Picosecond Mechanism of Metal-Ion-Sensitive Fluorescence of Phenylimidazoanthraquinone with Azacrown

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Dynamic mechanism of metal-ion-sensitive fluorescence of phenylimidazoanthraquinone with azacrown (PIAQ−AC) was investigated by time-resolved fluorescence and absorption spectra upon excitation with a femtosecond laser. PIAQ−AC showed marked fluorescence quenching, while the fluorescence intensity was greatly enhanced upon binding of either calcium or barium ions. The transient absorption of PIAQ−AC ascribed to the excited singlet decayed with a lifetime of 5.8 ps in the absence of calcium ions. The lifetime of the excited singlet increased to 200 ps upon binding of calcium ions to the azacrown. The transient absorption spectrum of the phenylimidazoanthraquinone anion radical was observed in the absence of metal ions. These results clearly indicate that the fluorescence was switched on and off by an intramolecular electron-transfer mechanism controlled with metal ions.

Introduction

Crown ethers and cryptands are well-known as ion-sensitive receptors.[1] Their ability for ion recognition has been utilized for various types of chemosensors. The design and synthesis of chemosensor systems are areas of growing interest because of their potential applicability to biomedical and environmental fields.[2] The biological significance of these sensors lies in the nondestructive determination of intracellular Na^+, K^+, Ca^{2+}, and Mg^{2+} ions.[3−9] The chemosensor systems are based on fluorescence or absorption, which will be triggered or modulated by metal ions. Fluorescent chemosensors for ions are usually much more sensitive than those based on light absorption because of the easy detection of fluorescence against a dark background.

The fluorescent chemosensor system should include a fluorophore and an ion receptor as essential components connected by an appropriate spacer. Such "fluorophore−spacer−receptor" systems are designed to show a very low fluorescence quantum yield in the absence of metal ions. Fluorescence quenching will be due to photoinduced intramolecular electron-transfer reactions or energy transfer between the ion-free receptor and the fluorophore. The photoinduced electron-transfer process can be suppressed by metal cations captured into the receptor by the cation-induced change of the ionization or oxidation potential of the receptor.

Recently, such characteristics have been developed not only as molecular fluorescent chemosensors but also as molecular digital devices for electronics and ionics.[10−12] de Silva et al. designed a cyanoanthracene system having both a benzocrown ring and a tertiary amino group that will function as an AND logic gate.[10] The fluorescence intensity of the cyanoanthracene increased in the presence of the sodium cation and proton. Two receptor sites, benzocrown ether for alkali metal ions and the tertiary amino group for protons, are characteristic of the AND logic gate. The research groups of Ghosh and Credi have reported OR and exclusive OR (XOR) logic gates.[11,12]

We have demonstrated a new fluorescent sensing system in which an electron-accepting 2-phenylimidazoanthraquinone (PIAQ) chromophore was linked to an azacrown ether (AC) by a methylene spacer.[13] This system can recognize the charge and the size of alkali and alkaline-earth metal cations and transform its information precisely into highly and specifically enhanced fluorescence. When metal ions were bound by electrostatic interaction between the lone pair electrons in the azacrown and alkali or alkaline-earth ions, the fluorescence was increased depending on both the charge and the size. Alkaline-earth metal ions increased fluorescence more efficiently than alkali metal ions. The difference in the fluorescence quantum yields between the alkali metal ions and the alkaline-earth metal ions was interpreted as due to a stronger electrostatic interaction between the divalent metal ions and the lone pair electron in the azacrown, which would suppress the photoinduced electron-transfer reactions process more efficiently. Valeur et al.[14,15] and Lapouyade et al.[16] reported twisted intramolecular charge transfer (TICT) fluorescence that is affected by metal ions complexed by azacrown. The picosecond dynamics of photoejection of metal ions and the reversible nitrogen−calcium bond dissociation in the excited state are discussed in refs 15 and 16. In these fluoroionophores, a locally excited (LE) state is nonemissive and only the intramolecular charge transfer (ICT) is emissive. Metal cations were interpreted to steer the reduction of the efficiency of transfer from LE to ICT states. In the present study, we report the photoinduced electron-transfer process dynamics of metal-ion-sensitive fluorescence of PIAQ linked to AC investigated by time-resolved fluorescence and absorption spectra measurement with a femtosecond laser.

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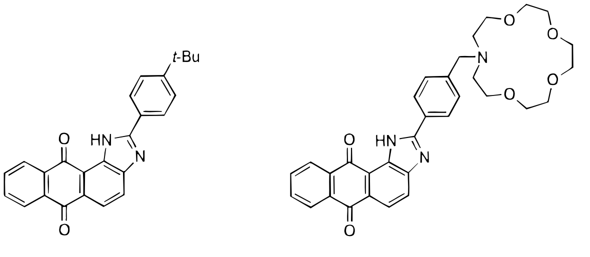

PIAQ-t-Bu **PIAQ-AC**

Figure 1. Chemical structures and abbreviation of phenylimidazoanthraquinones with a tertiary butyl group (PIAQ−*t*-Bu) and an azacrown (PIAQ−AC).

Experimental Section

Materials and Sample Preparation. 2-Phenylimidazoanthraquinone (PIAQ) linked to tertiary butyl (*t*-Bu) and azacrown ether (AC) was synthesized according to a similar method reported previously.[13] The structures of these compounds are shown in Figure 1 together with their abbreviations. Their structures and purity were confirmed by FT-IR, ^{1}H NMR, and elemental analysis. The compounds were dissolved in acetonitrile (Wako Pure Chemical Industries, guaranteed reagent). Five times excess amounts of alkaline-earth metal salts ($Ca(SCN)_2$, $Ba(SCN)_2$) were added to the azacrown ether compounds. All measurements were carried out at 25 °C.

Fluorescence Lifetime Measurement. The femtosecond laser system consists of a Ti:sapphire laser (Spectra-Physics, Tsunami, 800 nm) pumped with a solid-state visible CW laser (Spectra-Physics, Millennia) and a regenerative amplifier pumped with the second harmonic (532 nm) of a Nd:YAG laser (Spectra-Physics, GCR-170). The sample solution in a quartz cell of 1 cm path length was excited in air by the second harmonic (400 nm, 20 μJ/pulse) of a femtosecond laser. The fluorescence lifetimes were measured with an imaging spectrograph (Hamamatsu, C5094) and a streak scope (Hamamatsu, C2830) with a high-speed streak unit (Hamamatsu, M2547).

Femtosecond Time-Resolved Absorption Spectroscopy. Details of the femtosecond laser photolysis system were reported previously.[17,18] The sample solutions in a 4 mm path length cell were excited in air by the above-mentioned femtosecond laser system. A white light probe was obtained by focusing the residual 800 nm light after passing through a BBO crystal to obtain the second harmonics into a cell containing a D_2O/H_2O (2:1) mixture. The total time resolution of our system as determined by the transient bleaching of malachite green in methanol solution was about 1 ps. The transient absorption spectra and the dynamics were observed with a photonic multichannel analyzer (PMA; Hamamatsu Photonics) system with a dual MOS photodiode array (C6140) using an optical delay. The intensities of the probe light with and without the pump pulses were averaged with 20 measurements.

Electrochemical Measurement. Cyclic voltammograms were measured with a voltammetric analyzer (BAS CV-50W) using a glassy-carbon working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. All measurements were performed in acetonitrile solutions degassed with high-purity argon containing a substrate (1.0 mM) and tetraethylammonium perchlorate (0.1 M) as a supporting electrolyte.

Results and Discussion

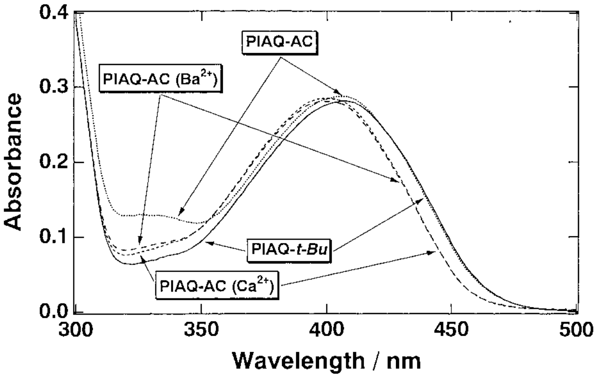

Figure 2. Absorption spectra of PIAQ−*t*-Bu and PIAQ−AC (25 μM) in acetonitrile before and after addition of metal salts (125 μM).

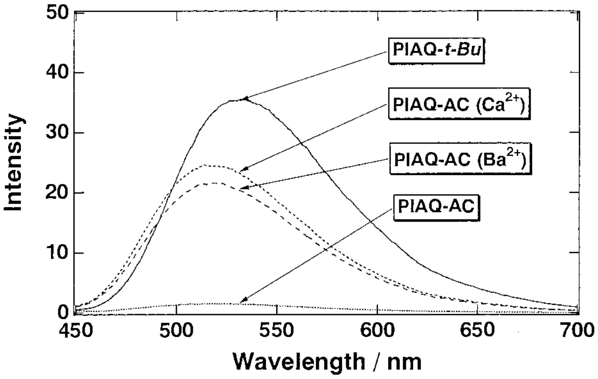

Figure 3. Fluorescence spectra of PIAQ−*t*-Bu and PIAQ−AC (25 μM) in acetonitrile excited at 400 nm before and after addition of metal salts (125 μM).

The absorption spectra of PIAQ−*t*-Bu and PIAQ−AC in acetonitrile solutions (25 μM) are shown in Figure 2. All compounds have absorption bands in the visible region with a peak at 405 nm due to the $\pi-\pi^*$ transition of the PIAQ chromophore. The absorption spectra were hardly affected by addition of various alkaline-earth metal salts to acetonitrile solutions of PIAQ−AC. The fluorescence spectra of PIAQ−*t*-Bu and PIAQ−AC in acetonitrile solutions (25 μM) are shown in Figure 3. PIAQ−*t*-Bu in acetonitrile solutions showed a very strong fluorescence with a peak at 529 nm by excitation of PIAQ chromophore. However, the fluorescence at 515 nm of metal-free PIAQ−AC in acetonitrile solutions was extremely weak. The fluorescence intensity was considerably enhanced upon binding of alkaline-earth ions (Ca^{2+} and Ba^{2+}) to the azacrown unit of PIAQ−AC, slightly depending on the metal ions as shown in Figure 3. The peak fluorescence intensity of metal-ion-bound PIAQ−AC was about 62−70% of that for PIAQ−*t*-Bu. Metal ions were found to be completely bound to PIAQ−AC at 5 times excess conditions.[13] These results suggested that slight fluorescence quenching still remained in metal-ion-bound PIAQ−AC.

de Silva et al. proposed that fluorescence quenching observed in the “fluorophore−spacer−receptor” was due to photoinduced intramolecular electron-transfer reactions on the basis of the consideration of the thermodynamic driving force (ΔG_{ET}).[3] The possibility of photoinduced intramolecular electron-transfer reactions from AC to excited PIAQ was investigated in a similar manner by a redox potentials measurement. The cyclic voltammograms for the reduction potential (E_{red}) of fluorophore (PIAQ) showed two reversible one-electron redox peaks. The first and the second reduction potentials were determined as −0.94 and −1.16 V (vs Ag/AgCl), respectively. The oxidation potential (E_{ox}) of the receptor (AC) in a cation-free state was estimated as +0.84 V (vs Ag/AgCl). The feasibility of photoinduced intramolecular electron-transfer reactions within this

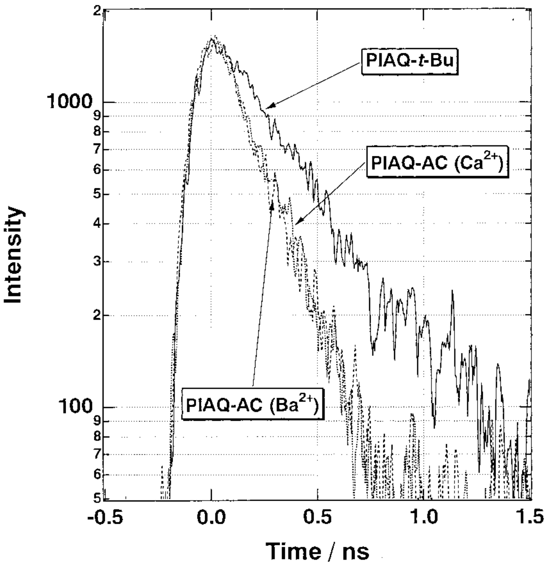

Figure 4. Fluorescence decay curves of PIAQ−*t*-Bu (25 μM) at 529 nm and PIAQ−AC with metal salts (125 μM) at 515 nm in acetonitrile solutions, excited with a 400 nm femtosecond laser pulse.

system can be assessed by means of the Rehm−Weller equation (eq 1).[19]

$$\Delta G_{\mathrm{ET}} = E_{\mathrm{ox}} - E_{\mathrm{red}} - \frac{e^2}{\epsilon r} - E_{00} \qquad (1)$$

The singlet energy of PIAQ (E_{00}) was calculated as 2.70 eV from the crossover point of the excitation and emission spectra. The attractive potential between the radical ion pair $-\ e^2/(\epsilon r)$ is approximately −0.1 eV.[20] Application of these values into eq 1 yields a ΔG_{ET} of −1.02 eV, which is a substantially negative value. It is thus indicated that the photoinduced intramolecular electron-transfer reaction is highly possible. When Ca^{2+} ions were bound, the values of E_{ox} and E_{00} were estimated to be 1.70 V and 2.67 eV, respectively. The E_{red} remained constant. Therefore, ΔG_{ET} was estimated as −0.13 eV, which suggested that the photoinduced intramolecular electron-transfer reactions might occur but with a much slower rate compared to the metal-ion-free condition.

The fluorescence decay curves of PIAQ−*t*-Bu and PIAQ−AC in acetonitrile solution (25 μM) excited with a femtosecond laser at 400 nm are shown in Figure 4. The decay for PIAQ−*t*-Bu is almost single exponential with a lifetime of 420 ps. The fluorescence lifetime of PIAQ−AC in acetonitrile solution in the absence of metal ions was too fast to be measured by our system. Meanwhile the fluorescence lifetime of PIAQ−AC in acetonitrile solution containing Ca^{2+} and Ba^{2+} was estimated from Figure 4 as 234 and 228 ps, respectively.

The time-resolved absorption spectra of PIAQ−*t*-Bu in acetonitrile (250 μM) femtosecond laser pulse excitation at 400 nm are shown in Figure 5a. Immediately after excitation, a transient absorption with peaks at 525 and 750 nm was observed. They showed a similar decay and disappeared after about 1 ns. The time profile of the transient absorption at 525 nm is shown in Figure 5b. The transient absorption at 525 nm of PIAQ−*t*-Bu decayed following single-exponential kinetics (τ = 470 ps) and an offset. The lifetime of the transient absorption almost agreed with the fluorescence lifetime, 420 ps, as shown in Figure 4. From these results, the transient absorption bands at 525 and 750 nm are attributed to the excited singlet state of the PIAQ chromophore. In the concomitant decrease of the absorption bands at 525 and 750 nm until about 1 ns, a new absorption with a peak at 460 nm appeared as shown in Figure 5a. The excited triplet anthraquinone was reported to show an absorption peak around 390 nm in acetonitrile.[21] Although no reports have been made on the excited triplet of imidazoanthraquinone or phenylimidazoanthraquinone, it is expected to show an absorption at longer wavelength due to increased delocalization. From these results, it was attributed to the excited triplet state of the PIAQ chromophore.

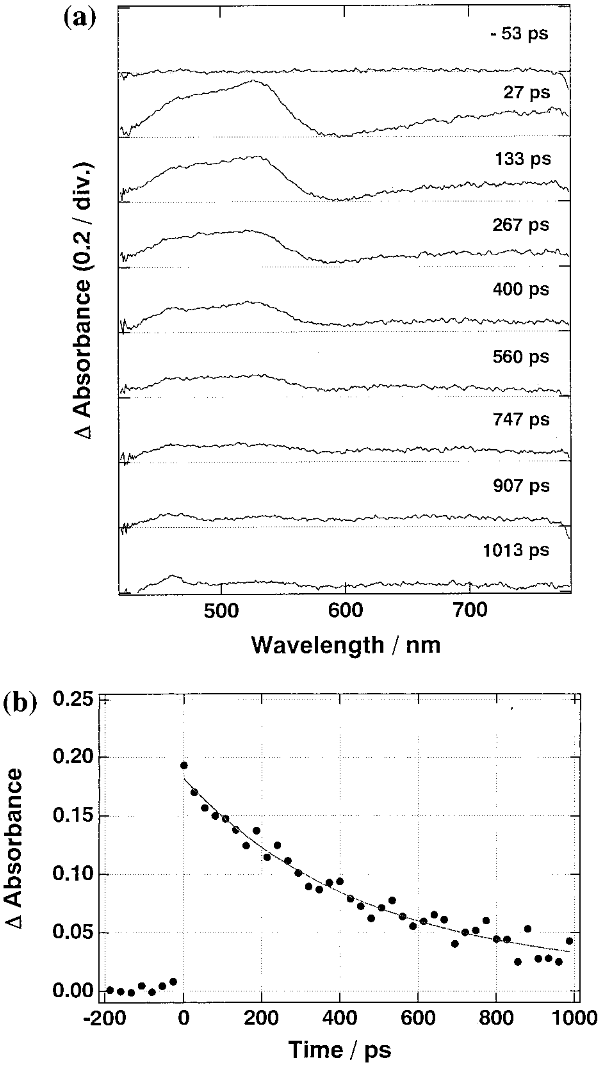

Figure 5. (a) Time-resolved transient absorption spectra of PIAQ−*t*-Bu in acetonitrile solution (250 μM), excited with a 400 nm femtosecond laser pulse. (b) Time profile of transient absorption at 525 nm of the same solution.

The transient absorption of PIAQ−AC in acetonitrile solution (250 μM) in the absence of metal ions was similar to that of the excited singlet of PIAQ−*t*-Bu shown in Figure 5a, but the decay was much faster. The time profile of the transient absorption at 500 nm of PIAQ−AC is shown in Figure 6. The decay of the transient absorption followed single-exponential kinetics (τ = 5.8 ps) with an offset. The time-resolved absorption spectra of PIAQ−AC in the absence of metal ions are shown in Figure 7 for a long time region. After the absorption bands at 500 and 750 nm decayed, a new absorption band with a peak at 610 nm was observed in addition to the absorption band at 460 nm due to the excited triplet PIAQ chromophore. This peak at 610 nm, which was not observed in PIAQ−*t*-Bu, almost disappeared until about 850 ps. The absorption bands of anion radicals of anthraquinone and tetraquinone were reported to show a peak at 543 and 595 nm, respectively.[22,23] Anion radicals

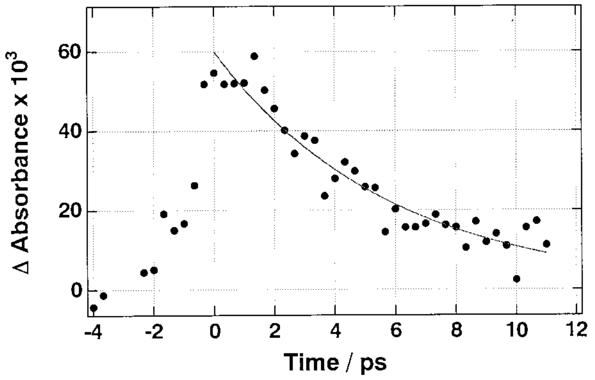

Figure 6. Time profile of transient absorption at 500 nm of PIAQ−AC in acetonitrile solution (250 μM), excited with a 400 nm femtosecond laser pulse.

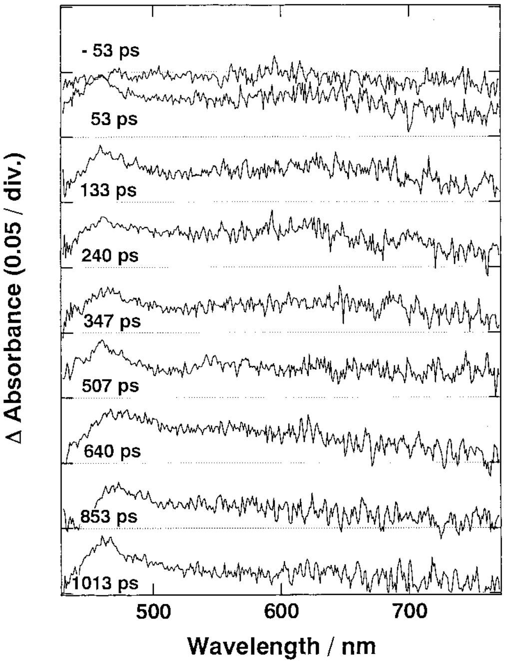

Figure 7. Time-resolved transient absorption spectra of PIAQ−AC in acetonitrile solution (250 μM), excited with a 400 nm femtosecond laser pulse.

of imidazoanthraquinone or phenylimidazoanthraquinone are again expected to show an absorption spectrum at longer wavelengths because of increased delocalization. From these results and the thermodynamic driving force mentioned above, the transient absorption species at 610 nm is most probably attributed to the phenylimidazoanthraquinone anion radical. The triethylamine radical cation, which is an equivalent of oxidized azacrown, showed a very broad weak absorption spectrum below about 380 nm.[24] Such shorter wavelength absorption is not detected in the present experiment even when the oxidized azacrown is found. The photoinduced electron-transfer reaction from AC to excited PIAQ was thus directly proved in PIAQ−AC.

Figure 8a shows the time-resolved absorption spectra of PIAQ−AC in acetonitrile solution (250 μM) in the presence of Ca^{2+} ion (1.25 mM). The result is very different from that shown in Figure 7 in the absence of metal ions. Transient absorption spectra up to about 267 ps resembled those for PIAQ−*t*-Bu shown in Figure 5a, which were attributed to the excited singlet PIAQ chromophore. The time profile of transient absorption at 500 nm was shown in Figure 8b, which was fitted with an exponential and an offset. The lifetime of the excited singlet PIAQ was estimated from it as 200 ps for PIAQ−AC (Ca^{2+}), which is much longer than that (5.8 ps) for metal-free PIAQ−AC. The lifetime of the transient absorption almost agreed with the fluorescence lifetime (234 ps) of PIAQ−AC containing Ca^{2+} ions shown in Figure 4. The lifetime of the excited singlet was increased to 200 ps, which strongly suggested that photoinduced electron-transfer reactions from AC to excited PIAQ were considerably inhibited by binding metal ions into AC. However, the absorption band of phenylimidazoanthraquinone anion radical due to the photoinduced electron transfer was slightly observed in Figure 8a in the presence of Ca^{2+} ions. Furthermore, the lifetime of the excited singlet of metal-ion-bound PIAQ−AC, estimated from time-resolved fluorescence and transient absorption, was shorter than that of PIAQ−*t*-Bu. These results can be attributed to the slightly negative value of ΔG_{ET} (− 0.13 eV) in metal-ion-bound PIAQ−AC. These results were also supposed by the fluorescence intensity shown in Figure 3 in the presence of metal ions.

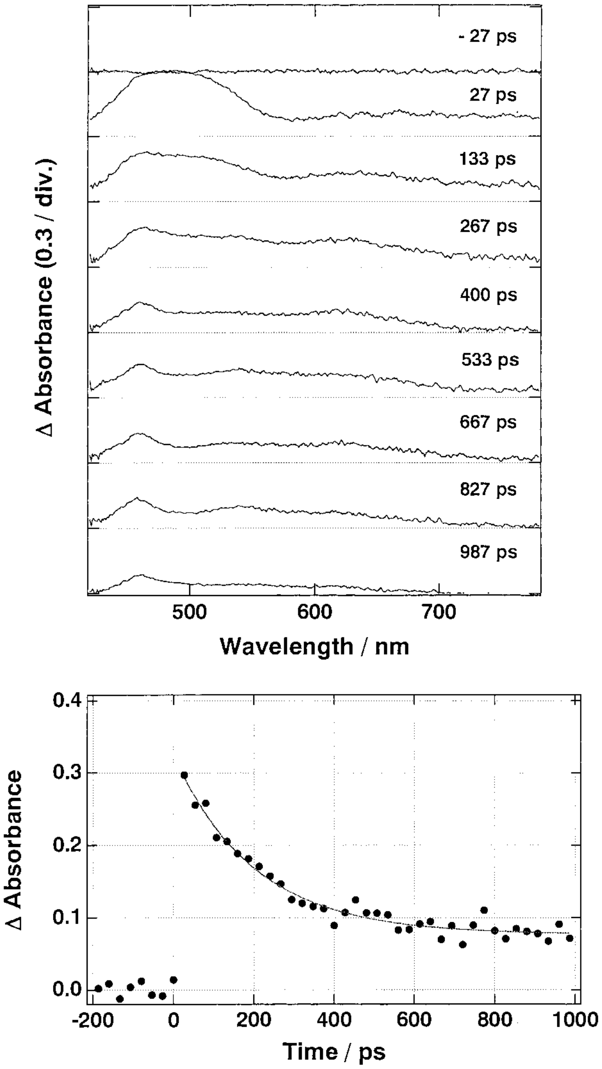

Figure 8. (a) Time-resolved transient absorption spectra of PIAQ−AC in acetonitrile solution (250 μM) in the presence of Ca^{2+} ion (1.25 mM), excited with a 400 nm femtosecond laser pulse. (b) Time profile of transient absorption at 500 nm of the same sample solution.

The reactions of PIAQ−AC after photoexcitation can be expressed in terms of the primary rate constants k_n, k_f, k_{isc}, and k_{et} according to eqs 2−7, where ^{1}PIAQ*−AC, ^{3}PIAQ*−AC, and $PIAQ^-$−AC^+ stand for the excited singlet state, the excited triplet state, and the charge-separated state, respectively.

$$k_0:\quad \mathrm{PIAQ{-}AC} \xrightarrow{h\nu} {}^1\mathrm{PIAQ^*{-}AC} \tag{2}$$

$$k_n:\quad {}^1\mathrm{PIAQ^*{-}AC} \rightarrow \mathrm{PIAQ{-}AC} + \Delta \tag{3}$$

$$k_f:\quad {}^1\mathrm{PIAQ^*{-}AC} \rightarrow \mathrm{PIAQ{-}AC} + h\nu_f \tag{4}$$

$$k_{isc}:\quad {}^1\mathrm{PIAQ^*{-}AC} \rightarrow {}^3\mathrm{PIAQ^*{-}AC} \tag{5}$$

$$k_{et}:\quad {}^1\mathrm{PIAQ^*{-}AC} \rightarrow \mathrm{PIAQ^-{-}AC^+} \tag{6}$$

$$k_b:\quad \mathrm{PIAQ^-{-}AC^+} \rightarrow \mathrm{PIAQ{-}AC} \tag{7}$$

The fluorescence quantum yields Φ_f for PIAQ−AC without and with Ca^{2+} ions are expressed by eqs 8 and 9:

$$\Phi_f = k_f/(k_n + k_f + k_{isc} + k_{et}) \tag{8}$$

$$\Phi_f(Ca^{2+}) = k_f/(k_n + k_f + k_{isc}) \tag{9}$$

The combination of eqs 8 and 9 leads to eq 10.

$$\Phi_f(Ca^{2+})/\Phi_f = 1 + k_{et}/(k_n + k_f + k_{isc})$$
$$= 1 + k_{et}\tau_s$$

Equation 10 can be solved for k_{et} by using the fluorescence quantum yields and the excited singlet lifetime. Φ_f and $\Phi_f(Ca^{2+})$ were estimated as 0.21×10^{-3} and 6.8×10^{-3}, respectively, using quinine sulfate in sulfuric acid (0.1 N) as the standard with $\Phi_f = 0.546$. On the basis of these values and $\tau_s(Ca^{2+}) =$ 200 ps, k_{et} was determined to be 1.57×10^{11} s^{-1}, which gives $\tau_{et} = 6.4$ ps. This value coincides well with the lifetime ($\tau_{et} =$ 5.8 ps) of the excited singlet observed for PIAQ−AC in the absence of metal ions. These results support the dynamic mechanism of PIAQ−AC fluorescence quenching due to photoinduced intramolecular electron-transfer controlled by metal ions.

Conclusion

The transient absorption of the excited singlet phenylimidazoanthraquinone (PIAQ) showed peaks at 500 and 750 nm. In the absence of metal ions, the excited singlet PIAQ decayed with a lifetime of 5.8 ps most probably because of the photoinduced electron-transfer reactions from AC ether to excited PIAQ. The absorption band at 610 nm was observed in PIAQ−AC in the absence of metal ions, which was attributed to the phenylimidazoanthraquinone anion radical that was observed. Upon addition of metal ions, the lifetime of the excited singlet was increased to 200 ps because of the considerable retardation of electron-transfer reactions. The present study directly proved, for the first time, the mechanism and dynamics of fluorescent chemosensors based on intramolecular photoinduced electron transfer where the fluorescence from a locally excited state of PIAQ is dramatically controlled by the metal cations complexed to the AC unit attached to the PIAQ unit.

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