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# Excited state intramolecular hydrogen atom transfer of phenylethynyl-substituted 2′-hydroxychalcones

**Satomi Tasaki · Atsuya Momotake · Yoko Kanna · Tatsuo Arai**

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**Abstract** (*E*)-1-[2-Hydroxy-4-(phenylethynyl)phenyl]-3-[4-(phenylethynyl)phenyl] prop-2-en-1-one (**1**), (*E*)-1-[2-hydroxy-4-(phenylethynyl)phenyl]-3-phenylprop-2-en-1-one (**2**), and (*E*)-1-(2-hydroxyphenyl)-3-[4-(phenylethynyl)phenyl]prop-2-en-1-one (**3**), which belong to a new class of 2′-hydroxychalcones with phenylethynyl group(s) at the *para* position of the phenyl ring, were synthesized, and their photochemical properties were investigated. The lowest energy absorption band of **1** peaks at a longer wavelength (383 nm) with a much larger molar extinction coefficient ($5.0 \times 10^4$ $M^{-1}$ $cm^{-1}$) than that of the parent 2′-hydroxychalcone (**2′HC**) ($2.0 \times 10^4$ $M^{-1}$ $cm^{-1}$ at 318 nm). Upon photoexcitation, all three compounds underwent excited-state intramolecular hydrogen atom transfer (ESIHT) to produce an excited tautomer that emitted fluorescence with a large Stokes shift in the longer wavelength region at 600–700 nm. The quantum yield of the tautomer fluorescence of **1** was not high at 298 K ($\Phi_f = 9.1 \times 10^{-5}$), but was highest among **2′HC** and its analogues. The $\Phi_f$ values of **1**–**3** increased 10–30 fold upon reducing the temperature from 298 to 77 K.

**Keywords** Excited-state hydrogen atom transfer · Adiabatic reaction · 2′-Hydroxychalcone · Fluorescence · Photostability

## Introduction

Excited-state intramolecular hydrogen atom transfer (ESIHT) is a fundamental photochemical process that occurs upon photoexcitation of intramolecularly

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S. Tasaki · A. Momotake · T. Arai (✉)
Graduate School of Pure and Applied Sciences, University of Tsukuba,
Tsukuba, Ibaraki 305-8571, Japan
e-mail: arai@chem.tsukuba.ac.jp

Y. Kanna
Faculty of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan

hydrogen bonded compounds in which the hydrogen donating and accepting groups are in the appropriate geometry to form a pseudo aromatic ring system [1–9]. Upon photoexcitation, the excited state (**N***) of the original normal form (**N**) immediately undergoes ESIHT to produce the excited state tautomer form (**T***) that decays by radiative or non-radiative processes, and the resulting ground state tautomer (**T**) rapidly reverts back to **N** by reverse hydrogen atom transfer (Fig. 1). We have synthesized a variety of ESIHT compounds, for example salicylidene anilines [10–12], 2-(2′hydroxyphenyl)benzazoles (including benzoxazole [13–16], benzimidazole [17], and benzothiazole [17]), hemiindigos [18], pyrrole-pyridine [19], and pyrrole-quinoline [20–22] hydrogen-bonding systems, and have studied their excited state dynamics.

Among intramolecularly hydrogen bonded molecules, 2′-hydroxychalcone (**2′HC**), an important compound distributed in plants and a precursor of flavonoids and isoflavonoids [23, 24], is regarded as relatively stable on photoirradiation. One reason for this low reactivity on photoreaction is believed to be the presence of an intramolecular hydrogen bond that induces immediate deactivation to the ground state before undergoing reaction to produce other photoproducts. Chou et al. [25] studied the excited state reaction of **2′HC** and discovered tautomer formation in the excited singlet state by observing the fluorescence emission in the longer wavelength region of ca 630 nm. This fluorescence emission could not be detected by conventional fluorescence spectroscopy. When we began our studies on the dynamic behavior of **2′HC** in the excited triplet state, there were no reports on either detection of the triplet state or on detailed reaction processes of the triplet state of **2′HC**. We found that **2′HC** underwent ESIHT and intersystem crossing to give the tautomer in the excited triplet state with an extremely long triplet lifetime of 1 μs, making observation of the T–T absorption spectra by transient spectroscopy possible [26]. Furthermore, by synthesizing the *cis* isomer of **2′HC**, we revealed that **2′HC** undergoes only one-way *cis*-to-*trans* isomerization by an adiabatic process in the excited state, with the help of ESIHT, to form a polyene-like structure [27].

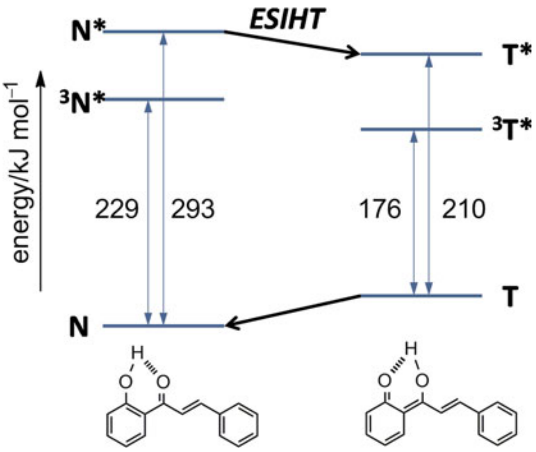


**Fig. 1** Potential energy surface of ESIHT of **2′HC**, where **N** and **T** indicate the normal and tautomer forms, respectively, as in the depicted structures. The energy values are from Ref. [27]

Thus, we revealed the triplet state of **2′HC** undergoes ESIHT and one-way *cis*-to-*trans* isomerization.

Another yet unresolved and important aspect of the excited state behavior of **2′HC** and related compounds is how to detect fluorescence of the tautomer by conventional fluorescence spectroscopy. Although the fluorescence efficiency of **2′HC** is very low ($\Phi_{\mathrm{f}} < 10^{-6}$), it can be enhanced by simple chemical modification. For example, fluorescence of the tautomer of naphthalene-fused **2′HC** analogues at approximately 600–700 nm can be detected by use of a commercially available fluorimeter [28–31]. Thus, extension of the $\pi$ electron system might be a simple way of facilitating spectroscopic observation of the tautomer. Recently, we have also successfully observed fluorescence of the tautomer of 2′-hydroxychalcone by introduction of electron-donating substituents, for example methoxy or dimethylamino groups, at the 4 or 4′ positions, which increase the efficiency of fluorescence of the tautomer [32]. However, the quantum yields of those substituted **2′HC** analogues were still low at 298 K ($\Phi_{\mathrm{f}} = 2.0 \times 10^{-6}$–$1.1 \times 10^{-5}$).

In this paper, we focus on a study of the effect of a phenylethynyl substituent on the photochemical properties of **2′HC**. The remarkable effects of the phenylethynyl substituent on the photochemistry of aromatic enediynes [33] and stilbene (unpublished data) have recently been investigated. A large red shift of the absorption and fluorescence spectra, dramatic enhancement of the fluorescence quantum yield, and a decrease of isomerization efficiency from the excited triplet state, because of the reduced triplet energy of planar conformations, were observed. The effect of the phenylethynyl unit on the photochemical and photophysical properties of **2′HC** should, therefore, also be of interest. Thus, three new phenylethynyl-substituted 2′-hydroxychalcones **1**–**3** were prepared for this study, as described below.

## Experimental

### Materials and general instrumentation

All reagents and solvents of the highest commercial quality were purchased from Tokyo Chemical Industry, Wako Pure Chemical Industries (Osaka, Japan), or Aldrich Chemical (Milwaukee, WI, USA) and were used without further purification. NMR spectra were recorded on a JNM-EX270 ($^{1}$H NMR at 270 MHz) or AV-400FT NMR ($^{1}$H NMR at 400 MHz; $^{13}$C at 100 MHz). $\delta$ values are given in parts per million relative to tetramethylsilane. Silica gel column chromatography was performed using silica gel 60N (Kanto Chemical, Tokyo, Japan). IR spectra were recorded on a Jasco FT-4100 spectrometer.

### Measurements

Absorption and fluorescence spectra were measured on Shimadzu UV-1600 and Hitachi F-4500 fluorescence spectrophotometers, respectively. The concentration for steady state fluorescence measurements was adjusted so that the absorption maximum of the excitation wavelength was 0.1 for each sample. Fluorescence quantum yields were determined relative to anthracene in ethanol ($\Phi_f = 0.27$) [34] and were corrected for the solvent refractive index.

## Materials

### *2-Hydroxy-(4-phenylethynyl)acetophenone (**4**)*

A mixture of 4-bromo-2-hydroxyacetophenone (2.73 g, 12.7 mmol), ethynylbenzene (1.93 g, 18.9 mmol), $Pd(PPh_3)_2Cl_2$ (461 mg, 0.657 mmol), $PPh_3$ (83 mg, 0.316 mmol), and triethylamine (2.54 g, 25.1 mmol) in 50 mL distilled THF was stirred for 30 min at room temperature, and CuI (74.9 mg, 0.393 mmol) was then added. After stirring for 24 h, the reaction was quenched by addition of water and then extracted with dichloromethane. The organic layer was washed with saturated sodium bicarbonate solution, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by silica gel column chromatography ($SiO_2$; chloroform–hexane, 1:2) to give **4** as a yellow solid (1.21 g, 40 %). mp 75–76 °C, $^1H$ NMR (270 MHz, $CDCl_3$), $\delta$ (ppm): 2.63 (s, 3H), 7.04 (d, $J = 8.2$ Hz, 1H), 7.13 (s, 1H), 7.37 (m, 3H), 7.54 (m, 2H), 7.70 (d, $J = 8.2$ Hz, 1H), 12.27 (s, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$), $\delta$ (ppm): 26.6, 88.3, 93.1, 119.2, 121.1, 122.1, 122.4, 128.4 (2C), 129.0, 130.1, 131.3, 131.8 (2C), 162.1, 203.9. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.15; H, 5.15. IR (KBr; 4000–400 $cm^{-1}$), $\nu$: 3444, 3241, 3069, 2922, 2337, 2206, 1763, 1639, 1544, 1367, 1269, 1215, 978, 805, 760, 691 $cm^{-1}$.

### *1-[2-Hydroxy-4-(2-phenylethynyl)phenyl]-3-[4-(2-phenylethynyl)phenyl]prop-2-en-1-one (**1**)*

To a solution of **4** (234 mg, 0.989 mmol) and (4-phenylethynyl)benzaldehyde (206 mg, 1.00 mmol) in methanol (15 mL), 2 mol/L KOH in methanol (6 mL) was added. The mixture was stirred at room temperature for 6 h and then at 40 °C for 18 h. The reaction mixture was poured into iced water, and 2 mol/L HCl was added until the mixture was acidic (pH 1–2). The mixture was extracted with dichloromethane and the organic layer was washed with saturated sodium bicarbonate solution, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by silica gel column chromatography ($SiO_2$; toluene) to give **1** as an orange solid (135 mg, 32 %). mp 162–163 °C, $^1H$ NMR (270 MHz, $CDCl_3$), $\delta$ (ppm): 7.09 (dd, $J = 8.3$, 1.5 Hz, 1H), 7.19 (d, $J = 1.5$ Hz, 1H), 7.37 (m, 6H), 7.59 (m, 9H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 15.3$ Hz, 1H), 12.86 (s, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$), $\delta$ (ppm): 88.5, 89.0, 92.2, 93.4, 119.6, 120.4, 121.3, 122.0, 122.5, 122.8, 126.0, 128.4 (2C), 128.5 (2C), 128.7, 128.7 (2C), 129.0, 129.5, 131.3, 131.7 (2C), 131.9 (2C), 132.2 (2C), 134.2, 144.7, 163.4, 192.8. Anal. Calcd for $C_{31}H_{20}O_2$: C, 87.71; H, 4.75. Found: C, 87.22; H, 4.56. IR (KBr; 4000–400 $cm^{-1}$), $\nu$: 3438, 3050, 2922, 2852, 2335, 2203, 1635, 1569, 1549, 1509, 1354, 1199, 1020, 753, 684 $cm^{-1}$.

### *1-[2-Hydroxy-4-(2-phenylethynyl)phenyl]-3-phenylprop-2-en-1-one (**2**)*

To a solution of **4** (238 mg, 1.01 mmol) and benzaldehyde (123 mg, 1.16 mmol) in methanol (15 mL), 2 mol dm$^{-3}$ KOH in methanol (5 mL) was added. The mixture was stirred at room temperature for 9 h and then at 40 °C for 15 h. The reaction mixture was poured into iced water, and 2 mol dm$^{-3}$ HCl was added until the mixture was acidic (pH 1–2). The mixture was extracted with dichloromethane and the organic layer was washed with saturated sodium bicarbonate solution, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by silica gel column chromatography ($SiO_2$; toluene) to give **2** as an orange solid (136 mg, 41 %). mp 135–136 °C, $^1$H NMR (270 MHz, $CDCl_3$), $\delta$ (ppm): 7.08 (dd, $J = 8.4$, 1.7 Hz, 1H), 7.17 (d, $J = 1.7$ Hz, 1H), 7.37 (m, 3H), 7.44 (m, 3H), 7.55 (m, 2H), 7.65 (m, 3H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 16.2$ Hz, 1H), 12.85 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$), $\delta$ (ppm): 88.5, 93.3, 119.6, 119.9, 121.3, 122.0, 122.5, 128.4 (2C), 128.7, 128.9 (2C), 129.0, 129.5 (2C), 131.0, 131.2, 131.8 (2C), 134.5, 145.7, 163.3, 193.0. Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 84.86; H, 5.09. IR (KBr; 4000–400 cm$^{-1}$), $v$: 3442, 3050, 2925, 2340, 2214, 1643, 1575, 1364, 1199, 1151, 979, 868, 755, 693 cm$^{-1}$.

### *1-(2-Hydroxyphenyl)-3-[4-(2-phenylethynyl)phenyl]prop-2-en-1-one (**3**)*

To a solution of 2-hydroxyacetophenone (149 mg, 1.08 mmol) and (4-phenylethynyl)benzaldehyde (213 mg, 1.03 mmol) in methanol (15 mL), 2 mol dm$^{-3}$ KOH in methanol (5 mL) was added. The mixture was stirred at room temperature for 7.5 h and then at 40 °C for 15 h. The reaction mixture was poured into iced water, and 2 mol dm$^{-3}$ HCl was added until the mixture was acidic (pH 1–2). The mixture was extracted with dichloromethane and the organic layer was washed with saturated sodium bicarbonate solution, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by silica gel column chromatography ($SiO_2$; toluene) to give **3** as an orange solid (157 mg, 47 %). mp 136–137 °C, $^1$H NMR (270 MHz, $CDCl_3$), $\delta$ (ppm): 6.96 (dd, $J = 8.2$, 7.1 Hz, 1H), 7.04 (d, $J = 8.2$ Hz, 1H), 7.36 (m, 3H), 7.57 (m, 8H), 7.91 (d, $J = 15.7$ Hz, 1H), 7.93 (d, $J = 7.3$ Hz, 1H), 12.78 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$), $\delta$ (ppm): 89.0, 92.1, 118.7, 118.9, 120.0, 120.6, 122.8, 125.9, 128.4 (2C), 128.6 (2C), 128.7, 129.6, 131.7 (2C), 132.1 (2C), 134.3, 136.5, 144.4, 163.6, 193.5. Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 85.07; H, 5.23. IR (KBr; 4000–400 cm$^{-1}$), $v$: 3442, 3032, 2922, 2337, 2214, 1639, 1568, 1490, 1445, 1338, 1206, 1163, 1025, 823, 762, 652 cm$^{-1}$.

## Results and discussion

### Molecular design and synthesis

In our previous study, the effect of phenylethynyl substituents at enhancing fluorescence emission was usually most remarkable when they were introduced at the *para* position of the photoresponsive unit [33]. In addition, the introduction of

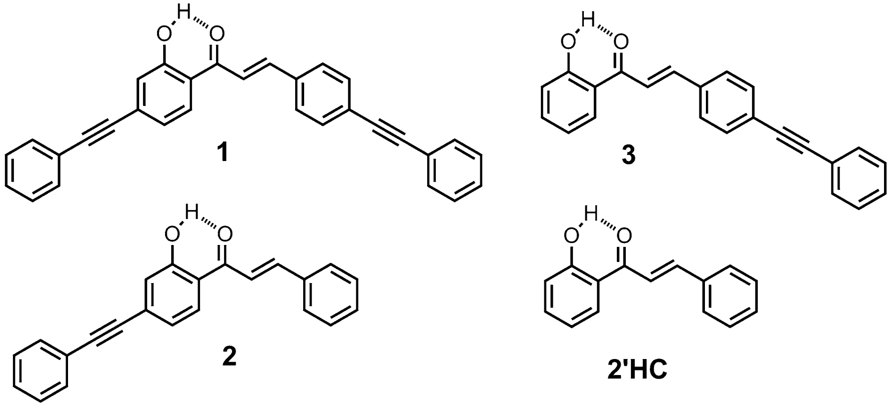


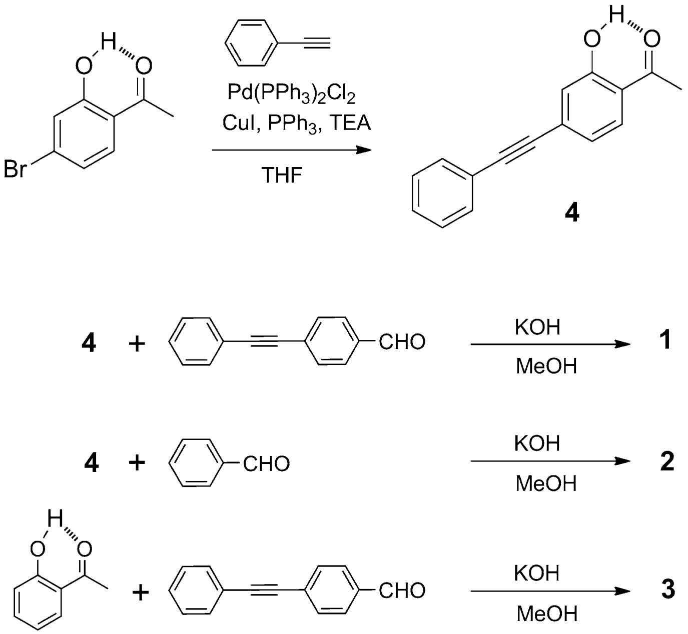
**Fig. 2** Chemical structures of the parent and phenylethynyl-substituted 2′-hydroxychalcones (**2′HC** and **1–3**)

electron-donating group(s) at the 4 or 4′ positions of **2′HC** was effective for fluorescence enhancement, as mentioned above. Thus, we designed the three 2′-hydroxychalcones having phenylethynyl units at the 4,4′ positions, the 4′ position, and the 4 position giving compounds **1**, **2**, and **3**, respectively, and their photochemistry and photophysics were compared with those of the parent **2′HC**. The chemical structures of all the compounds are depicted in Fig. 2.

The synthesis of **1** and **2** began with the Sonogashira coupling [35] of ethynylbenzene and 4-bromo-2-hydroxyacetophenone with $Pd(PPh_3)_2Cl_2$ as catalyst to yield 2-hydroxy-(4-phenylethynyl)acetophenone (**4**), the precursor of both **1** and **2** (Scheme 1). Subsequent aldol condensation of the precursor **4** and 4-(phenylethynyl)benzaldehyde (for **1**) or benzaldehyde (for **2**) in KOH–methanol produced the desired products. Compound **3** was prepared by aldol condensation of 2-hydroxyacetophenone and (4-phenylethynyl)benzaldehyde under the same reaction conditions.

## Absorption and fluorescence spectra at 298 K

The phenylethynyl substituent introduced at the 4 and 4′ positions has a significant effect on the spectroscopic properties of the 2′-hydroxychalcones (Table 1). The UV absorption spectrum of the parent **2′HC** in benzene at 298 K has a peak at 318 nm with a shoulder at approximately 350 nm, and the molar extinction coefficients are $2.0 \times 10^4$ and $1.0 \times 10^4$ $M^{-1}$ $cm^{-1}$ at 318 and 355 nm, respectively (Fig. 3). The absorption spectrum of **1**, having two phenylethynyl groups at the 4,4′ positions, is the most substantially red-shifted to 383 nm with a large ε value ($\varepsilon_{383} = 5.0 \times 10^4$ $M^{-1}$ $cm^{-1}$) at the peak wavelength. The shape of the spectrum of **2**, in which a phenylethynyl group is introduced at the 4′ position, is somewhat similar to that of the parent **2′HC**, but red-shifted to 341 nm with a shoulder at approximately 375 nm, and the ε value is twice as high at the peak wavelength ($\varepsilon_{342} = 3.6 \times 10^4$ $M^{-1}$ $cm^{-1}$). Compared with the absorption spectrum of **2**, the spectrum of **3** is



**Scheme 1** Synthesis of phenylethynyl-substituted 2′-hydroxychalcones **1–3**

**Table 1** Spectroscopic, photophysical, and photochemical data of **1–3** and **2′HC** in benzene (298 K) and MTHF (77 K) solution

| Compd. | $\lambda_{abs}$ (nm) | $\varepsilon$ ($10^4$ $M^{-1}$ $cm^{-1}$) | $\lambda_{fl}$ (nm) | $\Phi_f$ (298 K) | Stokes shift ($cm^{-1}$) | $\Phi_f$ (77 K) |
|---|---|---|---|---|---|---|
| **1** | 383 | 5.0 | 641 | $9.1 \times 10^{-5}$ | 11,000 | $1.0 \times 10^{-3}$ |
| **2** | 342, 372 | 3.6, 2.8 | 629 | $6.7 \times 10^{-5}$ | 13,000 | $1.5 \times 10^{-3}$ |
| **3** | 363 | 3.9 | 630 | $1.1 \times 10^{-5}$ | 12,000 | $2.5 \times 10^{-4}$ |
| **2′HC** | 318, 355 | 2.0, 1.0 | – | $<1.0 \times 10^{-6}$ | | |

further red-shifted to 363 nm, despite having only a single phenylethynyl substituent, and its shape is changed, indicating that the π electrons of the phenylethynyl unit at the 4 position are delocalized on to the **2′HC** moiety.

Although the intensity of the fluorescence emission was weak, it could be observed at room temperature in benzene for **1–3** (Fig. 4). The Stokes shift of the fluorescence of **1–3** at approximately 600–700 nm is as large as 10,000 $cm^{-1}$. In addition, the excitation spectra depicted in Fig. 3 are similar to the corresponding UV absorption spectra. These results indicate that the observed fluorescence originates from the excited tautomer that is populated through the ESIHT reaction upon photoexcitation of the normal form. It should be noted that, even if the quantum yield of the tautomer fluorescence of **1** was not high ($\Phi_f = 9.1 \times 10^{-5}$), it has the highest value among **2′HC** and its

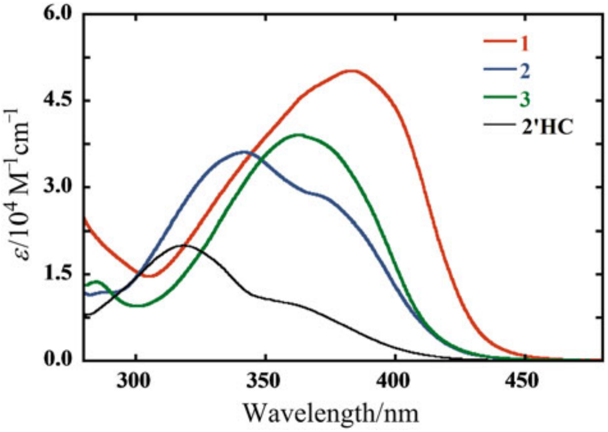


**Fig. 3** Absorption spectra of **1** (*red line*), **2** (*blue line*), **3** (*green line*), and **2′HC** (*black line*) in benzene at 298 K. (Color figure online)

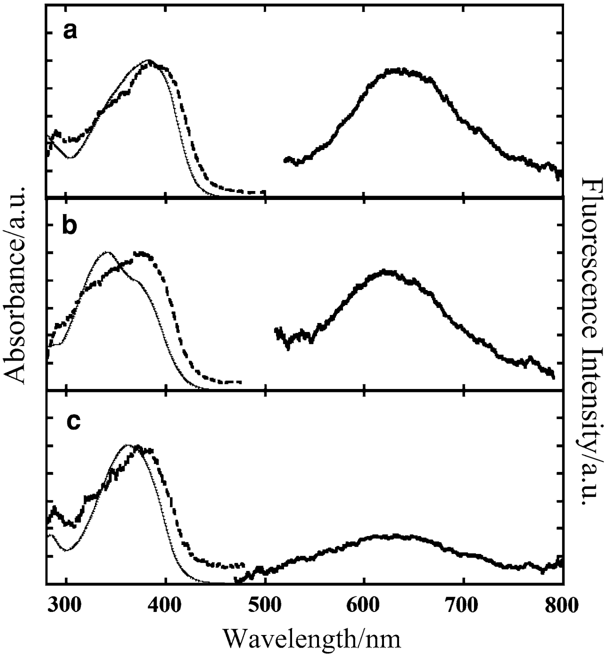


**Fig. 4** Absorption spectra (*thin lines*), fluorescence spectra (*bold lines*), and fluorescence excitation spectra (*dotted lines*) of **1** (**a**), **2** (**b**), and **3** (**c**) in benzene at 298 K. The concentrations of the compounds were 2.0 × $10^{-6}$, 2.8 × $10^{-6}$, and 2.6 × $10^{-6}$ mol/L for **1**, **2**, and **3**, respectively. The excitation wavelengths were 383, 342, and 362 nm for **1**, **2**, and **3**, respectively. The monitoring wavelengths were 640, 625, and 630 nm for **1**, **2**, and **3**, respectively

analogues in solution at 298 K. As already mentioned, detection of the fluorescence of the parent **2′HC** by use of our fluorimeter was unsuccessful, because of its very low quantum yield ($\Phi_f < 10^{-6}$).

Interestingly, despite the marked red-shifts observed in the absorption spectra, the fluorescence spectra of **1–3** are not very different, or even blue-shifted, compared with that of the parent **2′HC**, which had a peak at 635 nm, as reported by Chou et al. [25], on excitation by an Nd:YAG laser. These similar results, i.e., the significant absorption red-shift upon introduction of electron-donating groups at the *para* position of **2′HC**, with a blue-shift of the fluorescence spectra, were also observed in our previous study [32]. These results may indicate that the electron-donating or $\pi$-conjugated substituents affected the ground-state normal form to shift the absorption spectra of **2′HC** to a longer wavelength region, whereas the substituent effect is much less in its tautomer form in the excited state.

## Laser flash photolysis

Laser flash photolysis was performed to measure the transient absorption spectra of **1–3** at 298 K. Upon Nd:YAG laser excitation at 355 nm, no transient absorption spectra for **1–3** were observed, including the excited triplet state that had been observed for the parent **2′HC** [27] and for naphthalene-fused analogues of **2′HC** [30]. These results indicate that intersystem crossing from the singlet excited state to the triplet excited state was not significant and the phenylethynyl substituted 2′-hydroxychalcones **1–3** were predominantly deactivated from the excited singlet state non-radiatively at 298 K.

## Low-temperature fluorescence spectra

The fluorescence intensity of the tautomers of **1–3** increased in freezing MTHF glass at 77 K, as shown in Fig. 5. The fluorescence quantum yields of **1–3** at 77 K were determined to be $1.0 \times 10^{-3}$, $1.5 \times 10^{-3}$, and $2.5 \times 10^{-4}$, for **1**, **2**, and **3**, respectively; these are 10–30 times larger than those at 298 K. These results indicate that the non-radiative deactivation of **T*** was suppressed at low temperature; however, the $\Phi_f$ values for **1–3** at 77 K are still low. Unlike the behavior at 298 K, the $\Phi_f$ value of **1** was less than that of **2**. One possibility for the changing order of $\Phi_f$ values from 298 to 77 K is the different efficiency of intersystem crossing from **T*** between **1** and **2** at 77 K. In an ab-initio study of the excited state behavior of diphenylacetylene [36], the excited singlet (Franck–Condon) state undergoes intersystem crossing via several relaxation steps within the singlet lifetime. Similarly, **1–3** may undergo intersystem crossing at 77 K and the efficiency of **1** might be higher than that of **2**, resulting in the lower quantum yield of **1**. However, this could not be ascertained by use of our instruments.

## Photostability

Although **1–3** have large extinction coefficients in the near-UV to visible region and undergo ESIHT reactions quite efficiently, the main process that **T*** undergoes is non-radiative decay that does not involve a structural change, for example photo-decomposition by bond cleavage or reaction with surrounding molecules. Furthermore, **T**, although it cannot be detected, immediately reverts back to **N** in the ground

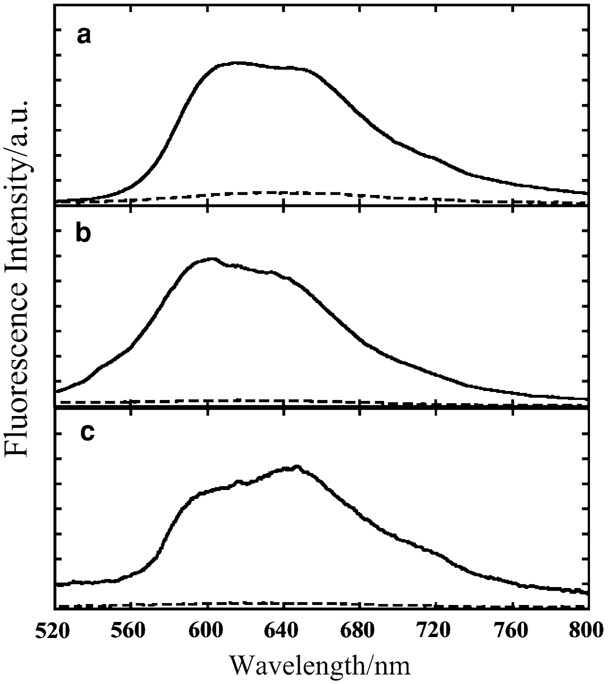


**Fig. 5** Fluorescence spectra of **1** (**a**), **2** (**b**), and **3** (**c**) in MTHF at 298 K (*dotted lines*) and at 77 K (*solid lines*). The concentrations of the compounds were $2.0 \times 10^{-6}$, $2.8 \times 10^{-6}$, and $2.6 \times 10^{-6}$ M for **1**, **2**, and **3**, respectively. The excitation wavelengths were 383, 342, and 362 nm for **1**, **2**, and **3**, respectively

state by thermal hydrogen atom transfer. This efficient reaction cycle, as depicted in Fig. 1, indicates that compounds **1–3** are photo-sensitive but highly photo-stable, which is in contrast to the parent compound **2′HC**. Photoirradiation of **2′HC** resulted in the formation of 3-hydroxyflavone, which is produced via oxygen-assisted photocyclization in the excited triplet state, to give 2-phenylchroman-3,4-dione followed by 1,3-hydrogen migration [25]. In deoxygenated polar solvents, irradiation of **2′HC** or methoxy-substituted **2′HC** causes facile photocyclization to give 4-flavanones [37]. For example, 2-methoxy-substituted **2′HC** photocyclized with a quantum yield of 0.3–0.4 in ethyl acetate [38]. This cyclization occurs via the *trans*-keto form which is produced by ESIHT to form **T*** followed by *cis–trans* isomerization of the newly produced C=C double bond [29, 38]. A similar reaction might occur with **1–3**, and the above non-radiative deactivation process may produce the *trans*-keto form. However, the *trans*-keto form could not be observed in the transient absorption measurements of **1–3**. Additionally, no detectable change of the absorption spectra was observed after laser flash photolysis in the diluted solution.

## Conclusion

In this paper we report the photochemical properties of a new class of 2′-hydroxychalcones, **1–3**, with phenylethynyl group(s) at the *para* positions of the phenyl rings. The lowest-energy absorption band of **1** peaks at a longer wavelength, and with a much larger molar extinction coefficient, than that of the parent 2′-hydroxychalcone. Upon photoexcitation, all three compounds underwent ESIHT to produce an excited tautomer that emitted intense Stokes-shifted fluorescence in the longer wavelength region at 600–700 nm. The quantum yield of the tautomer fluorescence of **1** was still low ($\Phi_f = 9.1 \times 10^{-5}$) at 298 K, but was improved, and the $\Phi_f$ value was the highest among **2′HC** and its derivatives. The $\Phi_f$ values of **1–3** were increased 10–30 fold on reducing temperature from 298 to 77 K. These measurements revealed that **1–3** were very photo-stable, even in dilute solution, because of the highly efficient four-cycle reaction process which involves photoexcitation, ESIHT reaction, non-radiative decay, and thermal back hydrogen atom transfer.

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