Oxa greatly increased with increasing concentration of Zn$^{2+}$, while the fluorescence intensity decreased with the addition of Cu$^{2+}$ or Cu$^{2+}$. On irradiation with 308 nm excimer laser, Oxa-ester underwent ESIPT to give E-NH isomer in the excited state in benzene, while Oxa did not undergo ESIPT probably due to the blocking of the intramolecular hydrogen bonding by solvent water.

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