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Control of photoisomerization of C═C double bond by hydrogen bonding and photoinduced hydrogen atom transfer

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ABSTRACT: Olefins with a phenathroline ring and a pyrrole ring were prepared and hydrogen atom transfer reaction in the excited singlet state was observed. The tautomer produced in the excited singlet state has lifetime of 30–50 ps for *cis*-**1** and *c,t*-**2** and with fluorescence maximum at longer wavelength region at 640 nm. The compound **1** exhibited photochromic behavior with its absorption maximum changing between 380 nm and 440 nm, while **2** exhibited only the small change of the absorption spectra on photoirradiation. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: isomerization; hydrogen atom transfer

INTRODUCTION

Hydrogen bonding can be observed in many chemical and biological materials and plays an important role to control the molecular properties and photochemical reactions.[1–19] We have been interested in preparing compounds with intramolecular hydrogen bonding to control photoisomerization,[8–18] energy transfer, and photoinduced electron transfer reactions.[19] For example, olefin with an indole ring and a pyridine ring showed one-way *trans*-to-*cis* photoisomerization in the excited singlet state.[9,10] In this case, *cis* isomer forms intramolecular hydrogen bonding and its excited state solely deactivates to the ground state *cis* isomer without giving the fluorescence emission as well as isomerization to the *trans* isomer (Scheme 1, **A**). In addition, an olefin with a pyrrole ring and a pyridine ring (**B**) also exhibited one-way *trans*-to-*cis* isomerization in the excited singlet state.[11] In these compounds the *cis* isomer gave fluorescence at considerably longer wavelength region at 580 nm due to the tautomer produced by intramolecular hydrogen atom transfer in the excited singlet state. Therefore, these photochemical properties depend on the molecular structures and the olefin with a pyrrole ring and a quinoline ring (**C**) exhibited *cis-trans* mutual isomerization and the excited state intramolecular hydrogen atom transfer in the excited state in *cis* isomer.[8]

We have also explored the hydrogen atom transfer induced one-way *cis*-to-*trans* isomerization in the excited state in 2′-hydroxychalcone (**D**) and its analogues by observing the adiabatic hydrogen atom transfer and isomerization processes by transient absorption spectroscopy.[17,18] The color change of hemiindigo derivatives (**E**) with photoirradiation has also been reported. Furthermore, the effect of intermolecular hydrogen bonding on the photoisomerization behavior of pyridone derivatives (**F**) was observed.

We have intended our research to move on the hydrogen-bonded system to develop compounds with plural hydrogen bonding parts. In this respect we have prepared the compounds with phenathroline ring and pyrrole ring. In these compounds, hydrogen atom transfer in the excited singlet state and some related photochemical properties were observed.

We wish to report here the synthesis of the new compounds (**1**, **2**) with two intramolecularly hydrogen bonding parts and the reference compound with one hydrogen bonding. By the preparation **1** was obtained as *cis* conformation (*cis*-**1**) and **2** was obtained as *cis*, *trans* conformation (*c,t*-**2**) as a main product. The structure was identified by ^{1}H-NMR spectroscopy and elemental analysis. The *cis*-**1** and *c,t*-**2** exhibited intramolecular hydrogen atom transfer in the excited state to give the fluorescence emission at 630–640 nm due to the tautomer with the lifetime of 30–50 ps in benzene. The *cis-trans* isomerization in *cis*-**1** was observed and *trans*-to-*cis* isomerization in *c,t*-**2** to *c,c*-**2** was suggested.

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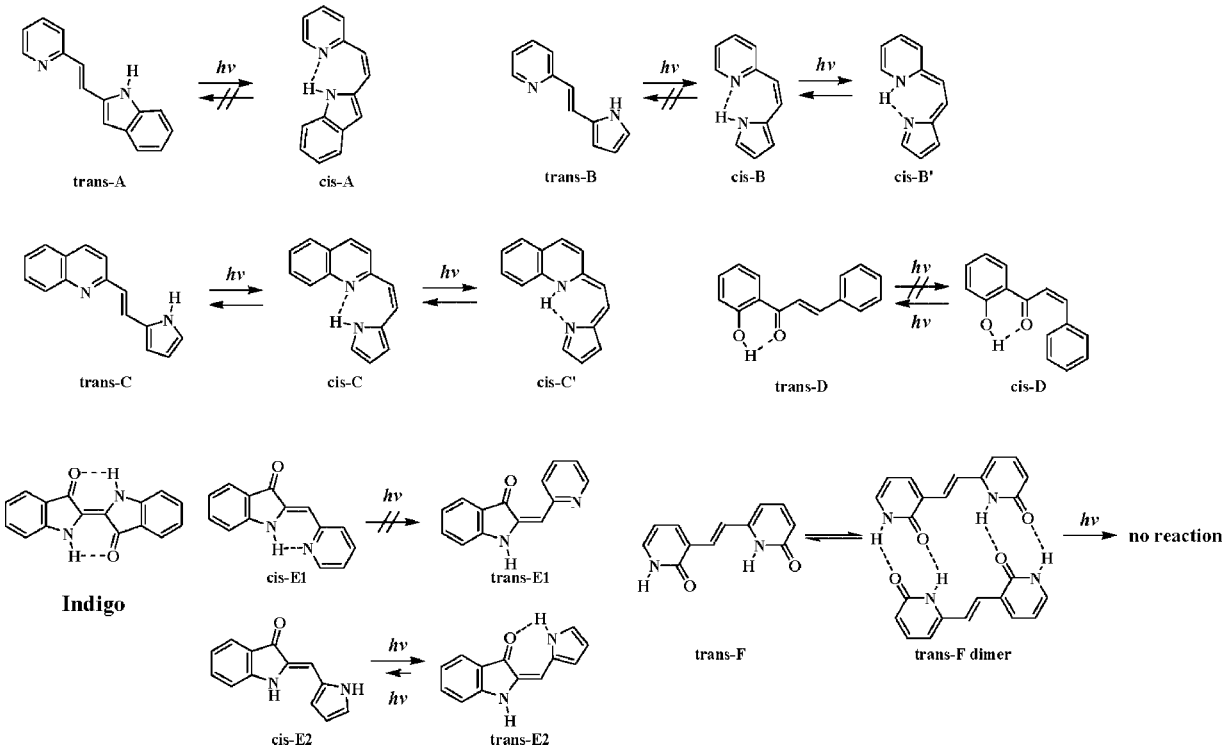

Scheme 1. Examples for the effect of hydrogen bonding on photoisomerization

EXPERIMENTAL

Neocuproine from Tokyo Kasei Kogyo Co., Ltd, Tokyo, Japan and pyrrole-2-carboxaldehyde from Lancaster were used as received. Solvents used for synthesis were dried and distilled (MeOH, DMF). Other solvents for measuring were of spectroscopic grade.

NMR spectra were recorded on Varian Gemini 200 or Bruker ARX-400 instruments. UV–vis absorption spectra and fluorescence spectra were recorded on a Shimadzu UV-1600 spectrophotometer and a Hitachi F-4500 fluorescence spectrometer, respectively. Photoisomerization was carried out by a Jasco FP-777 spectro fluorometer.

Fluorescence decay measurement was carried out by using the time-correlated single-photon counting method (TCSPC). The apparatus was assembled on the basis of previous paper,[20] and details were described elsewhere.[21] Laser excitation wavelength of 375 nm was achieved by a diode laser (PicoQuant, LDH-P-C-375) driven by a power control unit (PicoQuant, PDL 800-B) with a repetition rate of 2.5 MHz. Temporal profiles of fluorescence decay were detected by using a microchannel plate photomultiplier (Hamamatsu, R3809U) equipped with a TCSPC computer board module (Becker and Hickl, SPC630). Full-width at half-maximum (FWHM) of the instrument response function was 51 ps. Criteria for the best fit were the values of χ^2 and the Durbin–Watson parameters, obtained by nonlinear regression.[22]

Synthesis

To a solution of Neocuproine (2, 9-dimethyl-1, 10-phenanthroline) (0.975 g, 4.69 mmol) in 20 ml of MeOH at room temperature was added 35% HCl (1.0 ml, 11.7 mmol). The reaction mixture was stirred at room temperature for 1 h. After solvents were removed, the product was obtained as a white powder. To a solution of the white powder in 25 ml DMF was added pyrrol-2-carboxaldehyde (1.78 g, 18.7 mol) in 10 ml DMF and piperidine (0.93 ml, 9.39 mmol) at room temperature. The reaction mixture was stirred at 100 °C for 4 h. The resulting solution was washed with 0.5% aqueous $NaHCO_3$ (150 ml), extracted with $CHCl_3$, and dried over Na_2SO_4. After solvents were removed, the crude product was obtained as a brown powder. The product was purified with column chromatography on silica gel with CH_2Cl_2 as the eluent followed by precipitation with CH_2Cl_2 and hexane. After solvents were removed, two pure products (*cis*-**1** and *c,t*-**2**) were obtained.

Yellow solid of *cis*-**1** (187.0 mg, 14%) R*f* = 0.63, CH_2Cl_2. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 15.37 (s, 1H), 8.15 (d, 1H, $J = 2.8$ Hz), 8.13 (d, 1H, $J = 2.8$ Hz), 7.69 (s, 2H), 7.54 (d, 1H, $J = 2.2$ Hz), 7.52 (d, 1H $J = 1.5$ Hz), 7.44 (m, 1H), 6.80 (d, 1H, $J = 12.8$ Hz), 6.58 (m, 1H), 6.41 (m, 1H), 6.34 (d, 1H, $J = 12.8$ Hz), 3.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.5, 155.5, 145.2, 144.9, 136.3, 136.2, 131.2, 126.9, 126.5, 126.4, 125.4, 125.2, 125.0, 123.6, 122.4, 118.3, 116.3, 109.5,

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26.1; Anal. Calcd. for $C_{19}H_{15}N_3$: C, 78.98; H, 5.30; N, 14.73. Found: C, 79.73; H, 5.43; N, 14.63.

Yellow powder of *c,t*-**2** (69.0 mg, 4.1%) R*f* = 0.49, CH_2Cl_2. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 15.32 (s, 1H), 11.51 (s, 1H), 8.47 (d, 1H, *J* = 1.5 Hz), 8.45 (d, 1H, *J* = 1.5 Hz), 8.05 (d, 1H, *J* = 8.4 Hz), 7.92 (m, 2H), 7.80 (d, 1H, *J* = 8.4 Hz), 7.72 (d, 1H, *J* = 16.8 Hz), 7.35 (d, 1H, *J* = 16.8Hz), 7,20 (m, 1H), 7.00 (m, 1H), 6.82 (d, 1H, *J* = 8.4), 6.54 (m, 1H), 6.47 (d, 1H, *J* = 12.8 Hz), 6.41 (m, 1H), 6.28 (m, 1H), 6.20 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 156.4, 155.5, 145.7, 144.9, 136.3, 136.2, 131.6, 130.2, 127.4, 126.8, 126.5, 125.4, 125.2, 124.9, 124.7, 123.4, 122.2, 120.7, 120.5, 118.8, 115.9, 111.0, 110.6, 109.6; Anal. Calcd. for $C_{24}H_{18}N_4$: C, 79.54; H, 5.01; N, 15.46. Found: C, 79.26; H, 5.16; N, 15.38.

RESULTS AND DISCUSSION

Absorption and fluorescence spectroscopy and hydrogen atom transfer

Figure 1 shows the absorption spectra of *cis*- and *trans*-**1** in benzene, where the absorption maximum of *cis*-**1** (440 nm) is appeared at longer wavelength than that of *trans*-**1**. The absorption maximum and the extinction coefficient depend on the solvent properties as shown in Table 1. In polar solvent the absorption maximum shifted to the shorter wavelength compared to the nonpolar solvent, indicating that the lowest excited state should have n-π^* character. Usually the *cis* isomer with intramolecular hydrogen bonding exhibited absorption spectra at longer wavelength region compared to that of *trans* isomer with 30–40 nm. Thus, our findings regarding the spectral shift of the absorption spectra and the results of other intramolecularly hydrogen bonded compounds supported the spectral change observed.

Figure 2 shows the fluorescence and fluorescence excitation spectra of *trans*-**1** in acetonitrile. The fluorescence maximum appeared at 430 nm in benzene and in acetonitrile and their Stokes shift is calculated to be 3600, and 5600 cm^{-1}, where the longer wavelength absorption edge and the shorter wavelength fluorescence edge have some overlapping area.

Table 1. Absorption maxima and molar extinction coefficient of *cis*-**1** in polar and nonpolar solvent

	Solvent	λ/nm	ε/M-1 cm^{-1}
trans-1	Benzene	387	46 500
		367	41 500
		307	15 600
	Acetonitrile	379	35 100
		302	17 200
		271	32 200
		228	56 200
cis-1	Benzene	429	16 000
		329	3830
		283	27 800
	Acetonitrile	413	13 700
		322	4470
		277	26 200
		267	27 100
		227	41 200
	Methanol	415	16 000
		322	4470
		280	29 700
		263	32 600
		225	51 000

The fluorescence quantum yield of *trans*-1 was determined to be 5.2×10^{-3} and 2.5×10^{-3}, respectively in benzene and in acetonitrile.

Figure 3(a) shows the absorption spectra and fluorescence and fluorescence excitation spectra of *cis*-**1** in benzene. In benzene the fluorescence at shorter wavelength region with the maximum at 489 nm and at longer wavelength region with the maximum at 640 nm was observed on excitation at 340 nm. The excitation spectra observed at 640 nm are almost superimposed to the absorption spectra of *cis*-**1** and therefore, this emission is

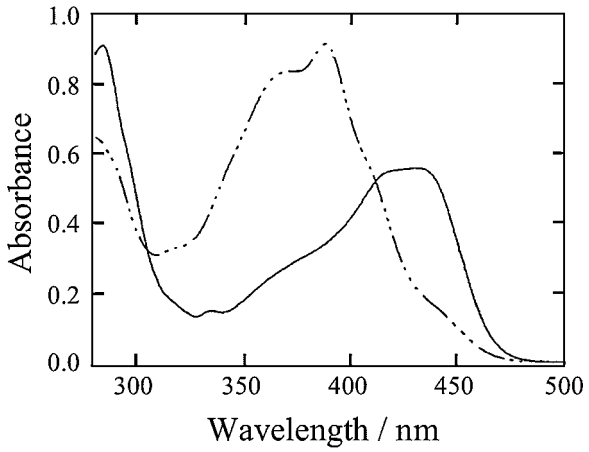

Figure 1. Absorption spectra of *cis*-**1** (solid line) and *trans*-**1** (three dots-dash line) in benzene

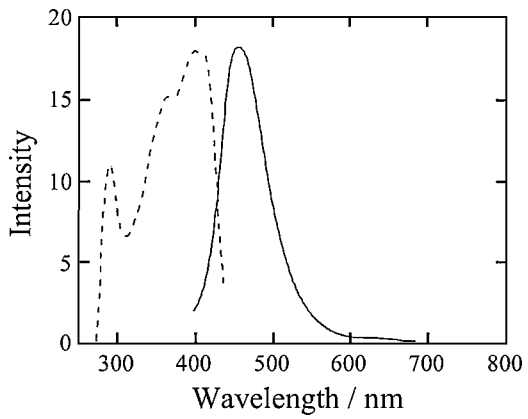

Figure 2. Fluorescence at 359 nm (solid line) and fluorescence excitation spectra at 480 nm (dash line) of *trans*-**1** in benzene

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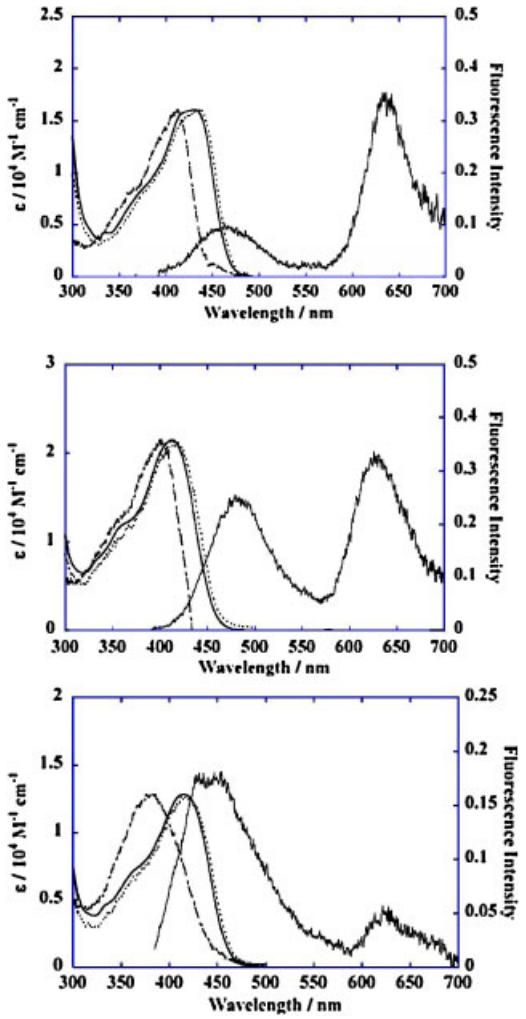

Figure 3. Absorption (thick line), fluorescence at 340 nm (thin line), and fluorescence excitation spectra at 510 nm (dot-dash line) and (a), (b) 640 nm (c) 638 nm (dotted line) of *cis*-**1** in benzene (a), in acetonitrile (b), and in methanol (c).

caused by the photoexcitation of *cis*-**1**. The fluorescence quantum yield (Φ_f) of *cis*-**1** was determined to be 5.2×10^{-4} and is very small. The Stokes shift between the absorption maximum at 400 nm and the emission maximum at 620 nm is calculated to be 7600 cm^{-1} indicating that the molecular structure and/or electronic structure of the emission species at 640 nm in the excited singlet state should be very much different from that of the ground state. Since the formation of the intramolecular hydrogen bonding in *cis*-**1** is suggested by the observation of the low field NH proton by NMR spectroscopy, the fluorescence spectra at 640 nm can be assigned to the tautomer produced by the excited state intramolecular hydrogen atom transfer in the excited singlet state. The Stokes shift calculated in acetonitrile and methanol is 8400 and 8300 cm^{-1}, respectively, but the fluorescence maximum of the tautomer is almost the same in varying solvents.

The fluorescence observed at 480 nm could be assigned to the normal form of *cis*-**1**, but the fluorescence excitation spectrum observed at 480 nm is different from the absorption spectra. One can explain by the following two possibilities. One of them is the existence of the ground state rotational isomer having no hydrogen bonding and the other is the fluorescence from the *trans*-**1** produced as a photoproduct of *cis*-**1**. The ^{1}H-NMR spectroscopy indicates that *cis*-**1** should exist as exclusively a hydrogen-bonded form, although the existence of a small amount of rotational isomer or *trans*-**1** cannot be ruled out.

In acetonitrile, the tautomer emission at 630 nm was also observed and indicates that the excited state intramolecular hydrogen atom transfer should take place not only in nonpolar solvent but also in polar solvent (Fig. 3(b)).

As shown in Fig. 3(c), in methanol *cis*-**1** gives similar fluorescence spectra to those in benzene, but the fluorescence intensity of 420 nm *vs*. 630 nm is reverse to that in benzene. Thus, the fluorescence intensity at 630 nm is smaller than that at 420 nm. In methanol solvent, methanol may form intermolecular hydrogen bonding with *cis*-**1** and methanol may affect the molecular conformation of *cis*-**1**, and therefore, the fluorescence band at 630 nm should be somehow affected by methanol. The effect of intermolecular hydrogen bonding with methanol may be the reason of smaller intensity at 630 nm relative to 420 nm compared to that in benzene. However, the maximum wavelength and the spectral profile of the emissive species at 630 nm is almost the same as that in benzene indicating that the intermolecular hydrogen bonding with solvent methanol does not affect the excited state properties of the tautomer produced by intramolecular hydrogen atom transfer.

The fluorescence spectra of *c,t*-**2** also give two bands at 480 nm and 640 nm (Fig. 4). The excitation spectra of both bands are superimposed to those of the absorption spectra of *c,t*-**2** indicating that the two fluorescence bands were observed on excitation of *c,t*-**2**. The Stokes shift of the longer wavelength band with the maximum at 640 nm and the absorption maximum at the longest wavelength region (450 nm) can be calculated to be 7000 cm^{-1}. Therefore, the fluorescence spectra were also assigned to the tautomer produced in the excited singlet state on photoirradiation.

Fluorescence lifetimes

Table 2 shows fluorescence lifetimes derived by the analysis of measured decay curves of *cis*-**1** and *c,t*-**2**. Lifetime of *cis*-**1** monitored at 630 nm gave almost single component manner of 46 ps, following negligible contribution of 506 ps as shown in Figs. 5 and 6. This is applicable to the lifetime of *c,t*-**2** in the same wavelength (Fig. 6). From the fluorescence measurement,

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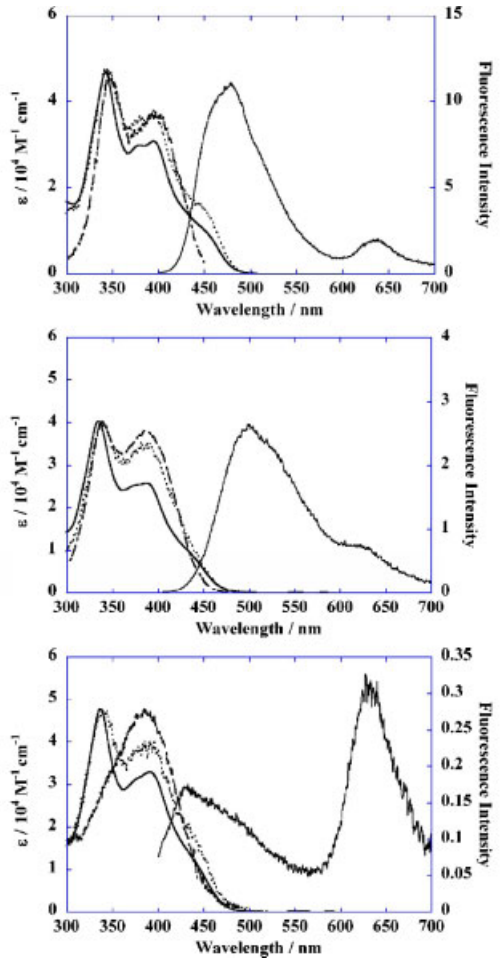

Figure 4. Absorption (thick line), fluorescence at (a) 330 nm, (b) 350 nm, (c) 340 nm (thin line) and fluorescence excitation spectra at (a) 480 nm, (b), (c) 510 nm (dot-dash line) and (a) 638 nm, (b), (c) 640 nm (dotted line) of *c,t*-**2** in benzene (a), in acetonitrile (b), and in methanol (c).

Table 2. Fluorescence lifetimes of *cis*-**1** and *c,t*-**2** in benzene under Ar atmosphere excited at 375 nm

	τ/ps	
Compound	480 nm	630 nm
cis-1	113 (0.877)	46 (0.993)
	380 (0.123)	506 (0.007)
c,t-**2**	138 (0.630)	28 (0.993)
	638 (0.370)	616 (0.007)

Values in parenthesis mean normalized ratio of the corresponding lifetime.

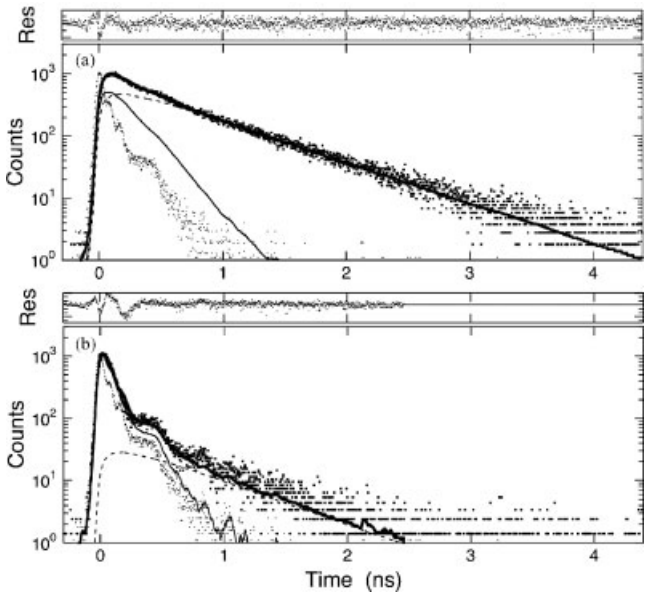

Figure 5. Fluorescence decay curves of *cis*-**1** monitored at (a) 480 nm and (b) 630 nm; observed decay (large dot), IRF (small dot), fitted curve (thick line), slow (thin line) and fast (broken line) components of fitted decay. Upper column is weighted residual

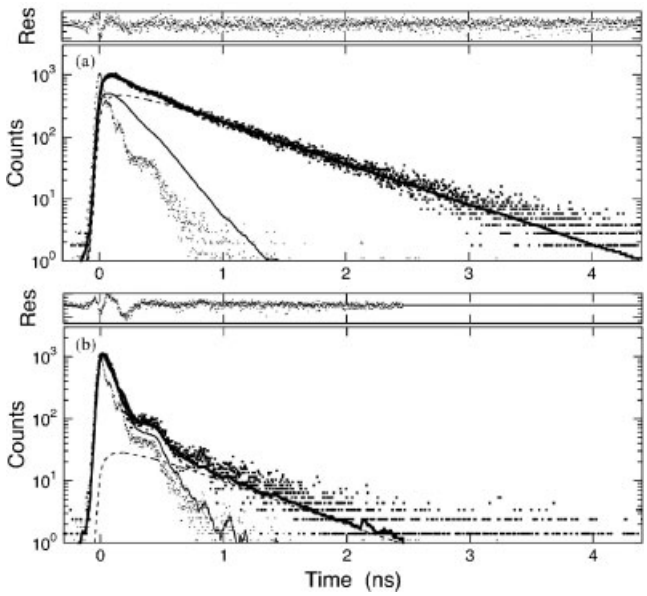

Figure 6. Fluorescence decay curves of *c,t*-**2** monitored at (a) 480 nm and (b) 630 nm; observed decay (large dot), IRF (small dot), fitted curve (thick line), slow (thin line) and fast (broken line) components of fitted decay. Upper column is weighted residual

this component seems to be the different component from the excited state of *cis*-**1** due to the large Stokes shift of 7400 cm^{-1} as described in the previous section. One may assign the lifetime of 46 ps and 28 ps to isomers *cis*-**1′** and *c,t*-**2′** formed by photoinduced hydrogen-atom transfer reaction as shown in Scheme 2. Since formation of *cis*-**1′** brings about very small structural changes during the reaction in the excited state, the formation time constant of *cis*-**1′** is considered to occur within Pico second time scale. This is why the rise component of *cis*-**1′** was not observed at 630 nm due to the lack of time resolution of the present TCSPC system. Meanwhile, the lifetime

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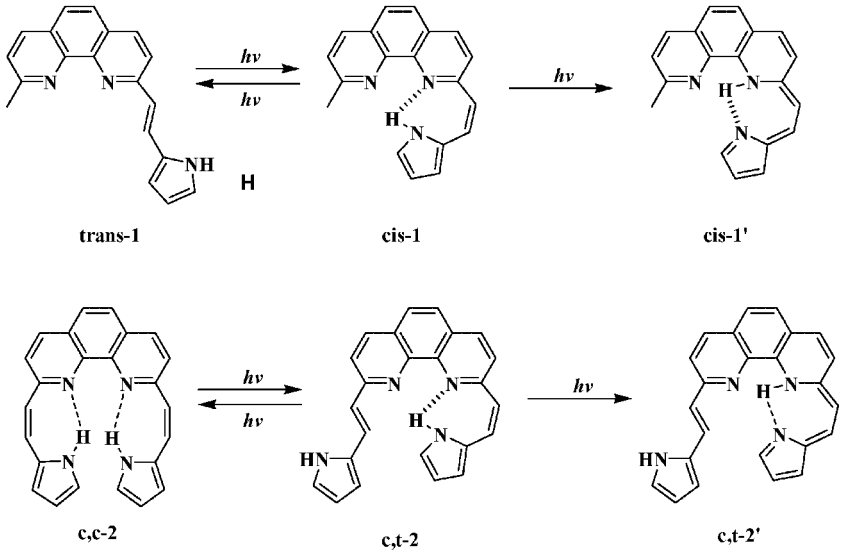

Scheme 2.

component monitored at 480 nm showed a relatively complicated fashion. τ of *cis*-**1** at 480 nm consisted of 113 and 380 ps, while that of *c,t*-**2** 138 and 638 ps. A major component of both *cis*-**1** and *c,t*-**2** was approximately 100 ps, which was 30–40% of τ monitored at 630 nm. The long lifetime of approximately 400 ps exists in the case of 480 nm decay in comparison with 630 nm decay. The spectral tail of emissive species may extend to 630 nm. In the present experiment, two possibilities for the assignment of emissive species monitored at 480 nm having approximately 100 ps may be considered: (1) the emission from *trans* form of *cis*-**1** formed by excitation laser during fluoresecence measurement, and (2) conformer of *cis*-**1** that cannot undergo hydrogen-atom transfer in the excited state (Scheme 2). To examine these two assumptions, fluorescence excitation measurement of *cis*-**1** was carried out monitored at 510 and 638 nm. Although the excitation spectrum monitored at 638 nm agreed with the corresponding absorption spectrum of *cis*-**1**, that at 510 nm gave an absorption spectrum close to *trans* form rather than an absorption spectrum of *cis*-**1**. We are now working on to complete the assignment of this emissive species.

Photoisomerization

On photoirradiation at 365 nm light the absorption spectra of *cis*-**1** were almost constant in benzene, while on irradiation at 465 nm light the absorption spectra changed very much and the maximum wavelength was shifted from 435 nm to 380 nm (Fig. 7).

$$([cis]/[trans])\,\mathrm{pss} = (\varepsilon_t/\varepsilon_c)(\Phi_{t-c}/\Phi_{c-t}) \qquad (1)$$

The photostationary state isomer ratio ([*cis*]/[*trans*]) pss was determined to be 99/1 on 365 nm excitation. The ratio of extinction coefficient of *cis*-**1** and *trans*-**1** at 365 nm $\varepsilon_t:\varepsilon_c = 3.6:1$. By using these values and Eqn 1, one can calculate the difference of quantum yield of *cis*-to-*trans* ($\Phi_{c\text{-}t}$) and *trans*-to-*cis* photoisomerization ($\Phi_{t\text{-}c}$) to be $\Phi_{t\text{-}c}/\Phi_{c\text{-}t} = 27.3$. Thus, the *cis*-to-*trans* isomerization is 27 times smaller than *trans*-to-*cis* isomerization in the excited state indicating the suppression of the isomerization by the deactivation through intramolecular N—H:N hydrogen bonding or by way of intramolecular hydrogen atom transfer. The spectral change by photoirradiation is also occurred with 415 nm irradiation at the isosbestic point to give the photostationary state.

Figure 8 shows the spectral change of the absorption spectra on excitation of *c,t*-**2** at 365 nm in benzene under argon atmosphere. The absorbance at the longer wavelength region increased with concomitant decrease with the absorbance at 300–400 nm.

As photochromic properties **1** exhibited absorption spectra change with photoirradiation between 380 nm (*trans*-**1**) and 440 nm (*cis*-**1**) depending on the irradiation wavelength. Usually, the *cis* isomer exhibited absorption spectra with smaller extinction coefficient with absorption maximum at slightly shorter wavelength. However, the presence of intramolecular hydrogen bonding affected the electronic structure to shift the absorption maximum of *cis* isomer by the extension of conjugation by intramolecular hydrogen bonding. This effect also contributes to extend the absorption maximum of *cis* isomer in **1**. The quantum yield of *cis*-to-*trans* isomerization is estimated to be 27 times smaller than that of *trans*-to-*cis* isomerization. Therefore, the intramolecular hydrogen bonding could control the efficiency and the mode of isomerization in phenanthroline derivatives.

Since the spectral change due to the photoirradiation is very small, **2** was obtained as *cis*, *trans* conformer (*c,t*-**2**)

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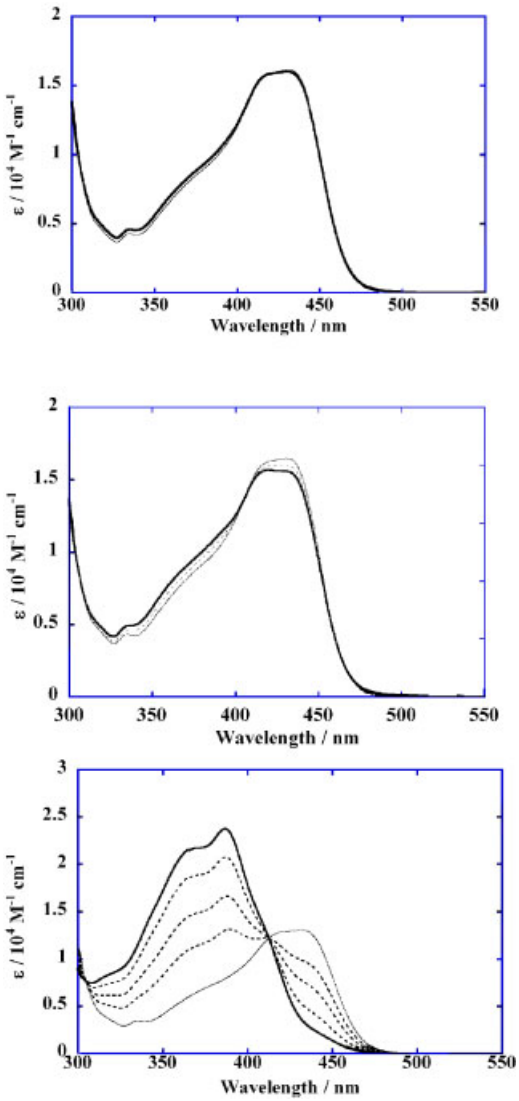

Figure 7. Change of absorption spectra on photoirradiation of *cis*-**1** in benzene under Ar at 365 for 0 and 60 min (a), 412 for 0, 30 sec, and 1 h (b), or 465 nm for 0, 30, 60,120 and 300 min (c).

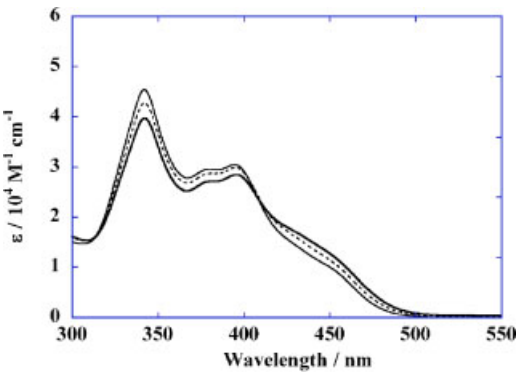

Figure 8. Change of absorption spectra on photoirradiation of *c,t*-**2** in benzene at 365 nm for 0, 10 and 30 min

and the photoirradiation did not seem to produce the *trans, trans* isomer (*t,t*-**2**). The observed spectral change by photoirradiation was tentatively assigned to the isomerization from *c,t*-**2** to *c,c*-**2**. We have expected that the introduction of the second intramolecular hydrogen bonding may affect the absorption spectra by further extending the electronic conjugation probably due to the intramolecular hydrogen bonding. However, the present finding indicates that only the presence of another intramolecular hydrogen bonding does not affect the absorption spectra.

Since **2** has two pyrrole NH groups and two pyridine N group and can introduce metal ions at the center, the study on photochemical properties of metal complexes of **2** is now in progress.

CONCLUSIONS

Effect of intramolecular hydrogen bonding in olefins of phenanthroline derivatives has been studied by the synthesis of desired compounds and steady state and time resolved spectroscopy as well as observation of photoisomerization behavior. The intramolecular hydrogen bonding induced the intramolecular hydrogen atom transfer to give the tautomers, which emit characteristic fluorescence spectra with large Stokes shift and quite short lifetime of 30–50 ps. The intramolecular hydrogen bonding affected the absorption spectral profile to give the photochromic properties depending on the conformation of *cis* isomer with hydrogen bonding and *trans*-isomer without hydrogen bonding.

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