Red fluorescence from tautomers of 2′-hydroxychalcones induced by intramolecular hydrogen atom transfer

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Received (in Montpellier, France) 5th January 2009, Accepted 17th April 2009
First published as an Advance Article on the web 5th May 2009
DOI: 10.1039/b823431k

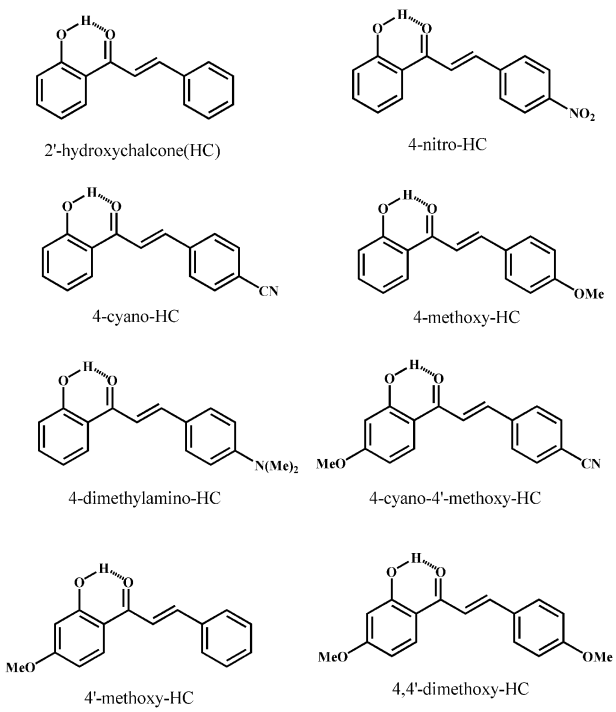
Tautomer fluorescence in the longer wavelength region at 600 nm produced by intramolecular hydrogen atom transfer was observed in several 2′-hydroxychalcones having an electron donating group at the *para* position of the phenyl ring. The quantum yield of tautomer fluorescence increased by 1000 times upon decreasing the temperature from room temperature to 77 K. The introduction of dendritic substituents also increased the intensity of the tautomer fluorescence. One can control the photochemical and photophysical properties of the olefins by introduction of intramolecular hydrogen bonding and photoinduced hydrogen atom transfer.

Introduction

Photoinduced hydrogen atom transfer is the fundamental photochemical process occurring in the excited singlet state of intramolecularly hydrogen bonded compounds.[1–17] We have prepared and studied various hydrogen bonded compounds and studied the fluorescence properties and the effect of hydrogen bonding on the *cis–trans* photochemical isomerization in the excited state. In 2′-hydroxychalcones, we have revealed that the intramolecular hydrogen atom transfer controlled the isomerization mode around the C=C double bond to induce only one-way *cis*-to-*trans* isomerization in the excited triplet state.[18–20] The molecular structure of 2′-hydroxychalcone was investigated by means of transient spectroscopies. Thus, we observed a T–T absorption spectrum of 2′-hydroxychalcone in its tautomer form with longer lifetime of 1 μs than 2′-methoxychalcone (30 ns) without intramolecular hydrogen bonding. This longer lifetime is ascribable to the molecular structure of the tautomer form in the excited triplet state, where a polyene like structure is produced by intramolecular hydrogen atom transfer.

Different from the spectroscopic studies of the tautomer of 2′-hydroxychalcone in the excited triplet state, the ground state tautomer has not been observed. In addition, the observation of the fluorescence spectra due to the tautomer produced by intramolecular hydrogen atom transfer is difficult for the parent 2′-hydroxychalcone, and only one study of the observation of the tautomer fluorescence was reported by using high power laser excitation.[11]

Studies on intramolecular hydrogen atom transfer in the excited state for chalcone analogues with a naphthalene ring were performed, where the tautomer fluorescence and the T–T absorption spectra as well as the ground state tautomer were successfully observed.[15,21–23] Thus, the introduction of a large aromatic group may accelerate the spectroscopic observation of the tautomers. However, as already mentioned above, the spectroscopic studies for 2′-hydroxychalcone were limited to the observation of T–T absorption spectra assigned to the tautomer,[18,20] with tautomer fluorescence only observable by high laser excitation.[11] Furthermore, the study of the effect of substituents on the hydrogen atom transfer dynamics was limited. Therefore, we were interested in observing fluorescence emission of the tautomer in 2′-hydroxychalcone by introduction of appropriate substituents. In this respect, we have prepared varying compounds of 2′-hydroxychalcone derivatives (Scheme 1 and 2). In these compounds the introduction of electron donating substituents such as methoxy or dimethylamino at the *para* position of the phenyl ring accelerates the efficiency of the tautomer emission produced by intramolecular hydrogen atom transfer in the excited



Scheme 1 Structure of 2′-hydroxychalcones.

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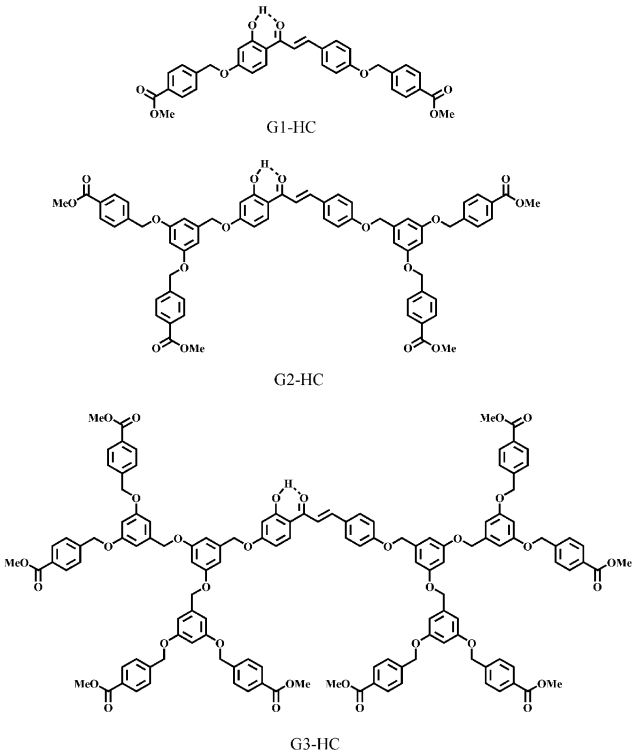


Scheme 2 Structure of 2′-hydroxychalcone dendrimers.

singlet state. Furthermore, one may expect an effect of dendritic structure on the excited state properties of hydrogen bonded compounds and we have prepared and studied dendrimers with 2′-hydroxychalcone structure at the core by using the 4,4′-dimethoxy-HC structure. Thus, we have focused on the study of the effect of a methoxy substituent and the temperature on the fluorescence properties of the tautomer produced by adiabatic hydrogen atom transfer. Furthermore, the effect of dendritic structure to increase the efficiency of the tautomer production and/or tautomer emission have been explored.

Results and discussion

Absorption and fluorescence spectra

Fig. 1 shows absorption spectra of 2′-hydroxychalcones having different substituents in benzene solution; Fig. 1(a) and (b) compare the spectra with electron donating and with electron accepting substituents, respectively. The absorption maximum appeared at around 320 nm for HC and 4-methoxy-HC with a shoulder at around 360 nm for HC, and absorption maxima at *ca.* 365 nm for 4′-methoxy- and 4,4′-dimethoxy-HC (Fig. 1(a) and Table 1). The absorption maximum appeared at a longer wavelength of 430 nm for 4-dimethylamino-HC (Fig. 1(a) and Table 1). The absorption maximum for 4-cyano-, 4-nitro- and 4-cyano-4′-methoxy-HC were observed at 315–323 nm with a shoulder at around 360 nm in benzene (Fig. 1(b) and Table 1). The absorption spectra are almost the same upon varying the solvent for 4,4′-dimethoxy-HC (Fig. 2(a)), but are slightly different for 4-dimethylamino-HC (Fig. 2(b)).

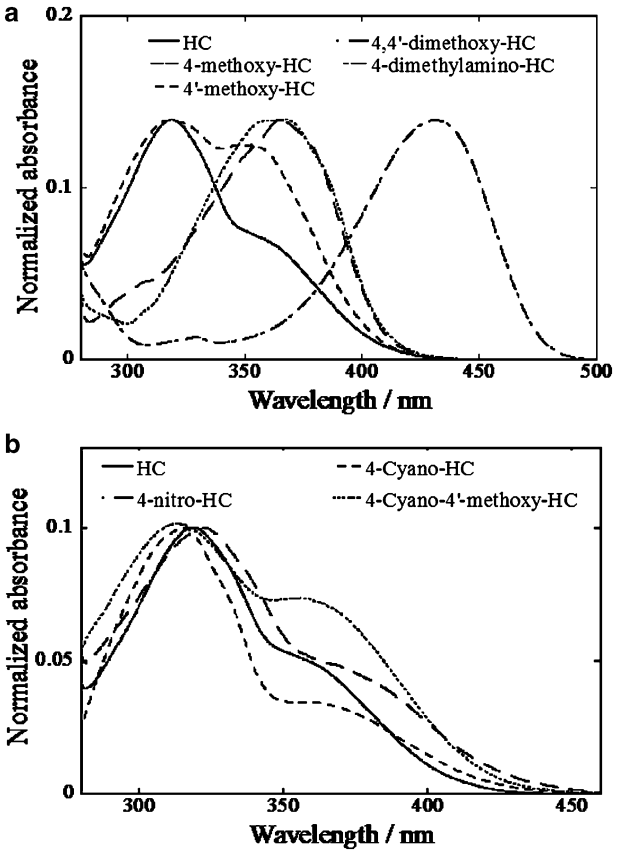


Fig. 1 Absorption spectra of 2′-hydroxychalcones (HCs) in benzene.

In the compounds examined in Scheme 1, the fluorescence emission at room temperature in benzene was observed for 4-methoxy-, 4′-methoxy-, 4,4′-dimethoxy- and 4-dimethylamino-HC, although the intensity of the fluorescence emission is weak (Fig. 3(a) and Table 1). Tautomer fluorescence was observed for these compounds in various solvents as shown in Fig. 3(b) for 4,4′-dimethoxy-HC. The fluorescence emission of 4,4′-dimethoxy-HC in EtOH appeared at slightly shorter wavelength compared with that in other solvents. The reason of this blue shift of the tautomer fluorescence in EtOH is not clear, though spectroscopic grade EtOH contains 0.5% H_2O and H_2O may influence the excited state properties of the tautomer to change the fluorescence wavelength. We could not observe fluorescence from other HCs studied in this paper due to their value being under the detection limit of our instrument. The Stokes shift calculated from the absorption maximum and fluorescence maximum for 4-methoxy-, 4′-methoxy-, 4,4′-dimethoxy- and 4-dimethylamino-HC in benzene are also listed in Table 1. The fluorescence maximum for 4,4′-dimethoxy-HC is almost the same in solvents with different polarities and the Stokes shifts are more than 10 000 cm^{-1} in all the solvents. However, the fluorescence spectra are changed with solvent properties for 4′-dimethylamino-HC, where the single peak appeared at 600 nm in benzene and methanol, but two maxima peaking at 500 and 600 nm were observed in THF (data not shown). The Stokes shift for 4-dimethyamino-HC is dependent upon the solvent polarity and is 5100 cm^{-1} in acetonitrile, 6300 cm^{-1} in

Table 1 Absorption maxima, fluorescence maxima, Stokes shifts and fluorescence quantum yield of 2′-hydroxychalcones having different substituents (in benzene solution)

	$\lambda_{max\ UV}$/nm	ε/M^{-1} cm^{-1}	$\lambda_{max\ FL}$/nm	Stokes shift/cm^{-1}	Φ_F
HC	318	19 900			$<10^{-6}$
4-O_2N-HC	323	12 900			$<10^{-6}$
4-NC-HC	315	22 000			$<10^{-6}$
4-MeO-HC	364	27 800	615	11 200	8.3×10^{-6}
4′-MeO-HC	319	18 200	610	14 900	1.1×10^{-5}
4-NC-4′-MeO-HC	318	16 800			$<10^{-6}$
4,4′-(MeO)$_2$-HC	365	32 000	605	10 500	2.0×10^{-6}
4-Me_2N-HC	430	36 900	620	7100	4.6×10^{-6}

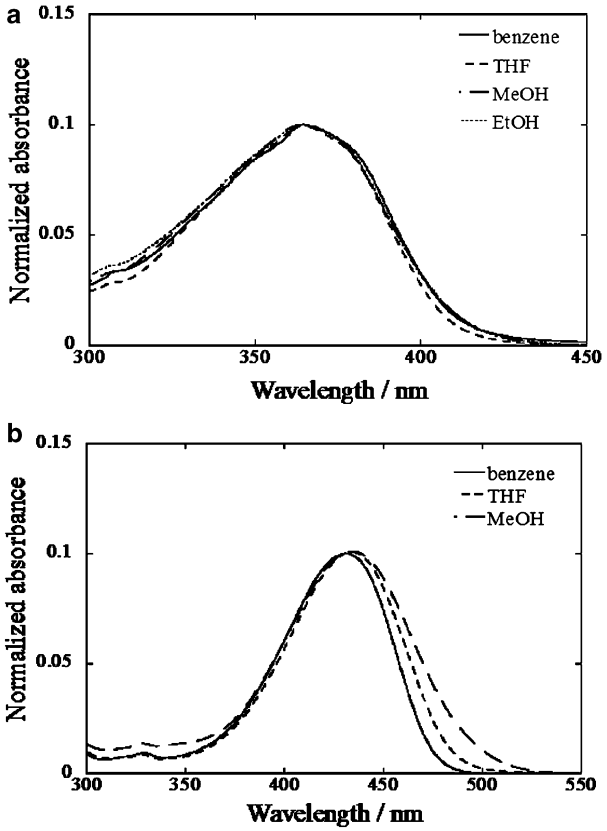


Fig. 2 (a) Absorption spectra of 4,4′-dimethoxy-HC in benzene, THF, MeOH and EtOH, and (b) absorption spectra of 4-dimethylamino-HC in benzene, THF and MeOH.

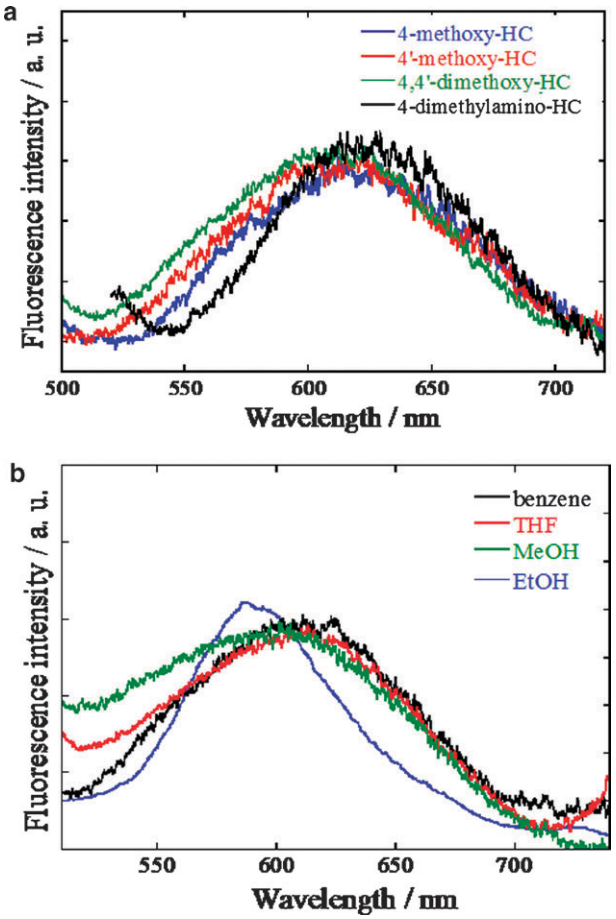


Fig. 3 (a) Fluorescence spectra observed in 2′-hydroxychalcones (HCs) in benzene and (b) fluorescence spectra of 4,4′-dimethoxy-HC in benzene, THF, MeOH and EtOH.

methanol, and 7100 cm^{-1} in benzene. Due to the rather small value of the Stokes shift observed for 4-dimethyamino-HC, we could not determine whether the observed fluorescence is due to the tautomer or not.

The fluorescence intensity of the tautomer increased with decreasing temperature. A typical example for 4,4′-dimethoxy-HC in EtOH is shown in Fig. 4. Thus, the quantum yields of fluorescence emission at 77 K in EtOH were determined to be 0.009, 0.013 and 0.023 for 4-methoxy-, 4′-methoxy- and 4,4′-dimethoxychalcones, respectively; the quantum yield at room temperature is almost 1000 times smaller than these values (Table 2).

Fig. 5 shows absorption spectra of 2′-hydroxychalcone dendrimers (4,4′-dimethoxy-HC (G0-HC), G1-, G2-, and G3-HC) compared to that of HC in THF at room temperature. The absorption profile at the longer wavelength region is almost the same among the dendrimers, but the absorbance at 280 nm increased with increasing generation due to the increase of the benzyl ether type dendron group. All of these dendrimers exhibited fluorescence emission (λ_{max} = 605 nm) with large Stokes shift (10 500 cm^{-1}) in THF under Ar (Table 3) and the fluorescence excitation spectrum was similar to the corresponding absorption spectrum. Fig. 6 summarizes and compares typical examples of absorption, fluorescence and fluorescence excitation spectra of 4,4′-dimethoxy-HC (G0-HC) and G2-HC in THF.

The fluorescence quantum yield for 4-methoxy-, 4′-methoxy-, 4,4′-dimethoxy- and 4′-dimethylamino-HC in benzene were

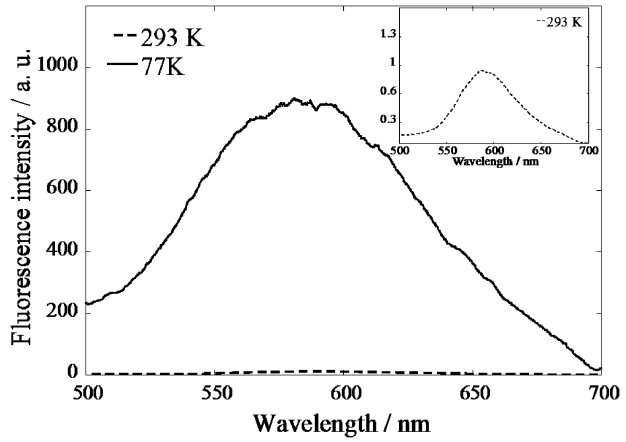


Fig. 4 Fluorescence spectra of 4,4′-dimethoxy-HC in EtOH at 77 K and room temperature (293 K). Inset: Fluorescence spectra of 4,4′-dimethoxy-HC at 293 K in EtOH (×1000).

Table 2 Fluorescence quantum yield of methoxy substituted-HCs in EtOH

	Φ_F (293 K)	Φ_F (77 K)
4-MeO-HC	9.0×10^{-6}	0.009
4′-MeO-HC	1.5×10^{-5}	0.013
4,4′-$(MeO)_2$-HC	2.0×10^{-5}	0.023

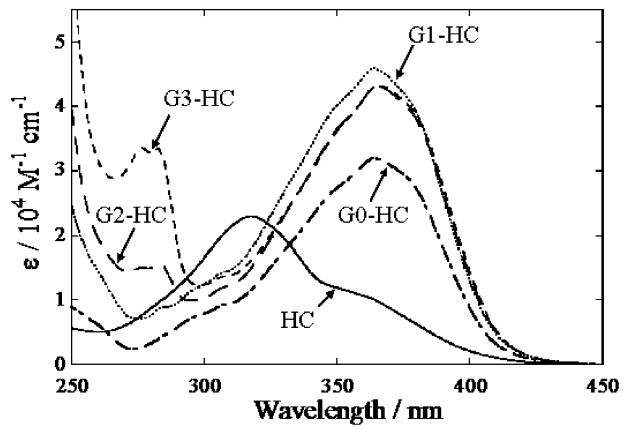


Fig. 5 Absorption spectra of 2′-hydroxychalcone (HC), 4,4′-dimethoxy-HC, G1-HC, G2-HC and G3-HC in THF.

determined as 8.3×10^{-6}, 1.1×10^{-5}, 2.0×10^{-5}, and 4.6×10^{-5}, respectively. The quantum yield is the highest for 4′-dimethylamino-HC.

The effect of dendritic structure is explored to determine the quantum yield of fluorescence emission in THF solution,

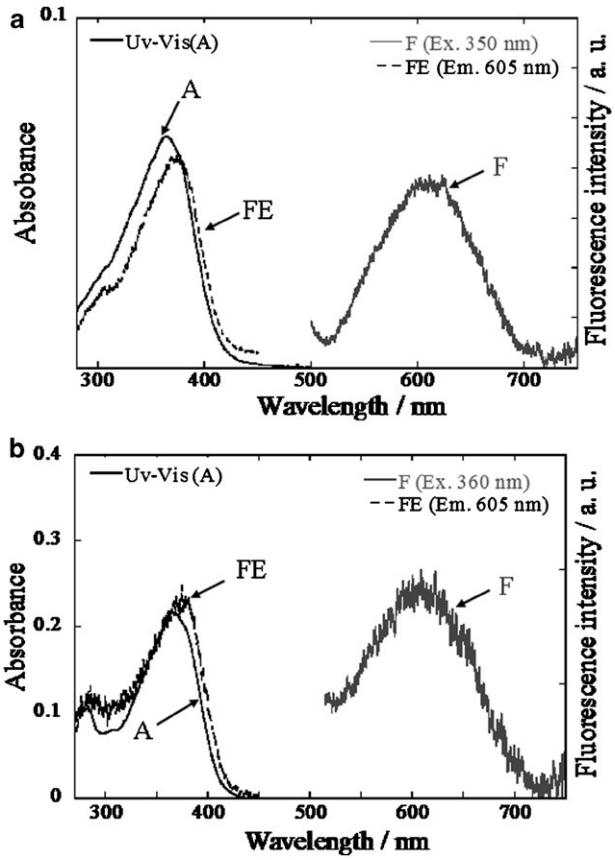


Fig. 6 (a) Absorption (A), fluorescence (F) and fluorescence excitation spectra (FE) of 4,4′-dimethoxy-HC in benzene and, (b) G2-HC in THF.

because the dendrimers dissolve in THF rather than in benzene. Thus, the fluorescence quantum yield slightly increased from 2.2×10^{-5} to 3.6×10^{-5} with increasing generation from 4,4′-dimethoxy-HC (G0-HC) to G3-HC.

Photochemical processes

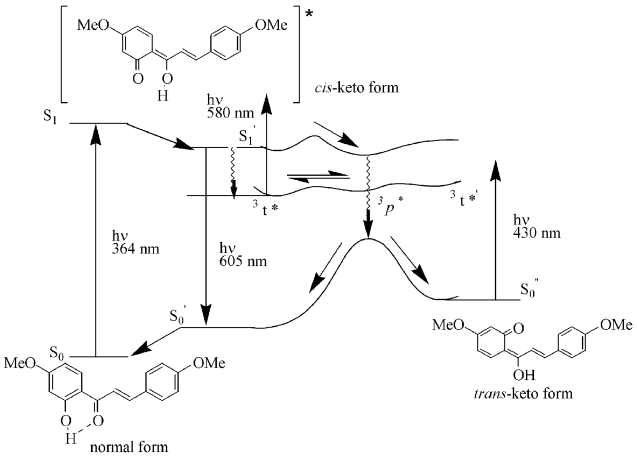
On photoirradiation of HCs, no appreciable change of the permanent absorption spectra was observed. Thus, the HCs are stable under steady-state photoirradiation conditions.

As discussed above, fluorescence spectra was observed at considerably longer wavelength region with a Stokes shift of 10^4 cm^{-1} for 4-methoxy-, 4′-methoxy- and 4,4′-dimethoxy-HC in benzene; the observed fluorescence emission was assigned to the tautomer produced by intramolecular hydrogen atom transfer in the excited singlet state (Scheme 3).

Previously, the fluorescence emission of the tautomer for the parent 2′-hydroxychalcone (HC) was reported by excitation

Table 3 Absorption maxima, fluorescence maxima, Stokes shift and fluorescence quantum yield of HC, 4,4′-dimethoxy-HC, G1-HC, G2-HC and G3-HC in THF under Ar

	$\lambda_{max\ UV}$/nm	ε/M^{-1} cm^{-1}	$\lambda_{max\ FL}$/nm	Stokes shift/cm^{-1}	Φ_F
HC	318	19 900			$<10^{-6}$
4,4′-$(MeO)_2$-HC	364	29 400	605	10 500	2.2×10^{-5}
G1-HC	364	45000	605	10 500	2.7×10^{-5}
G2-HC	364, 283	42 600, 18 500	605	10 500	3.2×10^{-5}
G3-HC	364, 283	43 100, 31 900	605	10 500	3.6×10^{-5}



Scheme 3 Mechanism of photoinduced hydrogen atom transfer in the excited state and decay processes.

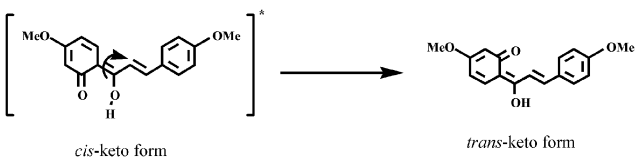
with laser light. However, in our experimental apparatus, we could not detect any fluorescence assigned to the tautomer for the parent 2′-hydroxychalcone and the maximum limit of the fluorescence emission of the tautomer of 2′-hydroxychalcone in the excited singlet state was thus estimated to be at the most 1×10^{-6}.

As summarized in Table 1, the introduction of the methoxy group increased the quantum yield of fluorescence emission by at least 10 times. The introduction of the dendritic structure also increased the quantum yield of fluorescence emission (Table 3) probably due to the inhibition of radiationless deactivation from the excited singlet state by structural change.

On irradiation of the normal form, intramolecular hydrogen atom transfer may take place to produce the tautomer (*cis*-keto form) in the excited singlet state, which can emit fluorescence at considerably longer wavelength or undergo intersystem crossing to the triplet state. In addition, radiationless deactivation by way of rotational isomerization around the quasi-double bond (Scheme 3 and 4) can take place to produce the *trans*-keto form in the ground state. The *trans*-keto form undergoes isomerization around the quasi-double bond to produce the *cis*-keto form in the ground state followed by reverse hydrogen atom transfer to give the normal form. Because of the low quantum yield of fluorescence emission at room temperature, the main deactivation pathway at room temperature seems to be the radiationless deactivation to the ground state or intersystem crossing to the triplet state.

Effect of substituent, temperature and dendritic structure on the tautomer emission

The introduction of an electron donating group such as a methoxy or dimethylamino group at the *para* position of the



Scheme 4 Rotational isomerization around the quasi-double bond in the excited state.

phenyl ring enabled us to observe the fluorescence emission from the tautomer produced in the excited singlet state as an adiabatic process. The reason of this substituent effect is not clear but the following points can be suggested. In order to observe the fluorescence emission from the tautomer, the intramolecular hydrogen atom transfer should proceed in the excited singlet state as an adiabatic process followed by the radiative deactivation from the tautomer. The radiative deactivation from the tautomer may compete with the deactivation by intersystem crossing to the triplet state and/or non-radiative deactivation by way of rotational isomerization around the quasi-double bond newly produced by intramolecular hydrogen atom transfer in the excited singlet state (Scheme 3). The electron donating substituent may change the excited state properties as observed in the tautomer fluorescence.[12,16,17] For example, the absorption shift depending upon the substituent on the benzene ring of 2′-hydroxychalcone has already been explored.[12] Furthermore, the increase of the quantum yield of tautomer fluorescence with the addition of an electron donating group at the benzene ring of hydrogen bonded compounds such as salicylideneanilines has been reported.[16,17] The origin of the enhancement of fluorescence emission was previously explained by the stabilization of the lowest excited singlet state (π,π^*) when increasing the electron-donor properties of the substituents.[16]

The temperature also affected the quantum yield of the fluorescence emission. Thus, the quantum yield increases more than 1000 times for methoxy-substituted chalcones, from *ca.* 10^{-5} to *ca.* 10^{-2}. This remarkable increase could be the consequence of the decrease of the non-radiative deactivation by means of rotation around the quai-double bond.

The large substituent may affect the deactivation processes from the excited singlet state. If one can assume that the occurrence of the intramolecular hydrogen atom transfer may need some special structure in the hydrogen bonded compounds, the dendritic structure may provide a suitable molecular arrangement for adiabatic intramolecular hydrogen atom transfer. Furthermore, in the deactivation processes, the isomerization around the quasi-double bond produced by hydrogen atom transfer in the excited state may take place to decrease the singlet lifetime of the tautomer and to decrease the quantum yield of fluorescence emission. The dendritic structure may decrease the isomerization around the quasi-double bond to increase the singlet lifetime and the quantum yield of fluorescence emission. Actually, one can observe the increase of fluorescence emission from the tautomer by introduction of the dendritic structure by 1.5 times, although the effect is small.

Photochromic properties of hydrogen bonded HCs

2′-Hydroxychalcones have two photoreactive parts, O–H:O intramolecular hydrogen bonding for hydrogen atom transfer and C=C double bond for *trans–cis* isomerization. The *trans–cis* isomerization may induce the color change of the compounds or at least the change of the absorption spectra. We could not observe the photochemical *trans–cis* isomerization in the 2′-hydroxychalcones examined in this study. Usually,

chalcones without O–H:O intramolecular hydrogen bonding undergo mutual *cis–trans* photoisomerization to give a mixture of *cis* and *trans* isomers. However, we have already reported that the parent compound 2′-hydroxychalcone underwent one-way *cis*-to-*trans* photochemical isomerization around the double bond controlled by photoinduced hydrogen atom transfer in the excited state to give 100% *trans* isomer at the photostationary state.[18,20] As mentioned above, the *trans* isomers of substituted HCs with O–H:O intramolecular hydrogen bonding are also practically stable on photo-irradiation. However, hydrogen atom transfer in the excited state did take place as observed spectroscopically. In particular, ultrafast intramolecular hydrogen atom transfer took place to produce the emissive tautomer giving fluorescence at a long wavelength region of red light. Thus, the photochromic tautomer deactivates by radiative and non-radiative processes to give the starting compound and this process might occur in very fast photochromic cycles due to the forward and backward intramolecular hydrogen atom transfer processes.

Conclusions

2′-Hydroxychalcones form intramolecular hydrogen bonding. The parent compound 2′-hydroxychalcone undergoes one-way *cis*-to-*trans* photochemical isomerization by way of intramolecular hydrogen atom transfer to produce the tautomer in the excited state followed by *cis*-to-*trans* isomerization and deactivation to the ground state. However, we could not observe fluorescence emission from the tautomer or any evidence for occurrence of hydrogen atom transfer in the excited singlet state in unsubstituted 2′-hydroxychalcone. In this paper, the tautomer fluorescence from 2′-hydroxychalcones was successfully observed by conventional fluorescence spectrometry. The effect of substituents with different electronic properties, introduction of dendritic structure, and temperature, on the efficiency of the tautomer emission produced by adiabatic intramolecular hydrogen atom transfer was evaluated. The introduction of the methoxy group as the electron donating substituent on the benzene ring made it possible to observe fluorescence emission from the tautomer. The quantum yield of the red light fluorescence from the transiently produced tautomer is 1000 times higher at 77 K than that at room temperature. Even if the effect is small, the fluorescence quantum yield of the tautomer increased with increasing generation of the dendrimer. Therefore, one could also increase the characteristic red fluorescence of the tautomer by introduction of the dendritic structure surrounding the 2′-hydroxychalcone core.

Experimental

Measurements

Absorption and fluorescence spectra were measured on a Shimadzu UV-1600 and on a Hitachi F-4500 fluorescence spectrometer, respectively. The quantum yields of fluorescence emissions were determined by using anthracene (Φ_f = 0.27) as a standard. A correction in the difference in refractive index among the solvents was made for each sample. The absorbance of the sample solution at the excitation wavelength was adjusted to less than 0.1, and the integration of the fluorescent spectra over all wavenumbers was plotted against absorbance at the excitation wavelength. The slope of these plots gives the relative value of the fluorescence quantum yield, and the quantum yield of fluorescence emission was then determined. All the solvents used in this experiments were of UV and fluorescence spectroscopic grade and were used without further purification. Only ethanol contains 0.5% H_2O (99.5% purity, Wako).

Synthesis

General procedure for the preparation of 2′-hydroxychalcones. Substituted 2′-hydroxychalcones (Scheme 1) were prepared by condensation of the appropriate ketones and aldehydes and the structures were determined by NMR and elemental analysis.[24–26]

4,4′-Dimethoxy-HC. The mixture of 4-methoxybenzaldehyde (1.71 g, 12.5 mmol) and 2′-hydroxy-4′-methoxyacetophenone (1.75 g, 10.5 mmol) was added in EtOH. 1.5 mol dm^{-3} KOH in EtOH (35 ml) was added and the mixture stirred under nitrogen at room temperature for 23 h. This reaction mixture was neutralized by addition of 1.2 mol dm^{-3} AcOH in EtOH. This mixture was extracted with ethyl acetate and the obtained organic layer was dried with Na_2SO_4. Then the solution was evaporated and recrystallized from EtOH to give 2′-hydroxy-4,4′-dimethoxychalcone as yellow crystals with a yield of 0.58 g (2.0 mmol, 19.3%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.87 (s, 6H, OMe), 6.47–6.52 (m, 2H; Ph–H), 6.95 (d, J = 8.9 Hz, 2H; Ph–H), 7.47 (d, J = 15.3 Hz, 1H; –HC═CH–), 7.62 (d, J = 8.9 Hz, 2H; Ph–H), 7.87 (d, J = 15.3 Hz, 1H; –HC═CH–), 7.86 (m, 1H; Ph–H), 13.56 (s, 1H; –OH). ^{13}C NMR (100 MHz, $CDCl_3$): 55.38, 55.52, 101.02, 107.55, 114.10, 114.41, 117.74, 127.46, 130.32, 131.08, 144.22, 161.75, 165.98, 166.57, 191.82. Anal. Calc. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.62. Found: C, 71.83; H, 5.68%.

4-Nitro-HC. ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.99 (t, J = 8.1 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 8.1 Hz, 1H), 7.79–7.96 (m, 5H), 8.30 (d, J = 8.1 Hz, 2H), 12.58 (s, 1H). Anal. Calc. for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20. Found: C, 65.98; H, 4.33; N, 5.20%.

4-Cyano-HC. ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.97 (t, J = 8.1 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 8.1 Hz, 1H), 7.69–7.74 (m, 5H), 7.85–7.92 (m, 2H), 12.59 (s, 1H). Anal. Calc. for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 76.61; H, 4.75; N, 5.53%.

4-Cyano-4′-methoxy-HC. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.88 (s, 3H), 6.49–6.53 (m, 2H), 7.64 (d, J = 15.4 Hz, 1H), 7.73 (s, 4H), 7.79–7.87 (m, 2H), 13.23 (s, 1H). Anal. Calc. for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.96; H, 4.91; N, 5.95%.

4-Methoxy-HC. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.87 (s, 3H), 6.91–7.04 (m, 4H), 7.46–7.65 (m, 4H), 7.88–7.94 (m, 2H), 12.93 (s, 1H). Anal. Calc. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55% Found: C, 75.36; H, 5.62%.

4′-Methoxy-HC. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.87 (s, 3H), 6.48–6.52 (m, 2H), 7.42–7.67 (m, 6H), 7.82–7.92 (m, 2H), 13.42 (s, 1H). Anal. Calc. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55 Found: C, 75.28; H, 5.66%.

4-Dimethylamino-HC. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.07 (s, 6H), 6.70 (d, J = 8.9 Hz, 2H), 6.92 (t, J = 7.0 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 7.43–7.60 (m, 4H), 7.90–7.95 (m, 2H), 13.19 (s, 1H). Anal. Calc. for $C_{17}H_{17}NO_2$:C, 76.38; H, 6.41; N, 5.24. Found: C, 76.2; H, 6.42; N, 5.53%.

General procedures for the preparation of G1–G3. Dendrimers used in this study (Scheme 2) were synthesized by condensation of 2,4,4′-trihydroxychalcone[27] (Scheme 5) and the corresponding dendrons as summarized in Scheme 6. The structures of the dendrimers were determined by several analytical data. Dendrons were synthesized according to a reported procedure.[28]

Synthesis of the core

Step 1. Protection of the 2′,4′-dihydroxyacetophenone. To a solution of 2′,4′-dihydroxyacetophenone (9.9 g, 65.1 mmol) and *N*-ethyl diisopropylamine (21.2 g, 164 mmol) in CH_2Cl_2 (120 ml), chloromethyl methyl ether (7.9 g, 98.1 mmol) was added. The mixture was stirred at room temperature for 1 h. Water (150 ml) was then added and the mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, and evaporated. Column chromatography (SiO_2, 15 : 1 *n*-hexane–acetone mixture) yielded 2′,4′-dihydroxyacetophenone as a clear and colorless oil. 10.9 g (55.9 mmol, 85.9%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 12.58 (s, 1H), 7.63 (d, 1H), 6.53–6.59 (m, 2H), 5.16 (s, 2H), 3.44 (s, 3H), 2.51 (s, 3H).

Step 2. Protection of 4-hydroxybenzaldehyde. To a solution of 4-hydroxybenzaldehyde (10.0 g, 81.9 mmol) and *N*-ethyl diisopropylamine (29.4 g, 22.7 mmol) in CH_2Cl_2 (70 ml), chloromethyl methyl ether (10.8 g, 134 mmol) was added. The mixture was stirred at room temperature for 2 h. Water was then added (100 ml) and the mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, and evaporated. Column chromatography (SiO_2, toluene) gave the derivative of 4-hydroxybenzaldehyde as light orange oil. 12.6 g (76.0 mmol, 93.0%). ^{1}H NMR (200 MHz, DMSO): δ 9.87 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 5.30 (s, 2H), 3.38 (s, 3H).

Step 3. Aldol condensation reaction. A mixture of 2′-hydroxy-4′-methoxyacetophenone (5.14 g, 26.2 mmol), 4-methoxybenzaldehyde (5.52 g, 33.2 mmol) and 1.5 mol l^{-1} KOH in EtOH (25 ml) was stirred at room temperature for 20 h. Then the mixture was filtered and the obtained solution was neutralized by addition of 10% AcOH in EtOH. To the mixture obtained by evaporation was added ethyl acetate. The remaining precipitate in this solution was filtered off and the filtrate was evaporated to give a yellow oil (7.03 g).

Step 4. Deprotection reaction. In the methanol solution (10 ml) of the mixture from step 3 (7.03 g), 10% HCl–MeOH (100 ml) was added. The mixture was stirred at room temperature for 7 h and then 10% HCl–MeOH (100 ml) was added. This mixture was stirred at room temperature for 4 h, neutralized with a saturated $NaHCO_3$ solution and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated. Column chromatography (SiO_2, ethyl acetate–toluene = 1 : 8) gave 2,2′,4′-trihydroxychalcone as a yellow solid (0.49 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.26 (d, J = 2.6 Hz, 1H), 6.39 (dd, J = 2.6,8.6 Hz, 1H), 6.83 (d, J = 8.6 Hz, 2H), 7.73–7.75 (m, 4H), 8.14 (d, J = 8.6 Hz, 1H), 10.12 (s, 1H), 10.66 (s, 1H), 13.60 (s, 1H).

Synthesis of dendrons

The dendrons used for the synthesis of G1–G3 were prepared according to the procedure reported elsewhere.[28]

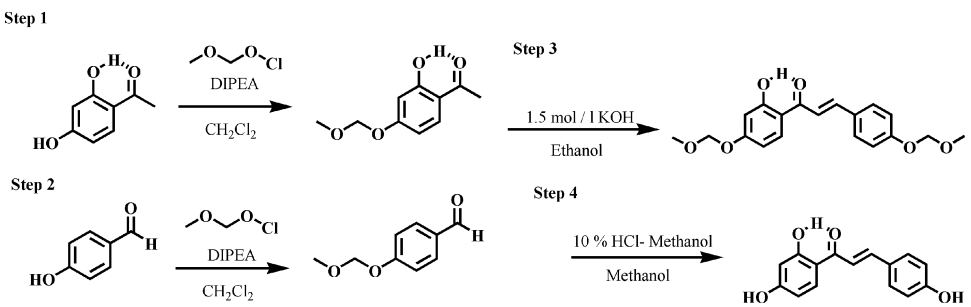
G1-Br. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.92 (s, 3H), 4.50 (s, 2H), 7.46 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H).

G2-OH. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.92 (s, 6H), 4.62 (s, 2 H), 5.09 (s, 4H), 6.52–6.63 (m, 3H), 7.47 (d, J = 8.0 Hz, 4H), 8.04 (d, J = 8.0 Hz, 4H).

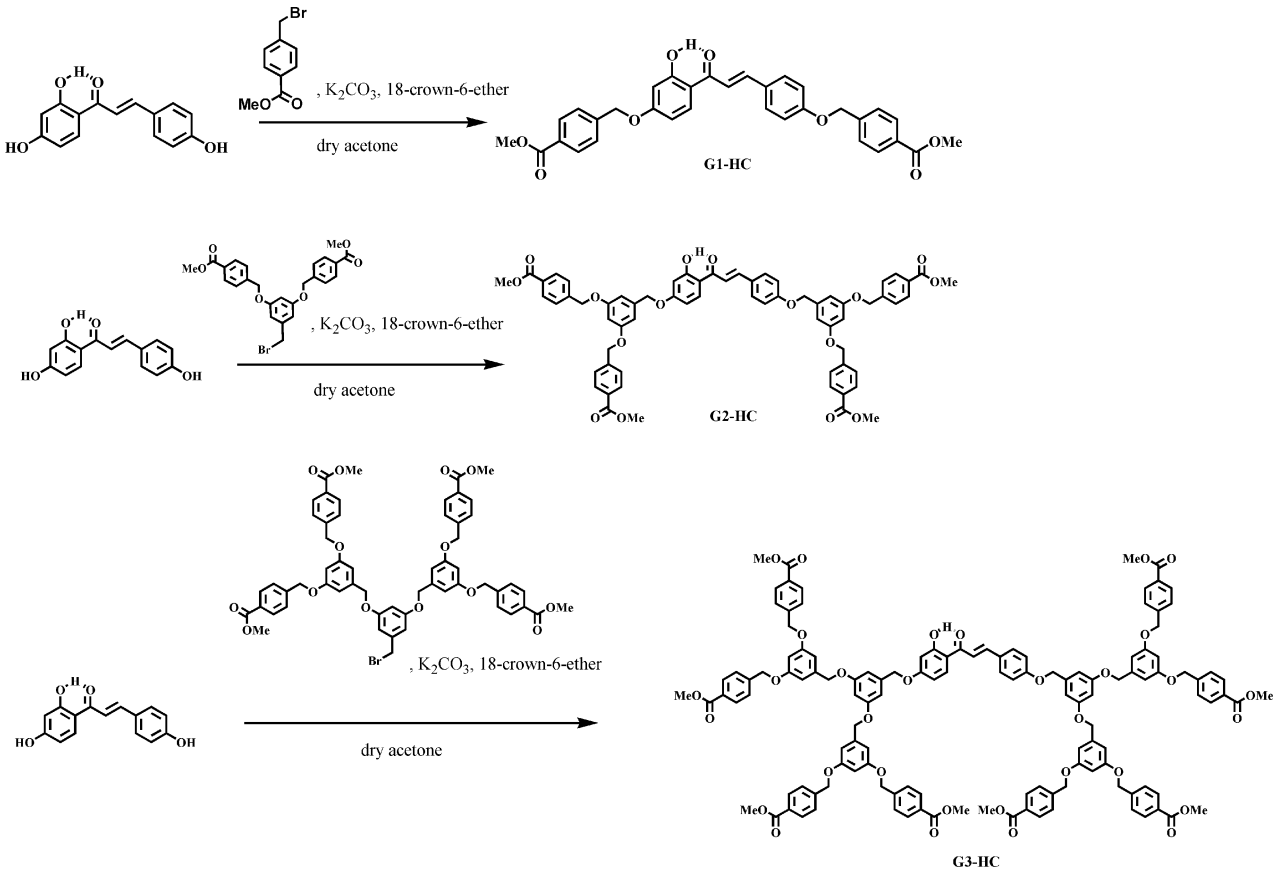
G2-Br. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.93 (s, 6H), 4.41 (s, 2 H), 5.10 (s, 4H), 6.51–6.65 (m, 3H), 7.50 (d, J = 8.1 Hz, 4H), 8.06 (d, J = 8.1 Hz, 4H).

G3-OH. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.90 (s, 12 H), 4.60 (d, 2 H), 4.95 (s, 4H), 5.05 (s, 8H) 6.50–6.66 (m, 9H), 7.42 (d, J = 8.0 Hz, 8H), 8.02 (d, J = 8.0 Hz, 8H).

G3-Br. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.92 (s, 12 H), 4.39 (s, 2 H), 4.95 (s, 4H), 5.09 (s, 8H), 6.49–6.66 (m, 9H), 7.47 (d, J = 8.0 Hz, 8H), 8.04 (d, J = 8.0 Hz, 8H).



Scheme 5 Synthesis of the core of 2′-hydroxychalcone dendrimers.



Scheme 6 Synthesis of 2′-hydroxychalcone dendrimers.

Synthesis of dendrimers

G1-HC. To a solution of 2′,4,4′-trihydroxychalcone (44.8 mg, 0.174 mmol) and G1-Br (86.1 mg, 0.38 mmol) in dry acetone (10 ml) was added potassium carbonate (2.09 g, 15.1 m mol) and 18-crown-6-ether (0.394 g, 1.49 mmol). The mixture was heated at reflux (60 °C) under nitrogen for 7 h. The reaction mixture was filtered and the filtrate was evaporated. The residue was recrystallized from ethyl acetate and *n*-hexane to give G1-HC as a yellow solid in 16.7% yield (16 mg, 0.03 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 6H; OMe), 5.18 (s, 4H; OCH_2), 6.54 (d, J = 2.4 Hz, 1H; Ph-H), 6.57 (dd, J = 2.4, 8.8 Hz, 1H; Ph-H), 7.01 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 15.6 Hz, 1H; –HC═CH–), 7.51 (d, J = 8.2 Hz, 4H), 7.62 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.8 Hz, 1H; Ph–H), 7.87 (d, J = 15.6 Hz, 1H; –HC═CH–), 8.08 (d, J = 8.2 Hz, 4H; Ph–H), 13.51 (s, 1H; –OH). ^{13}C NMR (100 MHz, $CDCl_3$): 52.09, 69.32, 69.37, 102.02, 107.90, 114.40, 115.02, 117.96, 127.89, 129.82, 129.87, 129.88, 130.32, 131.15, 140.92, 141.39, 144.14, 160.50, 164.63, 166.61, 166.64, 191.77. Anal. Calc. for $C_{33}H_{28}O_8$: C, 71.73; H, 5.11. Found: C, 71.41; H, 5.24. MALDI-TOFMS: Calc. for $C_{33}H_{28}O_8Na$ [M + Na]$^+$: m/z 575.2. Found: 574.8.

G2-HC. To a solution of 2′,4,4′-trihydroxychalcone (153 mg, 0.60 mmol) and G2-Br (597 mg, 1.20 mmol) in dry acetone (25 ml) was added potassium carbonate (244 mg, 1.77 mmol) and 18-crown-6-ether (62.3 mg, 0.24 mmol). The mixture was heated at reflux (60 °C) under nitrogen for 2.5 h. Water (120 ml) was then added and filtration gave a yellow solid. Column chromatography (SiO_2, CH_2Cl_2–diethyl ether = 20 : 1) and recrystallization from ethyl acetate and *n*-hexane gave G2-HC as a yellow solid in 51% yield (330 mg, 0.30 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 12H; OMe), 5.05 (s, 4H; OCH_2), 5.11 (s, 8H; OCH_2), 6.49–6.56 (m, 4H; Ph–H), 6.56–6.67 (m, 4H; Ph–H), 6.96 (d, J = 8.8 Hz, 2H; Ph–H), 7.47 (d, J = 15.6 Hz, 1H; –HC═CH–), 7.48 (d, J = 8.0 Hz, 8H; Ph–H), 7.59 (d, J = 8.8 Hz, 2H; Ph–H), 7.83–7.87 (m, 1H; Ph–H), 7.84 (d, J = 15.6 Hz, 1H; –CH═CH–), 8.04 (d, J = 8.0 Hz, 8H; Ph–H), 13.53 (s, 1H; –OH). ^{13}C NMR (100 MHz, $CDCl_3$): 52.17, 52.19, 69.44, 69.76, 69.83, 69.90, 101.70, 101.79, 102.11, 106.41, 108.06, 114.39, 115.31, 117.95, 126.97, 126.99, 127.82, 129.64, 127.82, 129.64, 129.75, 129.90, 130.40, 131.22, 138.60, 139.06, 141.80, 144.25, 159.92, 160.71, 164.86, 166.47, 166.80, 191.86. Anal. Calc. for $C_{65}H_{56}O_{16}$: C, 71.42; H, 5.16. Found: C, 71.20; H, 5.29. MALDI-TOFMS: Calc. for $C_{65}H_{56}O_{16}Na$ [M + Na]$^+$: m/z 1115.4. Found: 1115.6.

G3-HC. To a solution of 2,2′,4′-trihydroxychalcone (35.4 mg, 0.14 mmol) and G3-Br (300 mg, 0.29 mmol) in dry acetone (15 ml) was added potassium carbonate (81.5 mg, 0.59 mmol) and 18-crown-6-ether (14.7 mg, 0.06 mmol). The mixture was heated at reflux (50 °C) under nitrogen for 4 h. Water (10 ml) was then added and filtered to give a yellow solid. Column chromatography (SiO_2, CH_2Cl_2–diethyl

ether = 20 : 1) and the recrystallization from ethyl acetate and *n*-hexane gave G3-HC as a yellow solid in 54% yield (162 mg, 0.074 mmol). ^{1}H NMR (100 MHz, $CDCl_3$): δ 3.91 (s, 24H; –OMe), 4.98 (s, 8H; –OCH_2–), 5.04 (s, 4H; –OCH_2–), 5.09 (s, 16H; –OCH_2–), 6.50–6.53 (m, 8H; Ph–H), 6.62–6.66 (m, 12H; Ph–H), 6.96 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 15.2 Hz, 1H; –CH=CH–), 7.46 (d, J = 8.0 Hz, 16H; Ph–H), 7.56 (d, J = 8.0 Hz, 2H; Ph–H), 7.78–7.81 (m, 1H; Ph–H), 7.83 (d, J = 15.2 Hz, 1H; –CH=CH–), 8.03 (d, J = 8.0 Hz, 16H; Ph–H), 13.52 (s, 1H; –OH). ^{13}C NMR (100 MHz, $CDCl_3$): 52.04, 69.31, 69.75, 69.84, 69.90, 101.50, 101.53, 106.25, 106.34, 106.35, 107.91, 114.26, 115.21, 117.77, 126.87, 127.67, 129.62, 129.63, 129.78, 130.28, 138.31, 138.77, 139.28, 141.74, 141.77, 144.11, 159.77, 159.91, 160.70, 164.82, 166.38, 166.66, 191.69. MALDI-TOFMS: Calc. for $C_{129}H_{112}O_{32}Na$ $[M + Na]^+$: m/z 2195.7. Found: 2196.9.

Acknowledgements

This work was supported by a Grant-in-Aid for Science Research in a Priority Area "New Frontiers in Photochromism (No. 471)" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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