Photoinduced Proton Transfer in 2-(2′-Hydroxynaphthalenyl)-benzoxazole: Observation of Fluorescence with a Small Stokes Shift Induced by Excited-State Intramolecular Proton Transfer

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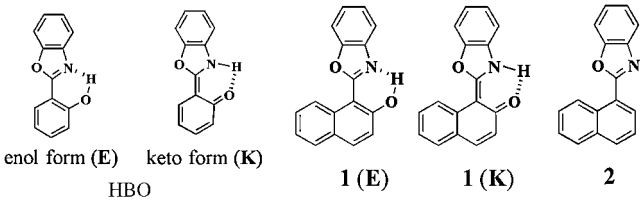
2-(2′-Hydroxynaphthalenyl)benzoxazole (**1**) emits fluorescence with small Stokes shift from its excited tautomer (**K***), produced by excited-state intramolecular proton transfer. Intramolecular hydrogen bonding may be responsible for this phenomenon on comparison with the results of 2-(2′-hydroxyphenyl)benzoxazole (HBO) and 2-(naphthalene-1-yl)benzoxazole (**2**) as a reference compound.

Intramolecular hydrogen-bonded molecules such as salicylates, oxazoles, and flavones have been known to exhibit excited-state intramolecular proton (or hydrogen atom) transfer in the singlet excited state (ESIPT).[1–4] ESIPT is a photo-tautomerization that yields an excited-state keto form (**K***) from the starting stable enol form (**E**) within 50 fs for salicylates, triazoles, and flavones.[5–8] The excited-state keto form relaxes radiatively to give a fluorescence spectrum with a large Stokes shift or nonradiatively to the ground-state keto form, which undergoes thermal re-enolization to give the stable original enol form.[9–12] The structural differences between light-absorbing species **E** and emitting species **K** in this reaction cycle result in a large Stokes-shifted fluorescence at longer wavelength and therefore is not reabsorbed even at high concentrations of chromophore. However, precise control of ESIPT by chemical modification allows us to make specific applications.[13,14]

The photochemistry of many 2-(2′-hydroxyphenyl)benzoxazole (HBO) analogs (Scheme 1), which undergo ESIPT, has been investigated experimentally and theoretically,[15–19] due to its chemical stability, structural simplicity, and facility for chemical modification.[6,20,21] Despite their unique character, practically important spectral properties depending on structural differences are still obscure. Recently, we reported the meta-effect on the photochemistry of HBO derivatives; i.e., the substituent position of methoxy groups strongly affects their photochemical behavior.[22] Because of the lack of experiments on the naphthyl analog of HBO, 2-(2′-hydroxynaphthalenyl)-benzoxazole (**1**)[23] was employed as naphthalene-fused HBO analogs. 2-(Naphthalene-1-yl)benzoxazole (**2**)[24] was also used as a model compound that does not form intramolecular hydrogen bonding. Here, we report fluorescence of **1** with unusually small Stokes shift.



Scheme 1. Chemical structures of HBO and its tautomer; enol form (**E**) and keto form (**K**), **1**, and **2**.

Results and Discussion

The absorption, fluorescence emission and excitation spectra of **1**, HBO, and **2** were measured in toluene at room temperature under argon. Compound **1** exhibited absorption bands at $\lambda_{max} = 361$ nm and $\lambda_{max} = 378$ nm (shoulder), which is red-shifted as compared to that of HBO ($\lambda_{max} = 335$ nm) because of extended π-conjugation caused by the aromatic ring expansion. Compound **1** showed dual fluorescence having maxima at 400 and 460 nm (Figure 1a) with the Stokes shift of 1460 and 4720 cm^{-1}, respectively. Unlike compound **1**, HBO exhibited sole fluorescence with a large Stokes-shift (10170 cm^{-1}) with a maximum at 508 nm (Figure 1b). Compound **2**, of which the structure is similar to that of **1** but has no intramolecular hydrogen bonding, gave fluorescence with the Stokes shift as small as 710 cm^{-1} (Figure 1c). The spectroscopic data including the values of Stokes shift and the fluorescence quantum yield are summarized in Table 1. Table 1 also lists the corresponding HOMO and LUMO energies calculated with density functional theory method (DFT) at B3LYP/6-31G* level.

In general, the expansion of the aromatic rings results in the red-shift of both absorption and fluorescence bands. Therefore, the absorption and fluorescence bands of **1** are expected to appear at longer wavelengths than those of HBO. Actually, the absorption maximum of **1** was observed at longer wavelength (378 nm) than that of HBO (335 nm). However, the major emission band of **1** in Figure 1a was located at much shorter wavelength (460 nm) than that of HBO (508 nm) in Figure 1b. In addition, **1** showed emission at shorter wavelength (400 nm) with smaller Stokes shift (1460 cm^{-1}). The light absorbing form of **1** and HBO are assumed to be **E**, since a single component is recognized in NMR spectra, and in more detail, the shape of the fluorescence excitation spectrum agreed with that of the absorption spectrum of **E**, which indicates the light emitting species of **1** and HBO are produced by single light-absorbing species. The fluorescence spectrum of HBO maximized at 508 nm was ascribed to the tautomer of HBO, resulting from ESIPT.[25,26] The observation of the dual fluorescence located at 400 and 460 nm for **1** indicates that the former and latter fluorescence can be assigned to the

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Table 1. Summary of the Spectroscopic Properties of **1**, HBO, and **2** in Toluene at Room Temperature under Argon Atmosphere, and HOMO–LUMO Energy Gaps of **1** and HBO Calculated by Density Functional Theory (DFT) at B3LYP/6-31G* Level

	λ_{max}^{abs}/nm	λ_{max}^{FL}/nm	Stokes shift/cm^{-1}	Φ_f	HOMO–LUMO gap/eV		
					E	**K**	**E–K**
1	378	460	4720	0.003	3.85	3.59	0.26
HBO	335	508	10170	0.02	4.36	3.53	0.83
2	353	362	710	0.56	—	—	—

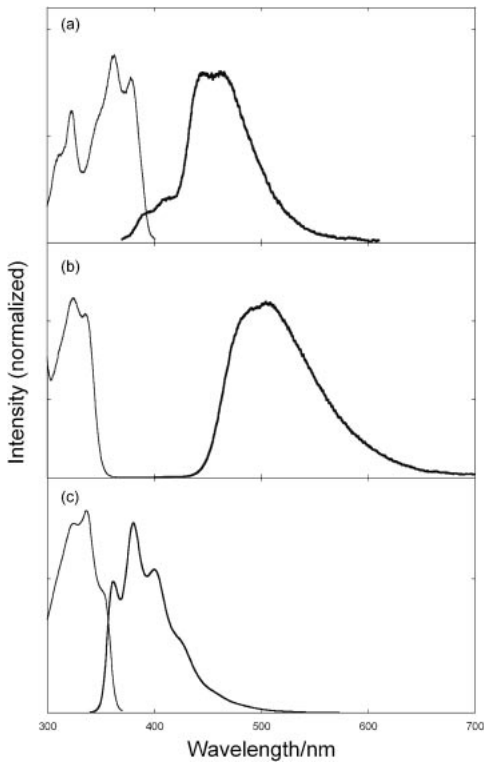

Figure 1. Fluorescence (FL) and the fluorescence excitation (FLE) spectra of (a) **1**, (b) HBO, and (c) **2** (1×10^{-6} M) in toluene under argon. Fluorescence spectra were measured with excitation at 380, 335, and 330 nm for **1**, HBO, and **2**, respectively. Fluorescence excitation spectra were measured monitoring the fluorescence emission at 450, 500, and 380 nm for **1**, HBO, and **2**, respectively.

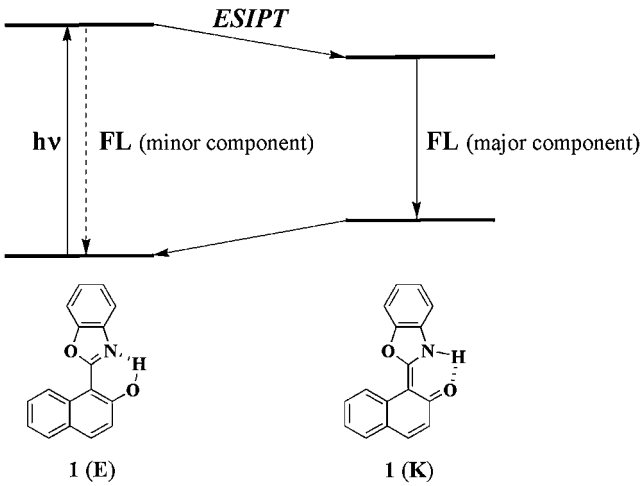

Figure 2. Energy diagram and the chemical structure of **1** and its tautomer.

fluorescence from the **E*** and **K*** of **1** (Figure 2). The possible emission species of the fluorescence spectra of **1** in Figure 1a are **E***, **K*** and the excited-state anion **E**$^{-}$*. However, the fluorescence emission from **E**$^{-}$*, produced by excited-state protolysis, is usually negligible in non-polar solvents such as toluene and is excluded from the possible species of fluorescence in Figure 1a. These assignments are also supported by the observation of the emission with considerably small Stokes shift (710 cm^{-1}) of the model compound **2**. Thus, **K*** gave fluorescence at 460 and 508 nm, respectively, for **1** and HBO, even if the absorption maximum appeared at shorter wavelength in HBO (335 nm) as compared to **1** (378 nm).

To gain insights into the considerable small Stokes shifted fluorescence from **K*** of **1**, we calculated the HOMO–LUMO energy gaps of **E** and **K** for both **1** and HBO, respectively, by density functional theory (DFT) at B3LYP/6-31G* level.[27] We can compare the HOMO–LUMO gap energies of **E** and **K** forms of each compound and can expect that the HOMO–LUMO gap energy of **1** is smaller than that of HBO. As Table 1 shows, the HOMO–LUMO energy gaps were calculated to be 3.85 (**E**) and 3.59 (**K**) eV for **1**, and 4.36 (**E**) and 3.53 (**K**) eV for HBO, respectively. The difference in HOMO–LUMO gap between **E** and **K** (ΔE) for **1** (0.26 eV) was smaller than that for HBO (0.83 eV). Therefore, the calculation supports the small Stokes shift of **1** as compared to HBO. The above discussion that the Stokes shift values could vary in similar ESIPT molecules depending upon small molecular structural change should be useful for developing fluorescent molecules with varying emission wavelength.

The fluorescence efficiency of HBO compounds is generally low because of the existence of efficient non-radiative processes of **K***, due to the photochemical E–Z isomerization to give *Z*-keto isomer.[28,29] In the case of **1**, the Φ_f value ($\Phi_f = 0.003$) is even one-order of magnitude smaller than that of HBO ($\Phi_f = 0.02$). The fluorescence lifetime of **1** was 22 ps in toluene, which is much shorter than that of HBO, reported to be 280 ps in non-polar solvent.[30] The shorter fluorescence lifetime of **1** indicates that the non-radiative process of **K*** is more efficient in **1** than in HBO, and/or a very fast non-radiative process from **E*** of **1** exist.

In summary, we can successfully observe unusually small Stokes shifted fluorescence from the excited tautomer (**K***) produced by ESIPT. These findings will be important information for the construction of fluorescent molecules exhibiting emission spectra at appropriate wavelength and color.

Experimental

Materials. All the solvents (spectrograde) were purchased from Aldrich or Wako and were used without further purification. HBO was obtained from TCI (Tokyo Kasei) and purified by recrystallization from ethanol.

2-(2′-Hydroxynaphthalenyl)benzoxazole (1).[23] *o*-Aminophenol (0.44 g, 4.1 mmol) and 2-hydroxy-1-naphthaldehyde (0.70 g, 4.1 mmol) in ethanol (70 mL) were refluxed for 24 h. After the solution was cooled to room temperature, the crude product was filtered off and washed with cold ethanol, followed by recrystallization from ethanol to give the desired product as yellow crystals (0.86 g), which was directly used in the next reaction without further purification. A mixture of the obtained yellow crystals (0.86 g) and DDQ (184 mg, 0.81 mmol) in chloroform (70 mL) was stirred for 3 h at room temperature. After evaporation to remove solvent, the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 4/1) to give **1** as a white solid (234 mg, 0.90 mmol) in 22% yield.

^{1}H NMR (DMSO-d_6, 400 MHz, Me_4Si): δ 12.14 (1H, s, OH), 8.42 (1H, d, $J = 8.8$ Hz, ArH), 8.08 (1H, d, $J = 8.8$ Hz, ArH), 7.95 (1H, d, $J = 8.4$ Hz, ArH), 7.92–7.90 (2H, m, ArH), 7.63–7.59 (1H, m, ArH), 7.50–7.48 (2H, m, ArH), 7.46–7.42 (1H, m, ArH), 7.35 (1H, d, $J = 8.8$ Hz, ArH). Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36%. Found: C, 77.88; H, 4.52; N, 5.02%.

2-(Naphthalene-1-yl)benzoxazole (2).[24] *o*-Aminophenol (0.44 g, 4.1 mmol) and 1-naphthaldehyde (0.72 g, 4.6 mmol) in ethanol (60 mL) were refluxed for 22 h. After the solution was cooled to room temperature, ethanol was evaporated to give dark-reddish oil, which was directly used for the next reaction without further purification. A mixture of the dark-reddish oil and DDQ (290 mg, 1.28 mmol) in chloroform (50 mL) was stirred for 4 h at room temperature. After evaporation to remove solvent, the residue was purified by recrystallization from ethanol to give yellow crystals (28 mg, 0.11 mmol) in 3% yield.

^{1}H NMR ($CDCl_3$, 270 MHz, Me_4Si): δ 9.47 (1H, d, $J = 8.5$ Hz), 8.44 (1H, d, $J = 7.2$ Hz), 8.04 (1H, d, $J = 8.2$ Hz), 7.95 (1H, d, $J = 7.8$ Hz), 7.93–7.85 (1H, m), 7.74–7.56 (4H, m), 7.44–7.38 (2H, m). Anal. Calcd for $C_{17}H_{11}NO$: C, 83.25; H, 4.52; N, 5.71%. Found: C, 83.08; H, 4.74; N, 5.66%.

Measurements. ^{1}H NMR spectra were measured with a JEOL EX-270 (270 MHz for ^{1}H NMR) or Bruker ARX-400 (400 MHz for ^{1}H NMR) spectrometer in solution of DMSO-d_6 with tetramethylsilane as an internal standard. UV absorption and fluorescence spectra were recorded on a Shimadzu UV-1600 spectrophotometer and on a Hitachi F-4500 fluorescence spectrometer, respectively. Fluorescence decay measurement was performed by using time-correlated single-photon counting.[31]

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