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# PHOTOCHEMICAL BEHAVIOR OF 2'-HYDROXYCHALCONE DERIVATIVES HAVING PYRIDYL AND QUINOLYL GROUPS

**Fumiya Aizawa, Yukino Shinozaki, Yuka Ishida, and Tatsuo Arai ***

Graduate School of Pure and Applied Science, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan; E-mail: arai@chem.tsukuba.ac.jp

**Abstract** – 2'-Hydroxy chalcone derivatives having heteroaromatic rings have been synthesized and their photochemical and photophysical properties have been examined in terms of tautomer produced by intramolecular hydrogen atom transfer reaction.

## INTRODUCTION

The aromatic compounds having the intramolecular hydrogen bonding are known to undergo photoinduced hydrogen atom transfer[1-14] and to give fluorescence with large Stokes shift in comparison with the compound which does not have intramolecular hydrogen bonding. This fluorescence is caused by the tautomer of the excited state produced from intramolecular hydrogen atom transfer reaction under light irradiation. Because one can change the wavelength of fluorescence emission by introducing the hydrogen bonding in molecules, it is expected to apply the intramolecular hydrogen-bonded compound to light emissive materials. 2'-Hydroxychalcone (**2HC**) has plural photoresponsive parts and shows the specific photochemical behavior including photoinduced hydrogen atom transfer reaction followed by one-way *cis*-to-*trans* isomerization[15-17] and photocyclization reaction.[12] Actually, we have elucidated

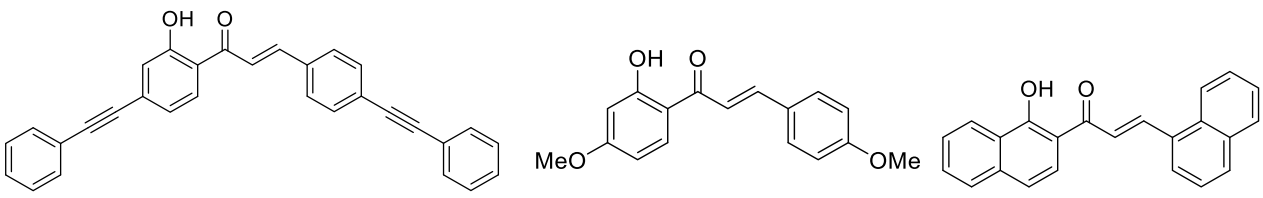



Figure 1. Structure of 2'-hydroxychalcones already reported

hydrogen atom transfer and *cis*-to-*trans* one way isomerization reaction in the excited triplet state by transient spectroscopy as well as steady state photoisomerization measurements.[15-18] Since the fluorescence quantum yield is small for **2HC**, we have tried to increase the quantum yield of fluorescence emission from the tautomer of **2HC** and its derivatives (Figure 1).[19-23] We have synthesized several compounds by introducing electron donating and/or electron accepting substituents or π conjugated system on the benzene rings of **2HC**, but still these compounds gave small value of fluorescence quantum yield (at most $2x10^{-5}$).[23]

Since the study of photoinduced hydrogen atom transfer in **2-HC** and its derivatives is limited to aromatic hydrocarbons, we are interested in studying the behavior of **2HC** derivatives having heteroaromatic rings. Therefore, we synthesized several compounds having heteroaromatic ring instead of benzene ring on the **2HC** to perform various spectrophotometric measurement for investigating photochemical behavior. We wish to report here the photochemical properties of **2HC** derivatives having pyridine and quinoline, as shown in Figure 2.

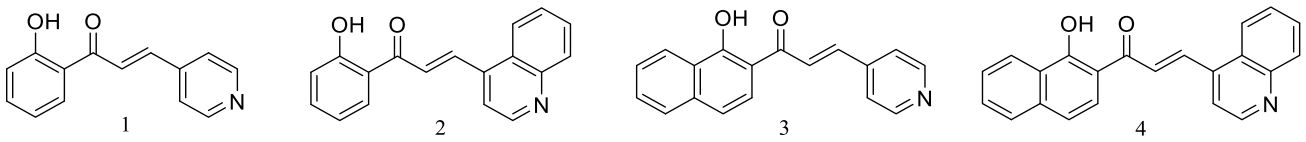



Figure 2. Structure of 2HC derivatives examined in this work

## RESULTS AND DISCUSSION

We have prepared **2HC** derivatives **1-4** listed in Figure 2 and did various spectroscopic and photoisomerization measurement in benzene. We compared the absorption spectra between **1** and **2** and between **3** and **4** (Figure 3). The extinction coefficient is higher for quinoline derivatives (**2** and **4**) compared to pyridine derivatives (**1** and **3**), but there were not significant differences between **1** and **2** and between **3** and **4** in the absorption profiles. However, the absorption maximum of the longer wavelength region from 360 nm for **1** and **2** to 415 nm for **3** and **4**. These results indicate that the change of the conjugation of aromatic ring from benzene to naphthalene at the intramolecular hydrogen bonding part considerably influenced the absorption profile of **2HC** derivatives. We have also measured the absorption spectra of **1-4** in polar solvent such as acetonitrile and polar protic solvent such as ethanol other than benzene. Almost no solvent effect was observed for all compounds **1-4**. Therefore, intramolecular O-H:O hydrogen bonding has scarcely influenced the electronic states even by polar protic solvent.

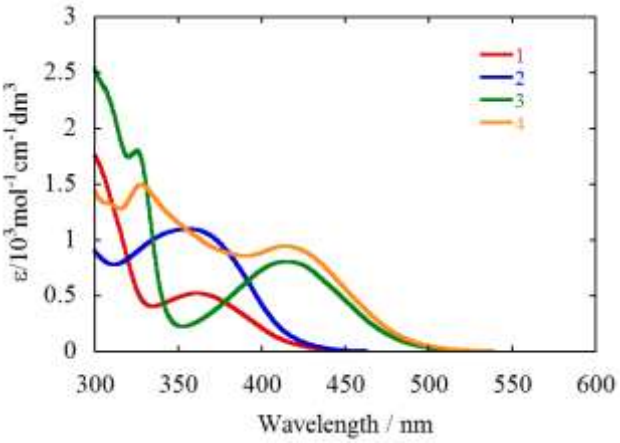



Figure 3. Absorption spectra of **1**-**4** in benzene

Fluorescence emission of large Stokes shift (approximately 8,000 $cm^{-1}$) was observed for **3** and **4** which are naphthalene-based **2HC** derivatives, as shown in Figure 4. Fluorescence spectra for **3** and **4** are almost the same for any excitation wavelength from 390-430 nm and the fluorescence excitation spectra are again almost the same for emission wavelength from 590-650 nm. Moreover, excitation spectra observed for **3** and **4** are almost superimposed to the absorption spectra of **3** and **4**. The experimental results strongly support that the fluorescence spectra come from the excitation of **3** and **4**. As summarized in Table 1, the fluorescence quantum yields of **3** and **4** are ca. $10^{-4}$ and is higher than the **2HC** derivatives already reported (at most $2x10^{-5}$).[23] However, the fluorescence emission could not be observed for **1** and **2** at room temperature.

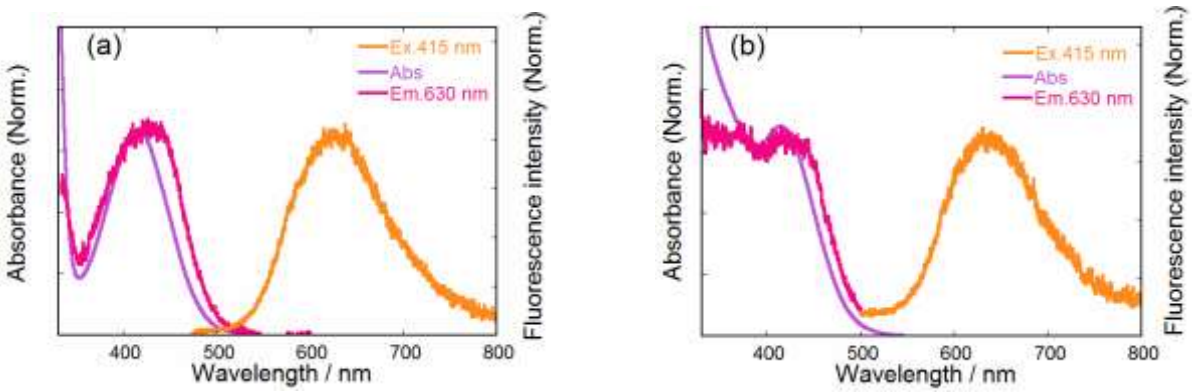
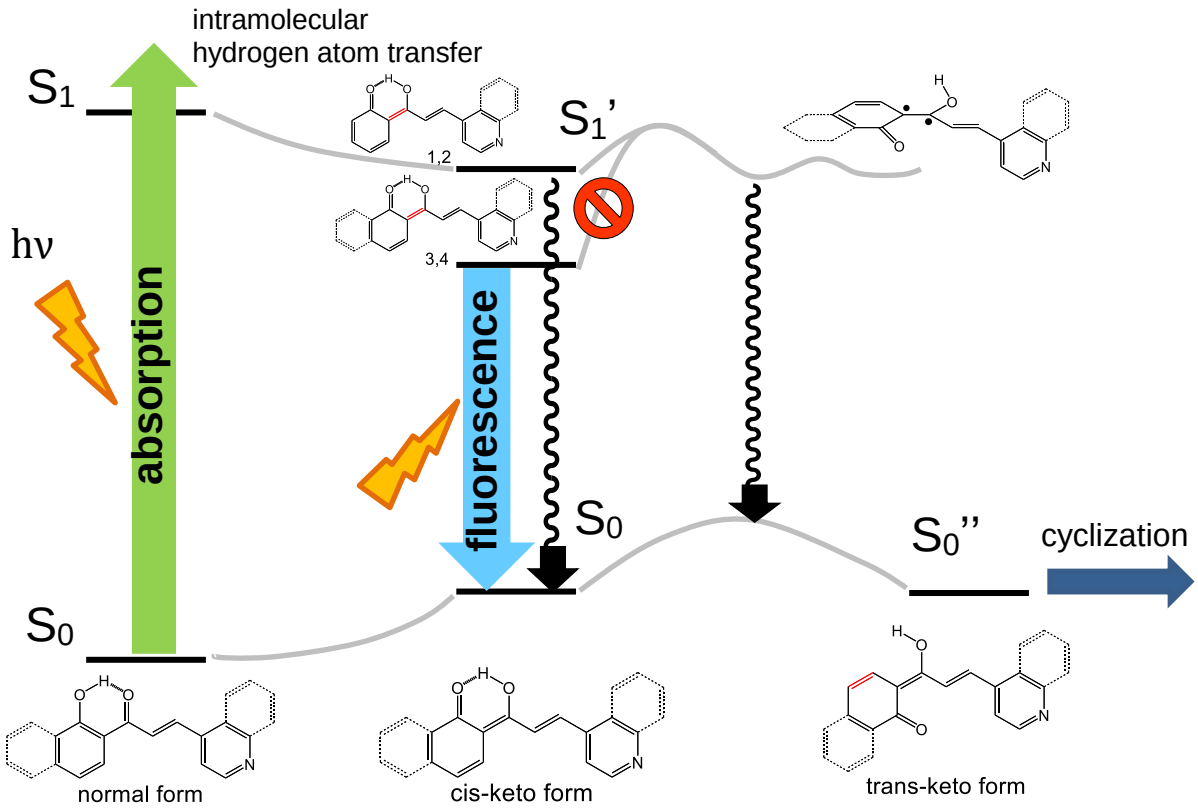



Figure 4. Fluorescence and fluorescence excitation spectra of **3** (a) and **4** (b) in benzene

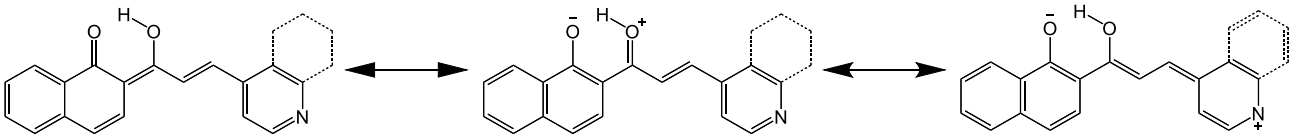
Table 1. Parameters of absorption and fluorescence spectra of **3** and **4** in benzene

| Compound | $\lambda_{abs}/nm$ | $\lambda_{FL}/nm$ | $\Delta E_{ss}/cm$ | $\Phi_{FL}$ |
|---|---|---|---|---|
| **3** | 415 | 630 | 8200 | $1.1\times10^{-4}$ |
| **4** | 415 | 635 | 8300 | $9.2\times10^{-5}$ |

Scheme 1 shows the potential energy surfaces of photochemical and photophysical behavior of **1-4**. The increase of fluorescence quantum yield for **3** and **4** could be explained by the resonance structure by electron accepting group pyridine and quinoline to stabilize the tautomer excited state (Scheme 2). In other word, since the normal form of **3** and **4** in the excited singlet state is lower in energy than that of **1** and **2**, it is thought that the energy of the tautomers **3'** and **4'** produced from **3** and **4** should be lower than the tautomers **1'** and **2'** (Scheme 1). Thus, it is proposed that energy barrier of isomerization around C=C double bond newly produced by intramolecular hydrogen atom transfer in tautomer **3** and **4** should be larger than that of **1** and **2**. It resulted in the suppression of non-radiative deactivation from the singlet excited state of **3** and **4** (Scheme 1).




Scheme 1. Potential energy surfaces of photoinduced hydrogen atom transfer and subsequent processes.



Scheme 2. Resonance structures of *cis*-keto form of **3** and **4**

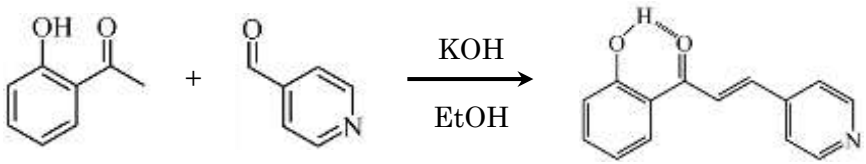
We should mention here the difference of fluorescence properties among **1**-**4**. At first we examined whether photoinduced hydrogen atom transfer takes place or not and the stability and deactivation processes of the tautomer. The occurrence of intramolecular hydrogen atom transfer could be related to the properties of excited singlet state whether the hydrogen bonded part is involved in the lowest excited state: if this is the case, photoinduced hydrogen atom transfer may take place. Second, the stability of the tautomer in the excited state is needed to observe the tautomer emission at longer wavelength region. When the energy of the tautomer is high enough to undergo isomerization around the newly produced C=C double bond in *cis*-keto form (Scheme 1), the observation of the tautomer emission seems to be difficult. Therefore, the main factor to observe the tautomer emission should be related to the efficiency of hydrogen atom transfer reaction and the subsequent non-radiative reaction processes such as isomerization to give the *trans*-keto form.

In conclusion, we have succeeded to increase the quantum yield of fluorescence emission of **2HC** derivatives by introducing heteroaromatic rings instead of benzene or naphthalene rings. Furthermore, as far as we are aware, the present compounds **3** and **4** give the highest fluorescence quantum yield at room temperature in 2'-hydroxychalcone and its derivatives.

## EXPERIMENTAL

### GENERAL INFORMATION

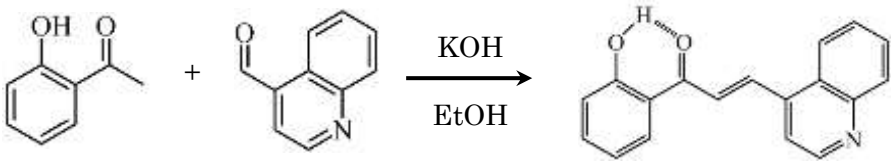
(2*E*)-1-(2-Hydroxyphenyl)-3-(4-pyridinyl)-2-propen-1-one (**1**)




To a solution of potassium hydroxide (1.63 g, 29.1 mmol) in EtOH (60 mL) was added 4-pyridinecarboxyaldehyde (0.95 mL, 10 mmol). Then, o-hydroxyacetophenone (1.2 mL, 10 mmol) was added to the solution at 0 ℃ under an atmosphere of nitrogen and the solution was stirred at 0 ℃ for 2.5 h. The solution was warmed to room temperature and stirred for additional 4.5 h. Acetic acid solution was added to the solution and the reaction was quenched. The red solid was collected by

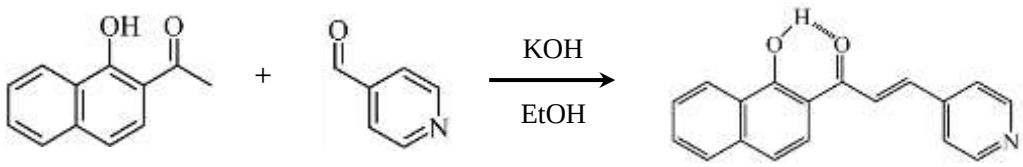
filtration followed by purification by silica gel column chromatography [eluent: $CH_2Cl_2$/EtOH (20:1)] to afford the compound **1** (233 mg, 10.3%) as red crystals; mp 124-125 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ12.2 (s, 1H), 8.68 (dd, *J* = 1.6, 4.5 Hz, 2H), 8.21 (d, *J* = 15.7 Hz, 2H), 8.21 (dd, *J* = 1.6, 8.2 Hz, 1H), 7.84 (dd, *J* = 1.6, 4.5 Hz, 1H), 7.75 (d, *J* = 15.7 Hz, 1H), 7.58 (dd, *J* = 1.6, 8.2 Hz, 1H), 7.02 (m, 2H). $^{13}$C NMR (400 MHz, DMSO-$d_6$): δ193.7, 162.0, 150.9, 142.0, 141.8, 137.0, 131.5, 127.1, 123.1, 121.5, 119.8, 118.2. Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.83; H, 5.20; N, 5.94.

(2*E*)-1-(2-Hydroxyphenyl)-3-(4-quinolinyl)-2-propen-1-one (**2**)



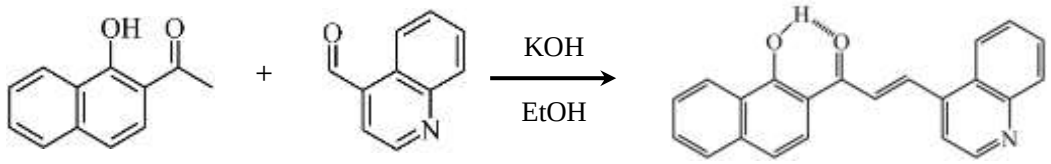

To a solution of potassium hydroxide (3.26 g, 58.1 mmol) in EtOH (60 mL) was added 4-quinolinecarboxyaldehyde(1.57 g, 10 mmol) and o-hydroxyacetophenone (1.2 mL, 10 mmol) under an atmosphere of nitrogen. The solution was stirred for 7 h at room temperature and then acetic acid solution was added to make the reaction mixture acidic. The resulting mixture was extracted with $CH_2Cl_2$. The combined organic phases were washed with water and brine, and then dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was recrystallized from $CH_2Cl_2$-hexane for two times and from EtOH for two times to give the compound **2** (223 mg, 8.1%) as a pink needle crystal; mp 106-107 ℃; $^1$H NMR(400 MHz, DMSO-$d_6$): δ12.1 (s, 1H), 9.02 (d, *J* = 4.5 Hz, 1H), 8.52 (d, *J* = 15.4 Hz, 1H), 8.35 (d, *J* = 8.7 Hz, 1H), 8.22 (d, *J* = 13.9 Hz, 1H), 8.22 (d, *J* = 4.5 Hz, 1H), 8.11 (m, 2H), 7.85 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.73 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.60 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.04 (m, 2H). $^{13}$C NMR (400 MHz, DMSO-$d_6$): δ193.4, 161.8, 150.8, 148.7, 139.8, 137.9, 137.0, 131.6, 130.3, 130.2, 129.3, 128.0, 126.1, 124.0, 121.8, 119.9, 119.3, 118.2. Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.67; H, 4.84; N, 5.02.

(2*E*)-1-(2-Hydroxynaphtyl)-3-(4-pyridyl)-2-propen-1-one (**3**)



To a solution of potassium hydroxide (3.26 g, 58.1 mmol) in EtOH (60 mL) was added 4-pyridinecarboxyaldehyde (0.94 mL, 10 mmol) and 1'-hydroxy-2'-acetonaphthone (1.86 g, 10 mmol) under an atmosphere of nitrogen. The solution was stirred for 8 h at room temperature and stirred for additional 12 h at 40 °C. Then acetic acid solution was added to make the mixture acidic. The red solid was collected by filtration followed by recrystallization from EtOH-water and from toluene to afford compound **3** (390 mg, 14.2%) as a red needle crystals; mp 144-145 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ14.8 (s, 1H), 8.71 (d, $J$ = 6.0 Hz, 2H), 8.42 (d, $J$ = 15.4 Hz, 1H), 8.39 (d, $J$ = 8.5 Hz, 1H), 8.33 (d, $J$ = 9.0 Hz, 1H), 7.96 (d, $J$ = 8.5 Hz, 1H), 7.93 (d, $J$ = 6.0 Hz, 2H), 7.90 (d, $J$ = 15.4 Hz, 1H), 7.77 (dd, $J$ = 7.5, 7.5 Hz,1H), 7.63 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.50 (d, $J$ = 9.0 Hz,1H). $^{13}$C NMR (400 MHz, DMSO-$d_6$): δ193.9, 163.9, 150.9, 142.7, 142.0, 137.7, 131.3, 128.2, 126.8, 126.0, 125.6, 124.8, 124.2, 123.2, 119.0, 113.8. Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.31; H, 4.75; N, 4.84.

(2*E*)-1-(2-Hydroxynaphtyl)-3-(4-quinolinyl)-2-propen-1-one (**4**)




To a solution of potassium hydroxide (3.26 g, 58.1 mmol) in EtOH (60 mL) was added 4-quinolinecarboxyaldehyde (1.57 g, 10 mmol) and 1'-hydroxy-2'-acetonaphthone (1.86 g, 10 mmol) under an atmosphere of nitrogen. The solution was stirred for 9 h at room temperature. Then acetic acid solution was added to make the mixture acidic. The red solid was collected by filtration followed by recrystallization from EtOH-water to afford compound **4** (96.0 mg, 3.0%) as a red powders; mp 120-121 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ14.8 (s, 1H), 9.06 (d, $J$ = 4.5 Hz, 1H), 8.69 (d, $J$ = 15.4 Hz, 1H), 8.45 (d, $J$ = 15.4 Hz, 1H), 8.41 (m, 2H), 8.35 (d, $J$ = 8.6 Hz, 1H), 8.25 (d, $J$ = 4.5 Hz, 1H), 8.13 (d, $J$ = 8.4 Hz, 1H), 7.98 (d, $J$ = 7.5 Hz, 1H), 7.87 (dd, $J$ = 8.4, 8.4 Hz, 1H), 7.79-7.73 (m, 2H), 7.66 (dd, $J$ = 7.9, 7.9, 1H), 7.51 (d, $J$ = 8.6 Hz, 1H). $^{13}$C NMR (400 MHz, DMSO-$d_6$): δ193.7, 163.9, 150.8, 148.8, 139.6, 138.8, 137.8, 131.3, 130.3, 130.3, 128.2, 128.1, 128.0, 126.9, 126.2, 125.7, 124.8, 124.3, 124.0, 119.5, 119.0, 113.9. Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30. Found: C, 81.34; H, 4.80; N, 4.18.

## MEASUREMENTS

Absorption and fluorescence spectra were measured on a Shimadzu UV-1600 and on a Hitachi F-4500 fluorescence spectrometer, respectively. All solvents of spectral grade for spectroscopy were purchased

and used without further purification. All measurements were carried out at room temperature under Ar. The concentration of solution for spectroscopy was adjusted so that the absorption maximum at the excitation wavelength was less than 0.1 for each sample. Fluorescence quantum yields were determined relative to anthracene ($\Phi_f$ = 0.27 in ethanol). $^1$H NMR spectra in $CDCl_3$ or DMSO-$d_6$ with TMS as an internal standard were measured on a 400 MHz NMR spectrometer, AV-400 (Bruker BioSpin).

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