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LETTERS

Rotational Isomerization of Phototautomer Produced in the Excited-State Proton Transfer of 2,2′-Bipyridin-3-ol

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Significantly Stokes-shifted fluorescence induced by the UV photoexcitation of 2,2′-bipyridin-3-ol in 3-methylpentane exhibits a dramatic temperature dependence such that dual fluorescence spectra ($\lambda_{max} = 560$ and 585 nm) at room temperature are replaced by a single fluorescence spectrum ($\lambda_{max} = 560$ nm) below 200 K. The respective emitting species responsible for the short- and long-wavelength bands may be ascribed to the excited-state primary phototautomer (S_1') and its rotamer (S_1''), which is generated by the rotational isomerization of S_1' with an activation barrier.

Introduction

Hydroxybipyridines such as 2,2′-bipyridin-3-ol, BP(OH), and 2,2′-bipyridin-3,3′-diol, $BP(OH)_2$, in which one or two O−H···N H-bonding interactions are involved, undergo a rapid $S_1 \rightarrow S_1'$ intramolecular proton transfer (ESIPT) upon $S_1 \leftarrow S_0$ excitation. In the UV steady-light excitation of BP(OH) and $BP(OH)_2$ in 3-methylpentane (MP) at room temperature, Bulska *et al.* have first reported[1,2] that the excited-state phototautomers (S_1'), generated by the $S_1 \rightarrow S_1'$ intramolecular proton transfer of BP(OH) and $BP(OH)_2$, emit significantly Stokes-shifted fluorescence spectra with peaks at 560 and 525 nm, respectively. For planar $BP(OH)_2$ with two O−H···N H-bondings, it has been reported[1−5] that a cooperative double proton transfer takes place to generate zwitterionic S_1' emitting intense green fluorescence, although a very recent study[6] with the fluorescence up-conversion technique demonstrated that a very short-lived fluorescent keto−enol tautomer is formed through a single proton transfer. On the other hand, only weak yellow fluorescence is induced by the $S_1 \leftarrow S_0$ excitation of BP(OH). The quantum yield of the $S_1' \rightarrow S_0'$ fluorescence has been estimated to be on the order of 10^{-3}, which is negligibly small compared to that (0.22) of $BP(OH)_2$. Assuming that the diketo tautomer of $BP(OH)_2$ is much more rigid in molecular planarity than the keto tautomer of BP(OH), Bulska *et al.*[2] demonstrated that the torsional motion around the C_2-C_2' axis is responsible for the nonradiative deactivation of S_1'. Because of such a low fluorescence yield for the keto tautomer of BP(OH), little attention has been paid to the phototautomerization of BP(OH) in contrast to various studies[7] on that of $BP(OH)_2$. However, we noticed that two emitting species are responsible for the significantly Stokes-shifted fluorescence spectra of BP(OH) in MP at room temperature. This finding stimulated us to elucidate the reaction of S_1' to yield an additional fluorescent species (S_1''). From the temperature-dependent steady-state fluorescence spectra and the time-resolved fluorescence spectra at room temperature, the rotational isomerization reaction of S_1' to S_1'' is demonstrated in this Letter.

Experimental Section

2,2′-Bipyridin-3-ol, BP(OH), was synthesized by a reported method[8] consisting of the ring transformation of 2-furyl 2-pyridyl ketone formed in the reaction of 2-Li-furan and 2-pyridine

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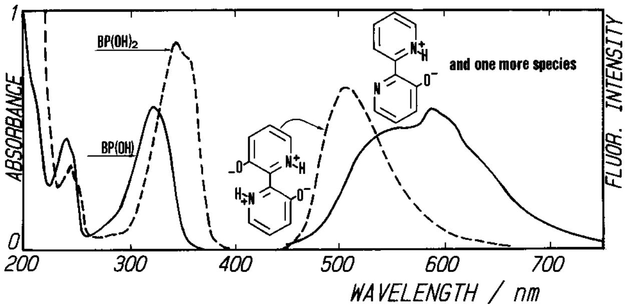


Figure 1. Absorption and uncorrected steady-state fluorescence spectra of 0.042-mM BP(OH) and 0.053-mM $BP(OH)_2$ in MP at room temperature, solid and broken curves, respectively. Fluorescence spectra are approximately normalized.

carbonitrile. MP (Aldrich), purified by distillation over $LiAlH_4$, was further treated with a potassium mirror to yield strictly anhydrous solvent. A solution of BP(OH) in MP was prepared by dissolving the appropriate amount of crystal, remained after evacuation of solvent from hexane solution of BP(OH), in anhydrous MP through a vacuum line without contacting air, and then was degassed by repeated freeze−pump−thaw cycles.

Fluorescence spectra of BP(OH) in MP at 118−300 K were recorded on a Hitachi 850 fluorescence spectrophotometer equipped with a photomultiplier (Hamamatsu Photonics R928). Fluorescence decay curves were determined by a picosecond time-resolved emission detection system. Our picosecond spectroscopic system is as follows: A dye laser (Coherent 701) is synchronously pumped by the second harmonic of a mode-locked Nd:YAG laser (Coherent Antares 76s), and the dye laser pulse is subjected to three-step amplification in a dye laser system (Continuum PTA 60) pumped by the second harmonic of a Nd:YAG regenerative amplifier (Continuum RGA 60). The 600-nm pulse (10 Hz, <20-ps fwhm) is available for the combination of Kiton red 620 (Exciton) and Sulforhodamine 640 (Exciton) selected as lasing dyes for the Coherent 701 and Continuum PTA 60, respectively. The 300-nm UV pulse of 0.5 mJ is finally obtained by frequency doubling of the red pulse. It is employed to induce the fluorescence of BP(OH). Fluorescence dispersed in a polychromator (Jobin-Yvon HR250) is time-resolved by a photon-counting streak camera system (Hamamatsu Photonics C2909) with a streak unit (M1952). Three-dimensional information regarding emission intensity, wavelength, and time is read in a cooled (−30 °C) CCD camera (C3140) interfaced with an A/D converter (C3366I/F unit). Digitized data are sent to a personal computer. Sample MP solution was contained in a 1-cm rectangular quartz cell set in a compact rectangular quartz Dewar. Low temperatures were controlled by adjusting the flow rate of cool nitrogen gas passing through the Dewar. Temperature was monitored by a copper-constantan thermocouple.

Results and Discussion

According to Bulska *et al.*,[2] proton transfer takes place to generate phototautomer in the excited state (S_1') following the $S_1 \leftarrow S_0$ excitation of BP(OH). A significantly Stokes-shifted $S_1' \rightarrow S_0'$ fluorescence spectrum with a single peak at 560 nm and a low fluorescence quantum yield of *ca.* 10^{-3} was reported.[2] In accord with this report, UV light excitation of BP(OH) in MP at room temperature reveals a weak yellow fluorescence. As shown in Figure 1, however, the uncorrected spectrum of a yellow fluorescence consists of the long-wavelength band (λ_{max} = 585 nm) superimposed on the broad short-wavelength band. Such a spectral feature is distinct from that of the Stokes-shifted fluorescence spectrum (broken curve) of $BP(OH)_2$, which consists of a single band.

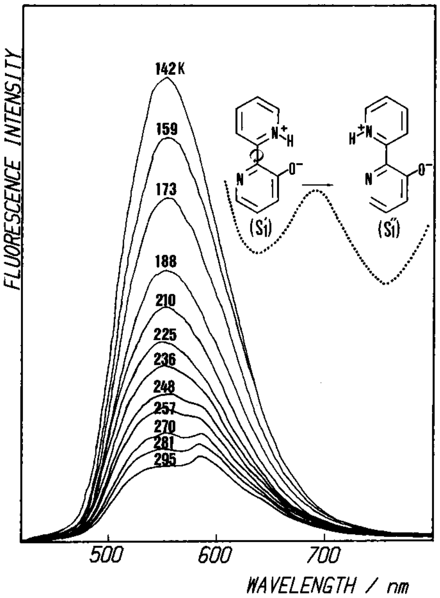


Figure 2. Temperature-dependent steady-state fluorescence spectra observed in the 320-nm steady-light excitation of 0.05-mM BP(OH) in degassed MP at 142−295 K. All the spectra are uncorrected.

Fluorescence excitation spectra of BP(OH) monitored at both 500 and 700 nm are the same as each other, and they are similar to the $S_n \leftarrow S_0$ absorption spectrum of BP(OH). A large Stokes shift of *ca.* 13 900 cm^{-1} was determined for the 585-nm band. It is thus implied that an additional fluorescent species is generated from the fluorescent phototautomer (S_1') through an adiabatic reaction. Provided a significant activation barrier exists in the adiabatic photoreaction, such a dual emission observed at room temperature will be altered with decreasing temperature. Indeed, a definite temperature effect was confirmed for the fluorescence spectra of BP(OH). Figure 2 shows the fluorescence spectra observed in the 320-nm excitation of BP(OH) in degassed MP at 118−295 K. Total emission intensity increases with decreasing temperature. A remarkable decrease in the contribution of the long-wavelength (585 nm) band with decreasing temperature from 295 to 200 K is observed. Fluorescence spectra at 140−200 K exhibit a single peak around 560 nm. Assuming that a rapid $S_1 \rightarrow S_1'$ ESIPT takes place for planar BP(OH) along the barrierless excited-state energy surface, the 560-nm band may be ascribed to the primary phototautomer (S_1') with planar structure. Furthermore, it is reasonable to assume a potential minimum for another planar excited species (S_1''), in which the phenoxy group no longer interacts with the protonated ring nitrogen. Namely, the rotational isomerization of S_1' produces planar rotamer (S_1''), and the rotamer may be responsible for the 585-nm fluorescence.

Fluorescence of BP(OH) was further examined by time-resolved spectroscopy. Figure 3 shows the time-resolved fluorescence spectra converted from the streak image, which was obtained by the 300-nm pulse excitation of BP(OH) in MP at 295 K. It should be noted that fluorescence decay curves are dependent on wavelength. The short-wavelength component decays much faster than the long-wavelength component. By analogy with excimer formation, the decay kinetics may be analyzed from the reaction scheme involving the two emitting species S_1' and S_1'' (Scheme 1).

$$[T^*] = ([T^*]_0/(\lambda_2 - \lambda_1))[(Y - \lambda_1)\exp(-\lambda_1 t) + (\lambda_2 - Y)\exp(-\lambda_2 t)] \quad (1)$$

$$[R^*] = k_3([T^*]_0/(\lambda_2 - \lambda_1))\,[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \quad (2)$$

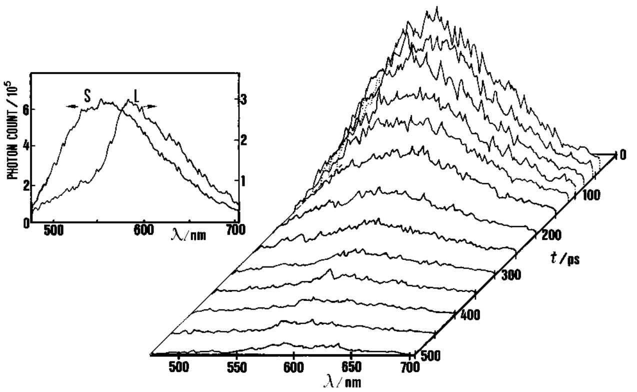
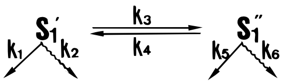


Figure 3. Three-dimensional fluorescence spectra converted by the streak image obtained by the 300-nm picosecond pulse excitation of 0.05-mM BP(OH) in MP at 295 K. Also shown are fluorescence spectra (S and L) integrated over the gate times of 36−88 and 300−550 ps, respectively.

SCHEME 1



Here, $X = k_1 + k_2 + k_3$, $Y = k_4 + k_5 + k_6$, $\lambda_2, \lambda_1 = (1/2)\{X + Y \pm [(X - Y)^2 + 4k_3k_4]^{1/2}\}$. In this scheme, k_1 and k_2 are radiative and nonradiative decay rate constants of S$_1'$ and k_5 and k_6 are those of S$_1''$, respectively. Rate constants of the rotational isomerization and its reverse process are designated as k_3 and k_4, respectively. When k_4 is negligibly small, λ_2 and λ_1 are equal to X and Y, respectively. According to eq 1, therefore, the concentration of S$_1'$ should exhibit the decay of $\exp(-\lambda_2 t)$. Experimentally, an approximately single-exponential decay of 84 ps was determined for the decay signal observed in the 477−523 nm region. It is thus demonstrated that the reverse process is insignificant. On the other hand, the concentration of S$_1''$ should exhibit a rise and a decay according to eq 2. However, a double-exponential decay of 82 and 413 ps was determined for the S$_1''$ fluorescence. This is almost certainly because the spectrum of very weak S$_1''$ fluorescence severely overlaps with that of S$_1'$ fluorescence.

Fluorescence spectra integrated by time are also shown in Figure 3. The spectrum of the long-lived component was obtained by the integration between 300 and 550 ps after the pulse excitation. On the other hand, the spectrum integrated between 36 and 88 ps after the pulse excitation may be ascribed to the short-lived component, because the long-lived fluorescence intensity is far less than the short-lived fluorescence intensity. It is evident that the spectrum L of the long-lived component red-shifts compared to the spectrum S of the short-lived component. Then, resolution of the dual tautomer fluorescence spectra obtained by steady-light excitation was undertaken, as illustrated in Figure 4. Since only the fluorescence spectrum (λ_{max} = 560 nm) ascribable to the primary phototautomer (S$_1'$) is detected below 200 K, we selected the fluorescence spectrum at 188 K as the S$_1'$ fluorescence spectrum. First, the S$_1'$ fluorescence spectrum was multiplied by a factor to meet the spectral curve of the observed dual fluorescence spectra in the 19000−21000 cm^{-1} region. Then, a lower energy spectrum ascribable to S$_1''$ was obtained by subtracting the multiplied S$_1'$ fluorescence spectrum from the dual fluorescence spectrum. The S$_1''$ fluorescence spectrum is similar to the long-wavelength and long-lived fluorescence spectrum (spectrum L in Figure 3) obtained by picosecond pulse excitation. It is noteworthy that the S$_1''$ fluorescence spectrum exhibits a sharp drop in going from peak to higher energy side. This implies that the potential minimum of the rotamer in the excited state (S$_1''$) is little displaced from that of the rotamer in the ground state (S$_0''$). In this case, the Franck−Condon (FC) factor of the 0−0 transition is usually the greatest of all, and the FC factor decreases with increasing vibrational quantum number,[9] although the effect of solvent broadening on the vibrational structure results in a structureless fluorescence spectrum.

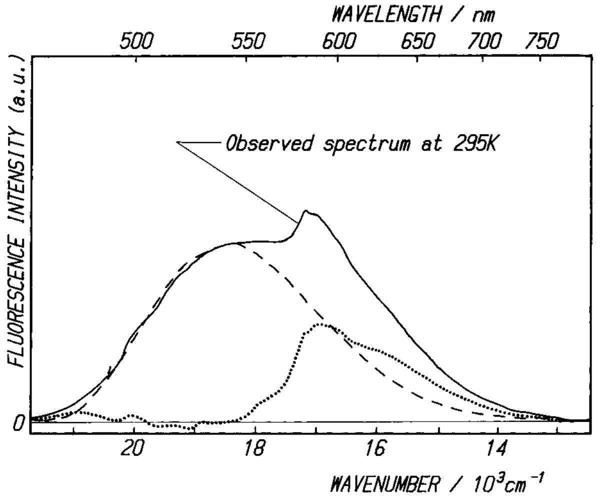


Figure 4. Resolution of dual fluorescence spectra (solid curve) observed at 295 K. Broken curve is the S$_1'$ → S$_0'$ fluorescence spectrum multiplied by an appropriate factor. Dotted spectrum is obtained by subtracting broken spectrum from solid spectrum.

Recently, photoisomerization of the primary phototautomer (cis-keto tautomer) of *o*-hydroxyphenylbenzazoles has been reported to generate trans-keto tautomer.[10] The trans-keto tautomer in the ground state was detected by transient absorption and two-step laser-induced-fluorescence (TS-LIF) spectroscopies. In contrast, dual tautomer fluorescence of BP(OH) is derived from the adiabatic S$_1'$ → S$_1''$ rotational isomerization along the excited-state potential energy surface. Time-resolved measurements of the temperature-dependent dual fluorescence will be reported. Furthermore, a TS-LIF study is now in progress to elucidate the reactivity and the molecular structure of the phototautomer in the ground state.

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