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# Proton-induced Quenching of Methoxynaphthalenes Studied by Laser Flash Photolysis and Inclusion Effect of β-Cyclodextrin on the Quenching

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Proton-induced quenching in both excited singlet and triplet states of methoxynaphthalenes in $H_2O$-$CH_3CN$ mixtures has been studied by means of laser flash photolysis. Inclusion effect of β-cyclodextrin (βCD) on the proton-induced quenching has been also examined. It is shown that the proton-induced quencing (the rate constant ${}^1k_q$) of 1-methoxynaphthalene (1RH) occurs effectively in the excited singlet state, but not in the triplet state on the basis of the $T_n \leftarrow T_1$ absorption measurements. There is no enhancement of triplet formation *via* the proton-induced quenching since the ${}^1k_q$ value obtained by the $T_n \leftarrow T_1$ absorption measurements agrees with that obtained by fluorimetry. It was unsuccessful to observe a protonated σ-complex produced by the excited-state protonation to the naphthalene ring. The 1:1 inclusion complex between 1RH and βCD is produced with the association constant $K_g$ (=27 mol$^{-1}$ dm$^3$ at 300K). In the presence of βCD, the ${}^1L_b$ character of 1RH increases in the fluorescent state and the proton-induced quenching of 1RH markedly decreases, which may be due to inclusion and environmental effects of βCD upon the behavior in the excited state of 1RH. As for 2RH having little or no intramolecular CT character (${}^1L_a$), there is no proton-induced quenching.

Proton association and dissociation in the excited state of aromatic compounds are elementary processes in chemistry. The acid-base properties in the excited state of aromatic compounds are closely related to electronic structure, which is considerably different from that in the ground state. A number of studies on the acidity constants p$K_a$* in the excited state of aromatic compounds have been reported showing that the p$K_a$* values are significantly different from the acidity constants in the ground state.[1–9] It is well-known that the p$K_a$* values can be estimated by means of the Förster cycle,[1–3,10] the fluorescence titration curve,[2,3] and the triplet-triplet absorbance titration curve.[11] These methods involve the assumption that proton transfer in the excited state is very fast, resulting in establishment of an acid-base equilibrium during the lifetime in the excited state.

However, it has been shown recently that proton-induced quenching (${}^1k_q$) is competitive with the proton transfer reaction in the excited state of naphthylamines (that is, simple acid-base equilibrium cannot be attained during the lifetime in the excited state of aromatic amines) and that a dynamic analysis containing the quenching process is, therefore, needed in order to obtain the accurate p$K_a$* values.[12] The dynamic analyses by means of nanosecond time-resolved spectroscopy with fluorimetry have been applied to 1-pyrenyl amine,[13] 1-anthrylamine,[14] phenanthrylamines,[15] and naphthols.[16] The Stuttgart group[17] has supported our method to determine the p$K_a$* values of naphthylamines. Similar experiments for excited naphthols have been reported by Harris and Selinger.[18] Establishment of prototropic equilibria at moderate acid conditions has been reported in the excited singlet state of 2-naphthol-6,8-disulfonate[19] and in the triplet states of benzophenone[20] and phenyl alkyl ketones.[21] For the triplet state, its lifetime is relatively long enough to accomplish the prototropic equilibrium.[21]

Thus, the proton-induced quenching is a very important process in the prototropic reaction in the excited state. For the quenching mechanism a complex in which a proton is shared between excited 2-naphthylamine and one water molecule[22] or a hydrated naphthylammonium cation in the ground state[23] was assumed as an intermediate for the quenching. However, it has been demonstrated that the proton-induced quenching proceeds *via* electrophilic protonation at one of carbon atoms of the aromatic ring in the excited singlet state, leading to proton exchange (or isotope exchange).[24] An intramolecular CT structure in the excited state is responsible for the quenching.[15,24,25] A linear relationship between the ${}^1k_q$ values and the charge densities in the excited state of aromatic compounds has been shown.[25]

In the course of a study on the excited-state proton transfer reaction,[26] we became interested in the proton-induced quenching of methoxynaphthalenes studied by laser flash photolysis in order to establish the proton-induced quenching mechanism. Inclusion effect of βCD on the quenching has been also examined. This work was studied to answer the following questions:
(1) Is there any enhancement of triplet formation induced by the quenching? (2) Is there any proton-induced quenching in the triplet state? (3) Is there any transient produced by protonation in the excited

state? (4) What is the relation between electronic structure and proton-induced quenching? and (5) What about the inclusion efect of βCD upon both the quenching and the fluorescent state?

## Experimental

*Materials.* Both 1- and 2-methoxynaphthalenes were the same as those reported elsewhere.[24] β-Cyclodextrin (Wako) and $H_2SO_4$ (97%, Wako) were used without further purification. Deionized water was distilled. Acetonitrile (reagent grade) was purified by the usual method.[27] The actual acid contents were determined by titration. Acetonitrile and water mixtures (1:4 or 4:1 by volume) were used as solvents. All samples were thoroughly degassed by freeze-pump-thaw cycles on a high vacuum line.

*Absorption and Fluorescence Measurements.* Absorption and fluorescence spectra were recorded with a Hitachi 200-10 spectrophotometer and a Hitachi M850 spectrofluorimeter respectively. The spectral corrections for the emission were made.

*Nanosecond Laser Flash Experiments.* Laser flash photolysis studies were carried out by using a $Nd^{3+}$-YAG laser equipped with a forth harmonic (266 nm) generator. The duration of a laser pulse was approximately 20 ns. The detection system for measurements of transient spectra consisted of a 150 W xenon lamp (Ushio UXL 150-D) as an analyzing light source, a monochromator (Ritsu Model MC-20N), a photomultiplier (Hamamatsu R758) and a transient memory (Kawasaki Electronica, MR-50E). The analyzing light beam was intensified by a factor of *ca.* 20 during the detection of the transient spectra. The transmitted light beam through a sample cell (10 mm) was led into the entrance slit of the monochromator. The output from the photomultiplier attached to the exit slit of the monochromator was recorded on the transient memory.

## Results and Discussion

*Proton-induced Quenching of Methoxynaphthalenes Studied by Laser Flash Photolysis.* Figure 1 shows the transient absorption spectra of (a) 1-methoxynaphthalene (1RH), (b) 1RH in the presence of acid ($[H_2SO_4]=0.5\ mol\ dm^{-3}$), and (c) 2-methoxynaphthalene (2RH) in $CH_3CN$-$H_2O$ (4:1) mixtures, obtained by laser flash photolysis at 266 nm. These spectra with peaks of 435 nm (1RH) and 430 nm (2RH) were assigned to those of $T_n \leftarrow T_1$ transitions, since they were the same as the $T_n \leftarrow T_1$ absorption spectra obtained by the triplet sensitization by acetophenone at 337 nm as can be seen in Fig. 1(d). These transient spectra were quenched effectively by dissolved oxygen. The absorbance of the $T_n \leftarrow T_1$ transient spectrum of 1RH was decreased with increasing the concentration of protons without any spectral change [*e.g.*, Fig. 1(b)]. However, for 2RH no change in the $T_n \leftarrow T_1$ absorbance dependent upon the concentration of protons was observed. The Stern-Volmer Plots of $A_T^0/A_T$ *vs.* $[H_3O^+]$ are shown in Fig. 2(a) and (b) for 1RH and 2RH respectively. Straight lines are obtained indicating that Eq. 1 fairly holds.

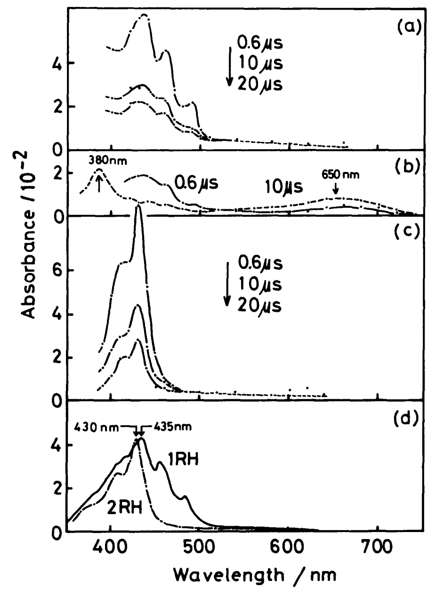


Fig. 1. Transient absorption spectra of (a) 1RH ($4.4\times10^{-4}\ mol\ dm^{-3}$), (b) 1RH ($4.4\times10^{-4}\ mol\ dm^{-3}$) in the presence of acid ($[H_2SO_4]=0.5\ mol\ dm^{-3}$), and (c) 2RH ($1.3\times10^{-3}\ mol\ dm^{-3}$) in $H_2O$-$CH_3CN$ (1 : 4) mixtures obtained by laser flash photolysis at 266 nm. (d) Reference $T_n \leftarrow T_1$ transient spectra of RH's ($2.5\times10^{-3}\ mol\ dm^{-3}$) obtained by triplet sensitization of acetophenone ($3\times10^{-2}\ mol\ dm^{-3}$) at 1 μs after laser pulsing at 337 nm.

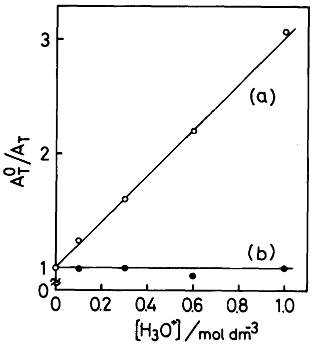


Fig. 2. Plot of $A_T^0/A_T$ of 1RH (a) or 2RH (b) as a function of $[H_3O^+]$. For detail, see text.

$$\frac{A_T^0}{A_T} = 1 + {}^1k_q\tau_0[H_3O^+] \qquad (1)$$

where $A_T$ and $A_T^0$ denote the $T_n \leftarrow T_1$ absorbances at the transient peaks at the delay time=100 ns with and without protons respectively, ${}^1k_q$ the rate constant for the proton-induced quenching in the excited singlet state, and $\tau_0$ the fluorescent life-time of methoxynaphthalenes. From the slope (a) in Fig. 2, the ${}^1k_q$ value is determined to be $1.5\times10^8\ mol^{-1}\ dm^3\ s^{-1}$ for

1RH using $\tau_0$=12.6 ns,[24] which is the same as that ($1.6\times10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$) obtained by fluorescence intensity measurements[24] within the experimental errors. As for 2RH, the $^1k_q$ value is very small (less than $1\times10^5$ mol$^{-1}$ dm$^3$ s$^{-1}$). The time trace of the transient $T_n\leftarrow T_1$ absorption monitored at the transient peaks are shown in Fig. 3, which decays with a single exponential function. The triplet lifetimes of 1RH and 2RH are obtained to be 10.2 (±0.4) and 10.2 (±0.2) μs, respectively. The triplet lifetimes were scarcely affected by protons, suggesting that there is little or no proton-induced quenching in the triplet state.

The introduction of electron-donating groups such as amino, hydroxyl, and methoxyl groups into the aromatic ring causes electron migration from the substituents to the ring in the excited singlet state.[28,29] This tendency is enhanced by solvation of the excited species in polar media, and the excited molecule has an intramolecular CT structure. As a result, the basicity of the aromatic ring increases appreciably in the excited state. This is the reason why the intramolecular CT structure is responsible for the proton-induced quenching.[15,24,25] The CT character in the excited species having electron-donating moieties at the $\alpha$-position of the naphthalene ring is larger than that at the $\beta$-position. In contrast, there is no CT character in the lowest triplet state of 1RH, resulting in little or no proton-induced quenching.[24] Therefore, the proton-induced quenching (*i.e.*, protonation to the carbon atoms of the aromatic ring) is attributed to a typical electrophilic reaction.[24,26] A possibility of enhancement of intersystem crossing due to the proton-induced fluorescence quenching was assumed in an early stage of this study.[30] The anion-induced quenching of aromatic compounds is to be the case.[31,32] However, the possibility for enhancement of triplet formation was completely ruled out since the $^1k_q$ value obtained by the $T_n\leftarrow T_1$ absorbance of 1RH agrees with that fluorimetry[24] as described above. It has been pointed out that there is relatively little correlation between $^1k_q$ and $I_P^*$ [the ionization potential for the excited singlet state of aromatic compounds ($^1A^*$) estimated from $I_P$ (ionization potential for the gorund state ($^1A$)) minus $E_A{}^\circ$ (0-0 transition energy for $^1A^*-^1A$)].[24] The quenching mechanism of $^1A^*$ by protons is different from that by inorganic anions $X^-$. The former involves a chemical interaction (protonation) at one of carbon atoms of the aromatic ring and the latter involves an electron transfer (or charge transfer).[31,32] An electronic interaction between $^1A^*$ and $H^+$ (or $D^+$) in the quenching is locally restricted to one of carbon atoms of the aromatic nucleus. This may be due to the following reasons: the radius of the proton ($10^{-5}$ A)[33] is too small to overlap widely with the $\pi$-electronic system of $^1A^*$ compared to those of $X^-$ (1.5—3 Å), and electrostatic and covalent interactions between $H^+$ [or $D^+$) and the proper carbon atom of $^1A^*$ become large enough to produce bond formation.[24] The experimental results can be accounted for by a schematic energy-state diagram in Fig. 4, showing that the proton-induced quenching $^1k_q$ occurs in the fluorescent state ($^1L_a$), but not in the $T_1$ state.

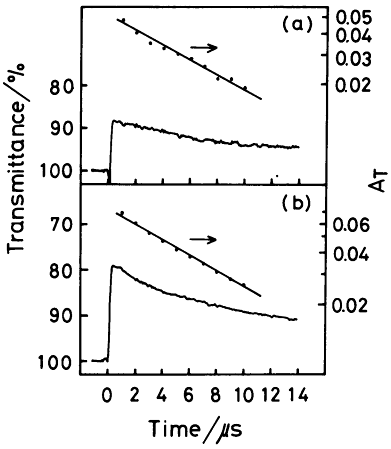


Fig. 3. Time traces of the transient $T_n\leftarrow T_1$ absorptions of 1RH (a) 2RH (b) monitored at 435 and 430 nm respectively, obtained by laser flash photolysis at 266 nm. The semilogarithmic plot of absorbance ($A_T$) gives a straight line, showing that the triplet species decays with a single exponential function. For the decay kinetics of 1RH, the absorbance ($1.26\times10^{-2}$) due to a transient having a long lifetime was subtracted from the absorbance at 435 nm. Similary, for 2RH the absorbance ($2.47\times10^{-2}$) due to a transient having a long lifetime was substracted from the absorbance at 430 nm. These absorbances may be due to photoproducts of RH.

Unfortunately, the detection of a protonated $\sigma$-complex produced by electrophilic attack mainly at position 5 of the excited 1RH was unsuccessful in the present laser flash experiments. This may be due to that the transient $\sigma$-complex may have a very weak absorption in the observed wavelength region and/or that its lifetime may be too short to detect the transient absorption. Anyway, it is unknown at the

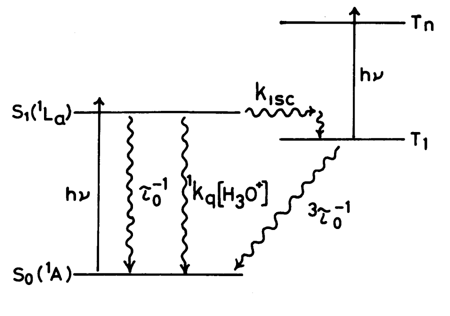


Fig. 4. A schematic energy-state diagram for the proton-induced quenching ($^1k_q$) of 1RH. For details, see text and Ref. (24).

present stage. A very weak absorption appeared in the longer wavelength region with a peak of 650 nm in the presence of protons, as shown in Fig. 1(b). The buildup time of the transient absorption was about 1 μs. The weak transient spectrum is very similar to that of the cation radical of 1RH.[34] It is obvious that this transient is not produced directly from the excited singlet state of 1RH because the rise (1 μs) and decay ($\tau_0$=12.6 ns) times are different from each other. There was no 650 nm transient formation without acid. Therefore, protons should be needed for formation of the longer wavelength transient. For direct excitation of 2RH, no 650 nm transient was observed. Further investigation on the transient species will be needed in future.

*Inclusion Effect of β-Cyclodextrin on Proton-induced Quenching of 1RH.* It has been demonstrated that the proton-induced quenching of 1RH proceeds *via* electrophilic protonation at the proper carbon atom of the aromatic ring in the lowest excited singlet state ($^1L_a$) in polar media, leading to proton exchange or isotope exchange mainly at position 5 (slightly at position 8) of the naphthalene ring.[24] Therefore, it was expected that if position 5 (or position 8) of the naphthalene ring would be protected by β-cyclodextrin the proton-induced quenching might decrease significantly. It is known to produce a 1:1 inclusion complex of β-cyclodextrin (βCD) with naphthalene derivatives.[35,36]

At first, spectroscopic studies of 1RH in the presence of βCD have been carried out. Figure 5(a) shows the absorption spectra of 1RH ([1RH]=1.4×10$^{-4}$ mol dm$^{-3}$) in a $H_2O$-$CH_3CN$ (4:1) mixture with(1) and without(2) βCD ([βCD]=2×10$^{-2}$ mol dm$^{-3}$); the differential spectrum of 1RH with and without βCD ([βCD]=2×10$^{-2}$ mol dm$^{-3}$) is also depicted in Fig. 5(b). An isosbestic point was observed at 282 nm at various concentrations of βCD, reflecting an equilibrium:

$$1RH + \beta CD \rightleftharpoons (1RH-\beta CD) \qquad (2)$$

The association constant in the ground state $K_g$ (=[1RH−βCD]{[1RH][βCD]}$^{-1}$), is calculated by[35]

$$(A_\lambda - A_\lambda^0)/C_\beta = K_g(A_\lambda^\infty - A_\lambda) \qquad (3)$$

where $C_\beta$ represents the concentration of βCD, $A_\lambda^0$, $A_\lambda$, and $A_\lambda^\infty$ stand for the absorbances of nil, $C_\beta$, and $\infty$, respectively. Figures 6 shows a plot of $(A_\lambda - A_\lambda^0)/C_\beta$ as a function of $A_\lambda$ at $\lambda$=300 nm at 300 K. The value of $K_g$ is determined to be 27 mol$^{-1}$ dm$^3$ from the slope.

The fluorescence spectra of 1RH([1RH]=1.4×10$^{-4}$ mol dm$^{-3}$) (1) with and (2) without βCD ([βCD]=2×10$^{-2}$ mol dm$^{-3}$) in $H_2O$-$CH_3CN$ (4:1) mixtures are also shown in Fig. 5(a). In the case of (1), the concentration of the 1RH-βCD complex is estimated to be 4.9×10$^{-5}$ mol dm$^{-3}$ at 300 K, which corresponds to 35% of the total concentration of 1RH (1.4×10$^{-4}$ mol dm$^{-3}$). The maximum concentration of βCD to add to the system is ≈2×10$^{-2}$ mol dm$^{-3}$, since the molecular weight of βCD is extremely large (1135) and its solubility is restricted. However, the effect of βCD on the fluorescence properties and the proton-induced quenching of 1RH were distinct. The fluorescence intensity at longer wavelengths decreases when βCD is added as shown in Fig. 5. It suggests that the addition of βCD decreases intramolecular CT character ($^1L_a$) in the excited state. The fluorescence quantum yield and apparent lifetime of 1RH in the presence of βCD (2×10$^{-2}$ mol dm$^{-3}$) in $H_2O$-$CH_3CN$ (4:1) were obtained to be 0.38 and 10.6 ns at 300 K, respectively. By addition of βCD to the system, the fluorescence quantum yield slightly decreased compared to that (0.43)[24] of free 1RH, whereas the lifetime became long in comparison with that (8.9 ns)[24] of free 1RH. It is noteworthy that the fluorescence spectrnm of 1RH with βCD is similar to that of free 1RH in less polar or nonpolar media. The vibrational structures of emission from the $^1L_b$ state (the locally excited state) appear at the shorter wavelengths with a peak of 338 nm. This observation can be explained in terms of a model of the 1RH-βCD inclusion complex, in

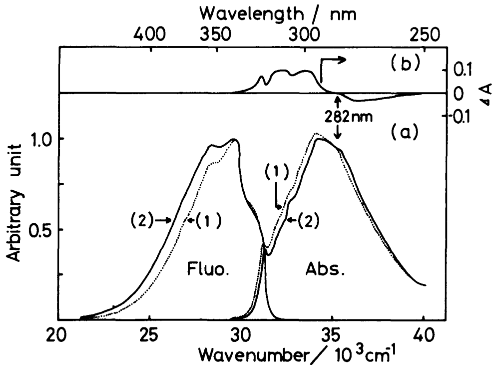


Fig. 5. (a) Absorption and fluorescence spectra of 1RH (1.4×10$^{-4}$ mol dm$^{-3}$) in $H_2O$-$CH_3CN$ (4 : 1) (1) with and (2) without βCD ([βCD]=2×10$^{-2}$ mol dm$^{-3}$). (b) The differential absorption spectrum of 1RH between (1) and (2). For detial, see text.

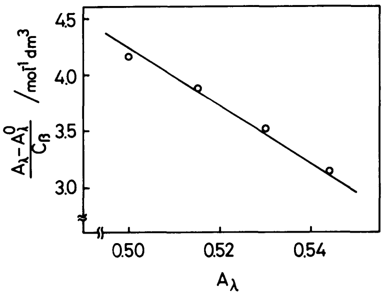
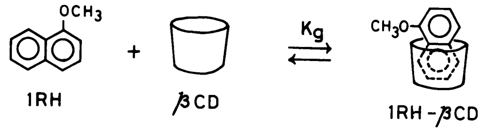


Fig. 6. Plot of $(A_\lambda - A_\lambda^0)/C_\beta$ *vs.* $A_\lambda$ at 300 K, where $\lambda$ is 300 nm. For detial, see text.

which a part of the naphthalene ring of 1RH (*i.e.*, positions 5 and 8) may be included as shown in Eq. 4:



(4)

A similar Corey-Pauling-Kolton molecular model has been proposed recently by Tran and Fendler.[36]

Electron migration from the methoxy group to the naphthalene ring decreases in the excited 1RH-βCD complex, since solvation of the excited 1RH [positions 5 and 8 having large charge densities in the excited state ($^1L_a$)][24] with polar solvent molecules may be prevented by βCD inclusion. As a result, the 1RH-βCD complex behaves as if it were in less polar media.

The plots of $I_0/I$ *vs.* [$H_3O^+$] are shown in Fig. 7, where $I$ and $I_0$ are the fluorescence intensities at 338 nm with and without protons respectively and (a) and (b) denote the absence and presence of βCD ([βCD]=$2\times10^{-2}$ mol dm$^{-3}$) respectively. This result shows that the proton-induced fluorescence quenching of 1RH ($^1k_q=1.1\times10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$) decreases markedly in the presence of βCD. This fact shows that the reactive positions [mainly 5 and slightly 8 in the excited state ($^1L_a$)] of 1RH are efficiently blocked by βCD inclusion. However, the experimental results of the fluorescence and proton-induced quenching cannot be explained only by the effect of the complex formation. In addition to this, one may take into account an environmental effect of βCD upon both fluorescence properties and the proton-induced quenching rate of 1RH, since the 1RH-βCD complex formation is 35% under the experimental conditions as described above. Probably, 1RH may be surrounded by βCD molecules, resulting in that the $^1L_b$ character of 1RH increases in the excited state. It should be noted that the $^1L_b$ state (locally excited state) is not susceptible of protons, as shown previously.[24]

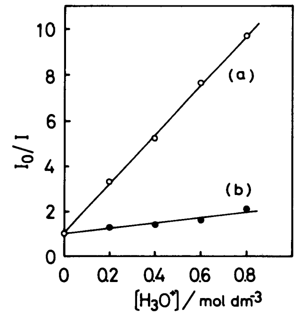


Fig. 7. Plots of $I_0/I$ of 1RH at 338 nm *vs.* [$H_3O^+$] in $H_2O$-$CH_3CN$ (4 : 1) (b) with and (a) without βCD ([βCD] = $2\times10^{-2}$ mol dm$^{-3}$).

## Summary

(1) The $T_n\leftarrow T_1$ absorbance of 1RH at 435 nm obtained by laser flash photolysis decreases considerably with increasing the concentration of protons, while its triplet lifetime (10.2 μs) is scarcely affected by protons, showing that the proton-induced quenching occurs in the excited singlet state, but not in the triplet state. There is no enhancement of triplet formation *via* the proton-induced quenching on the basis of the result that the $^1k_q$ value ($1.5\times10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$)in $H_2O$-$CH_3CN$ (1:4) at 300 K obtained by the $T_n\leftarrow T_1$ absorption measurements is nearly equal to that ($1.6\times10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$) obtained by fluorimetry[24] within the experimental errors. Unfortunately, the protonated σ-complex cannot be detected under the experimental conditions.

(2) The 1:1 complex between 1RH and βCD is produced with the association constant $K_g$ (27 mol$^{-1}$ dm$^3$ in $H_2O$-$CH_3CN$ (4:1) at 300 K). In the presence of βCD ($2\times10^{-2}$ mol dm$^{-3}$) the $^1L_b$ character of 1RH increases in the fluorescent state and the proton-induced quenching of 1RH markedly decreases. These effects of βCD may be due to not only the inclusion effect of βCD, but also the environmental effect of βCD upon the behavior of the excited 1RH species. The intramolecular CT character ($^1L_a$) in the excited state of 1RH also decreases by the βCD inclusion.

(3) For 2RH, proton-induced quenching in the lowest excited singlet state is scarcely observed. The difference in the quenching between 1RH and 2RH is caused by that in electronic structures in the excited singlet state; the former has an intramolecular CT structure ($^1L_a$), but not for the latter ($^1L_b$). It is confirmed that the intramolecular CT structure in the excited state is responsible for the proton-induced quenching.

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