

A Novel Approach to White-Light Emission Using a Single Fluorescent Urea Derivative and Fluoride

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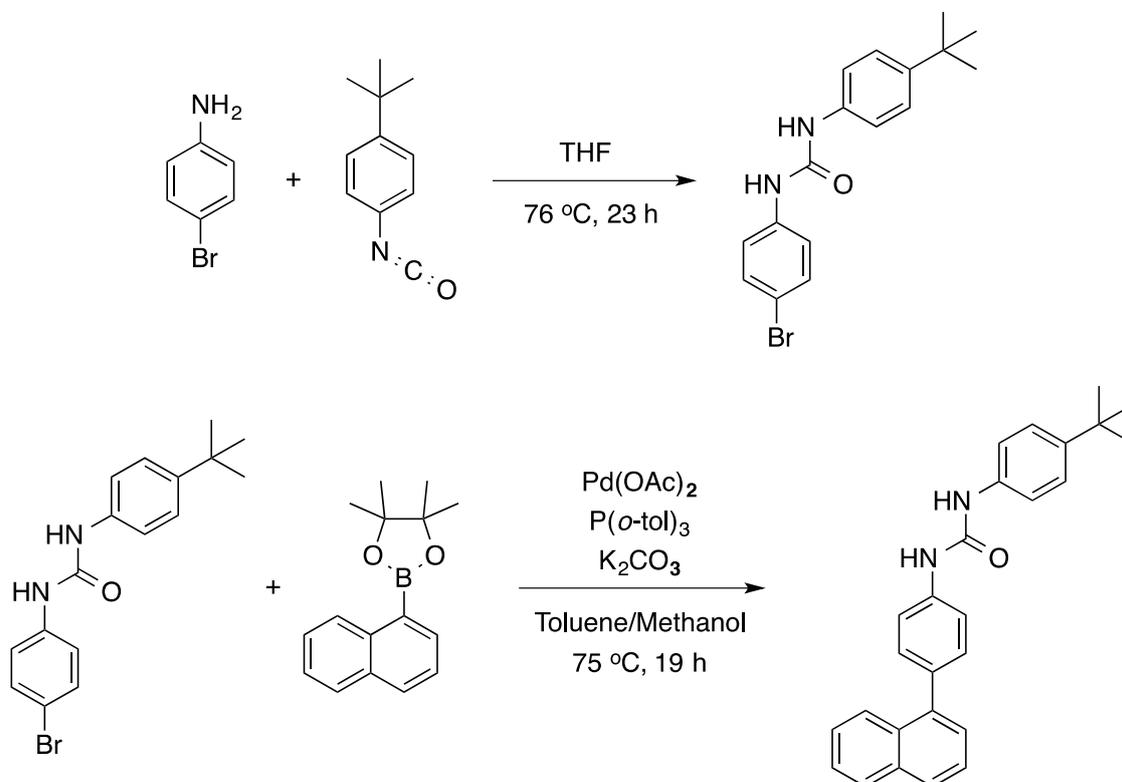
Materials

All chemicals were purchased from Kanto Kagaku Co., Ltd., TCI chemicals or Aldrich, and used without further purification and solvents for spectroscopic studies were of spectroscopic grade. Tetrabutylammonium fluoride (ca. 1 mol/L in Tetrahydrofuran) was purchased from TCI chemicals and used as dimethyl sulfoxide solution after tetrahydrofuran was removed under reduced pressure.

Spectral Measurements

Photochemical properties of urea derivative were investigated in detail by UV-vis absorption, ¹H NMR, fluorescence. Unless otherwise noted, urea derivative (1.5×10^{-4} M) were measured in DMSO at 25 °C. Absorption spectra were measured on JASCO V-570 spectrometer. Fluorescence spectra were measured on JASCO FP-6500 fluorescence spectrometers. ¹H NMR spectra were measured on Bruker Ascend 500 NMR. Fluorescence lifetime measurements were performed using a Hamamatsu Photonics model C11367 Quantaaurus-Tau spectrometer. The

fluorescence quantum yields were measured by a Hamamatsu Photonics C9920-02 absolute PL quantum yield measurement system at room temperature. The ESI-TOF MS data were obtained using a Bruker micrOTOF II mass spectrometer in the positive ion mode.



Scheme S1. Synthesis of **1H**.^{1,2}

N-[4-*tert*-butylphenyl]-N'-4-(naphthalen-1-yl)phenylurea (1H)

4-Bromoaniline (72.2 mg, 0.419 mmol) and 4-*tert*-Butylphenyl isocyanate (74.5 mg, 0.427 mmol) were stirred in tetrahydrofuran (THF; 3.7 mL) at 76 °C under N₂ for 21 h. After the solvent was removed under reduced pressure, the residue was washed with hexane three times and was concentrated under reduced pressure to give N-[4-bromophenyl]-N'-4-*tert*-Butylphenylurea as a yellow viscous body. The residue of N-[4-bromophenyl]-N'-4-*tert*-Butylphenylurea, which was used for the subsequent Suzuki-Miyaura coupling step without further purification. To a three-neck round-bottom flask (200 mL) were added N-[4-bromophenyl]-N'-4-*tert*-Butylphenylurea (141 mg, 0.409 mmol), 4,4,5,5-Tetramethyl-2-(1-naphthyl)-1,3,2-dioxaborolane (160 mg, 0.631 mmol), Tri-*o*-tolylphosphine (13.8 mg, 0.0453 mmol), Pd(OAc)₂ (4.87 mg, 0.0217 mmol), K₂CO₃ (243 mg, 1.76 mmol), toluene (84 ml), and methanol (3.3 ml). The resulting reaction mixture was stirred at 75 °C under N₂ for 21 h. Water was added to the reaction mixture and organic materials were extracted with ethyl acetate three times. The separated organic layer was dried with anhydrous Na₂SO₄ and solvent was removed

under reduced pressure. Purification of the residue by a Recycling Preparative HPLC (Japan Analytical Industry Co. Ltd., LC-908) equipped with GPC columns (JAIGEL-2H, 2.5H) using chloroform as an eluent yielded white solid (93.5 mg, 57 % in 2-steps total yield). ^1H NMR (DMSO- d_6 , 500 MHz): δ 8.78 (s, 1H, -NH), 8.63 (s, 1H, -NH), 7.98 (d, 1H, $J = 8.0$ Hz, naphthyl), 7.91 (d, 1H, $J = 8.0$ Hz, naphthyl), 7.87 (d, 1H, $J = 8.5$ Hz, naphthyl), 7.61 (d, 2H, $J = 8.5$ Hz, phenyl), 7.57-7.47 (m, 3H, naphthyl), 7.42-7.38 (m, 5H, naphthyl and phenyl), 7.30 (d, 2H, $J = 9.0$ Hz, phenyl). ^{13}C NMR (DMSO- d_6 , 125 MHz): δ 31.5, 34.1, 118.3, 118.3, 125.5, 125.6, 125.8, 126.1, 126.4, 127.0, 127.5, 128.5, 130.4, 131.2, 133.4, 133.7, 137.2, 139.4, 139.5, 144.4, 152.8. HRMS (ESI): m/z calcd. for $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$), 395.2118; found 395.2115.

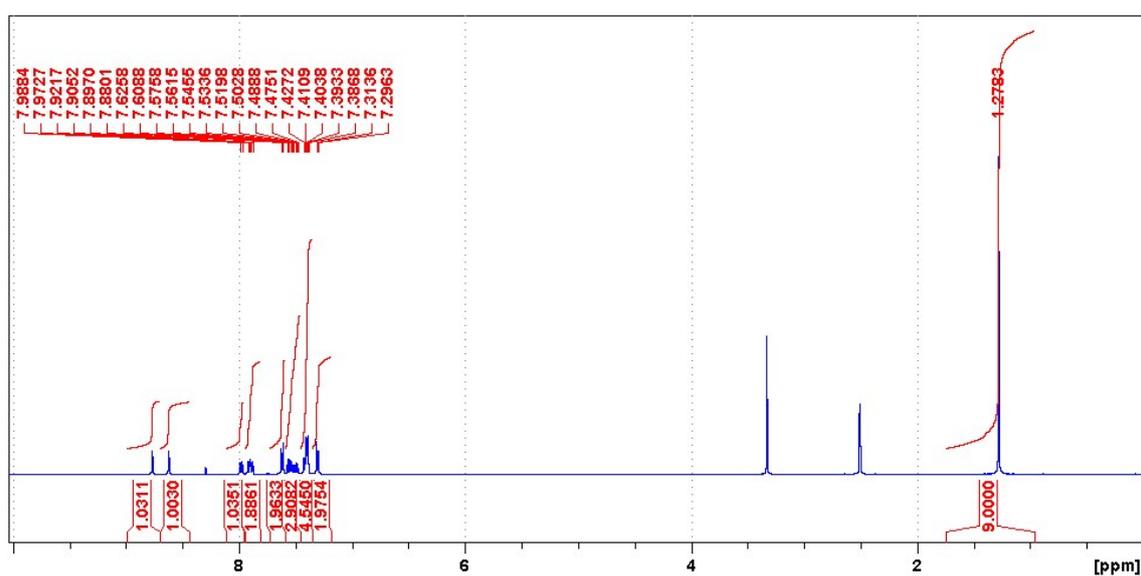


Fig. S1. ^1H NMR spectra (500MHz, DMSO- d_6 , 298K) of **1H**.

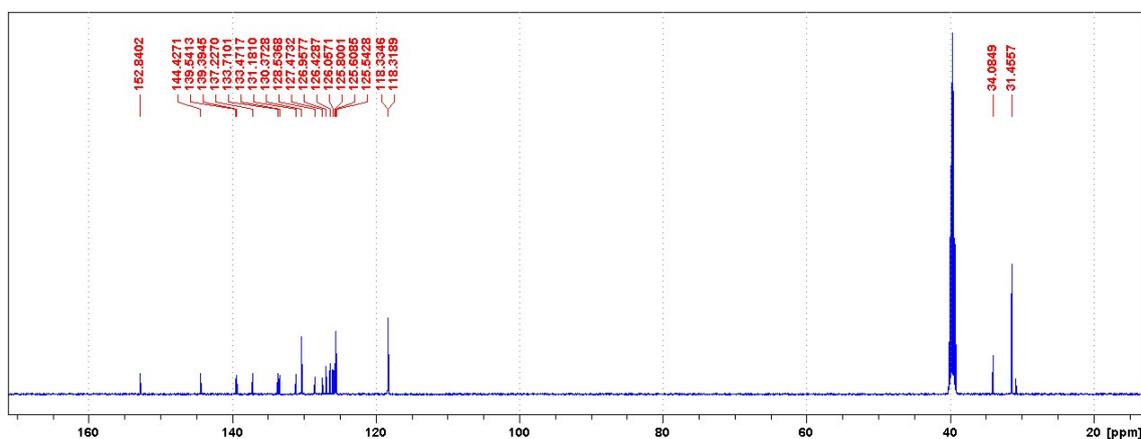


Fig. S2. ^{13}C NMR spectra (125MHz, DMSO- d_6 , 299K) of **1H**.

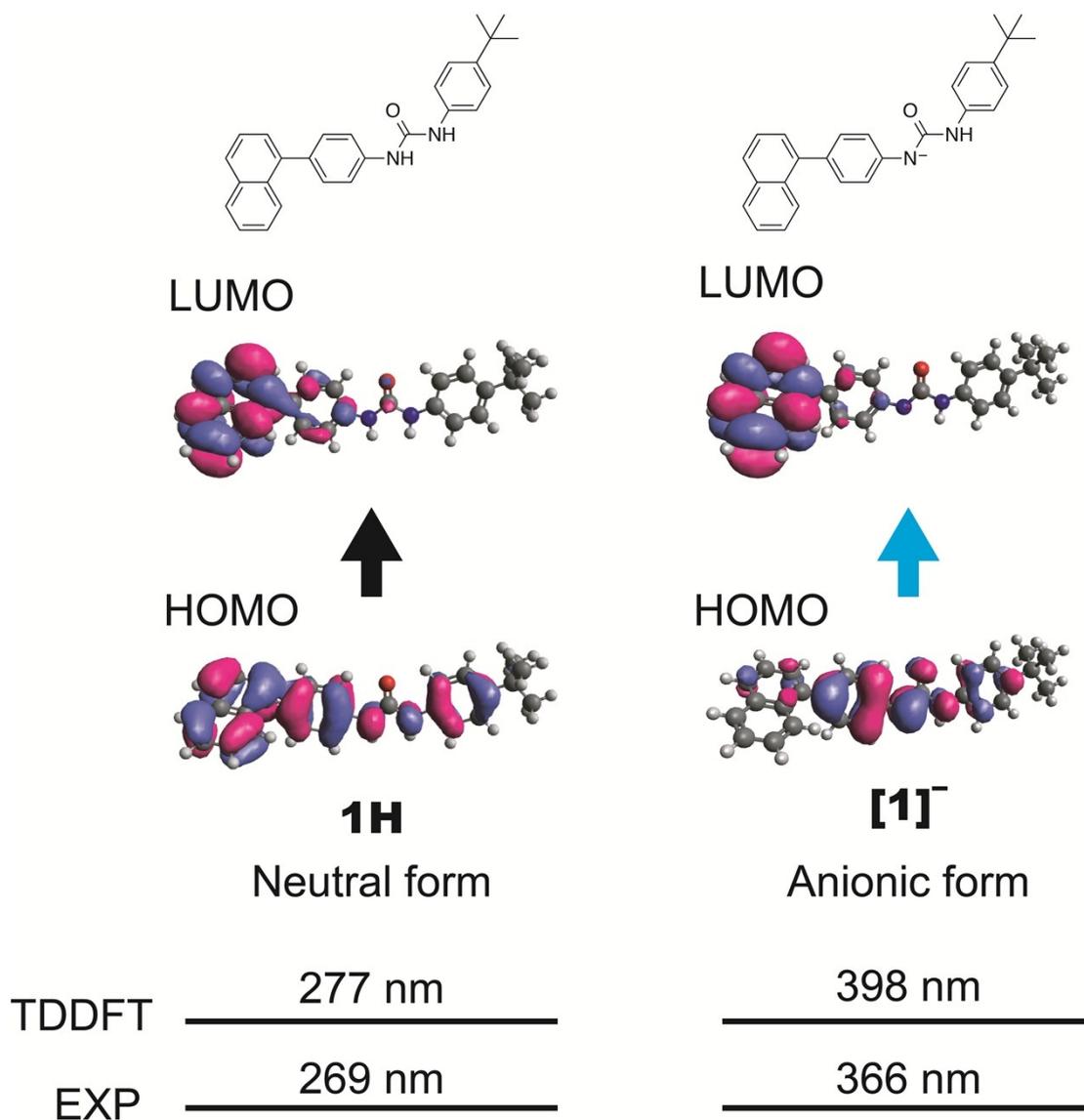


Fig. S3. Calculated and experimental values of main absorption bands of neutral form and anionic form of urea derivative **1H** and the main orbitals of (left) **1H** and (right) **[1]⁻** species, calculated at the TDDFT level (CAM-B3LYP/6-31+G**). Gray, white, blue, and red atoms indicate C, H, N, and O atoms, respectively. Purple and pale red parts on the molecular orbitals refer to the different phases of molecular wave functions.

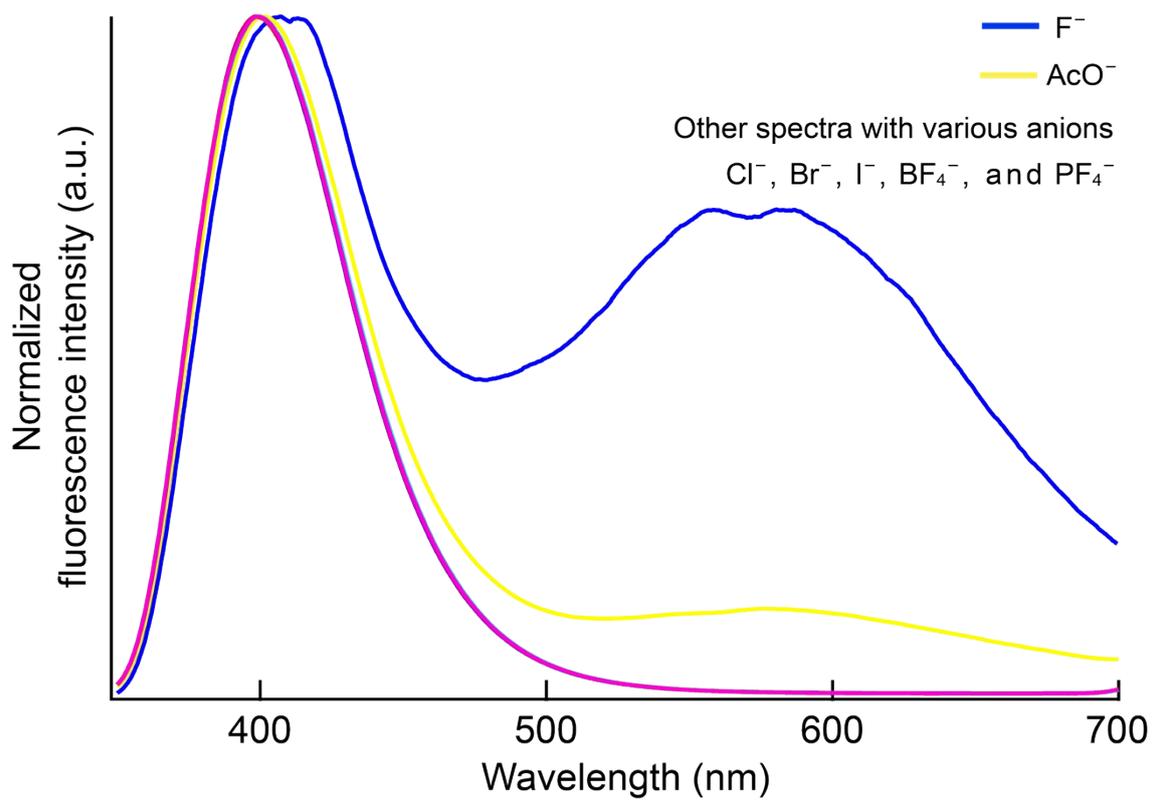


Fig. S4: Fluorescence spectra of **1H** DMSO solution (1.5×10^{-4} M) in the presence of 10 equiv of tetrabutylammonium salts of various anions.

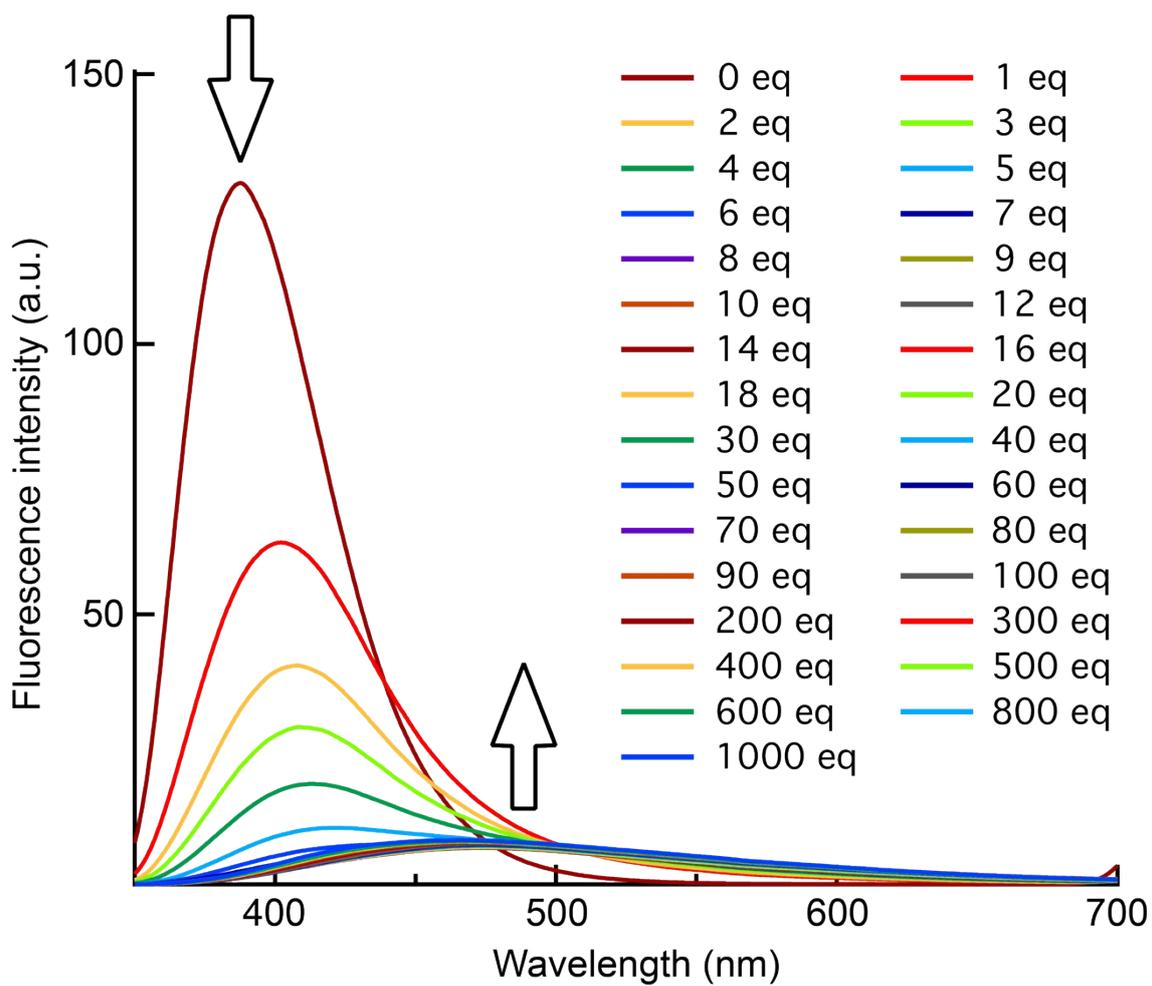
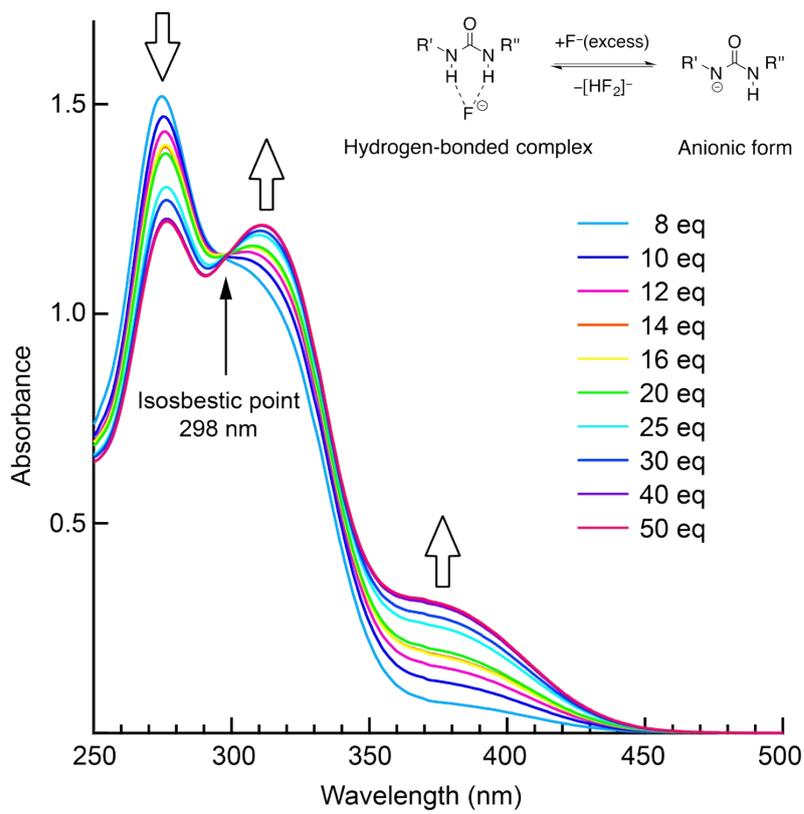
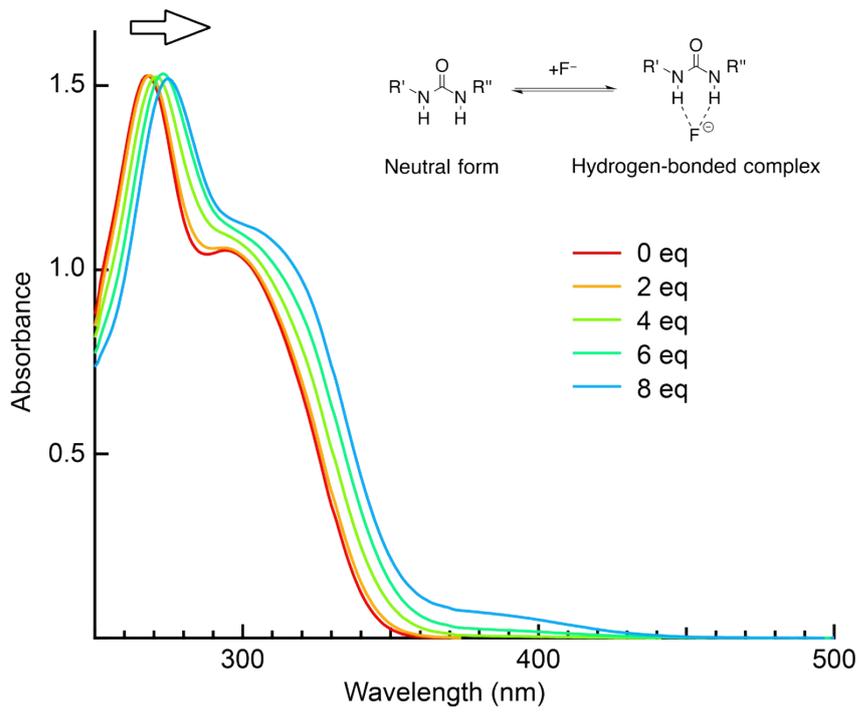


Fig. S5: Fluorescence spectra taken in the course of the titration of **1H** acetonitrile solution ($1.5 \times 10^{-4}\text{M}$) with TBAF.



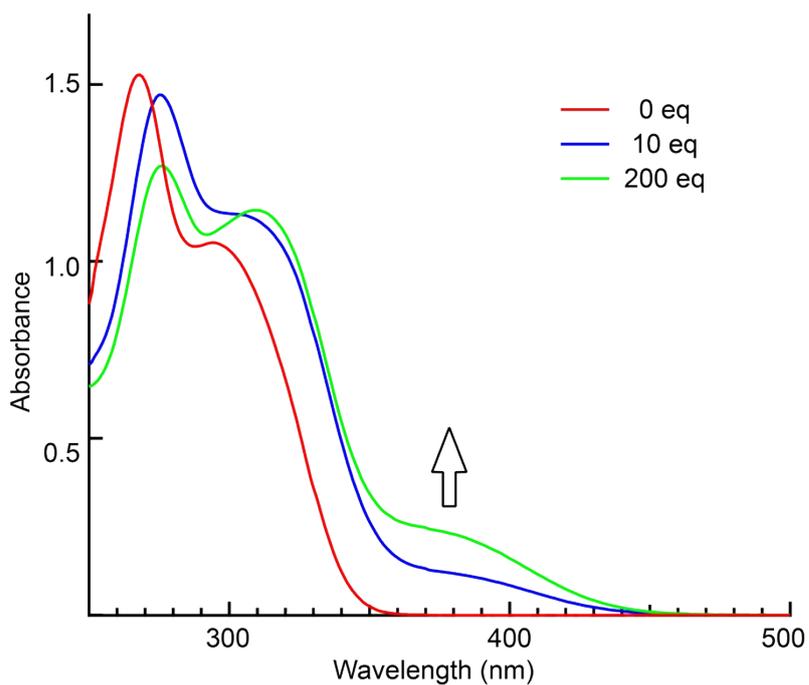
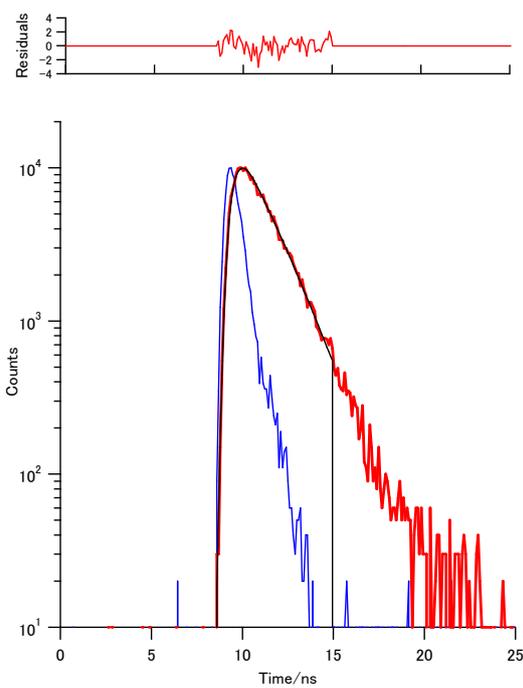
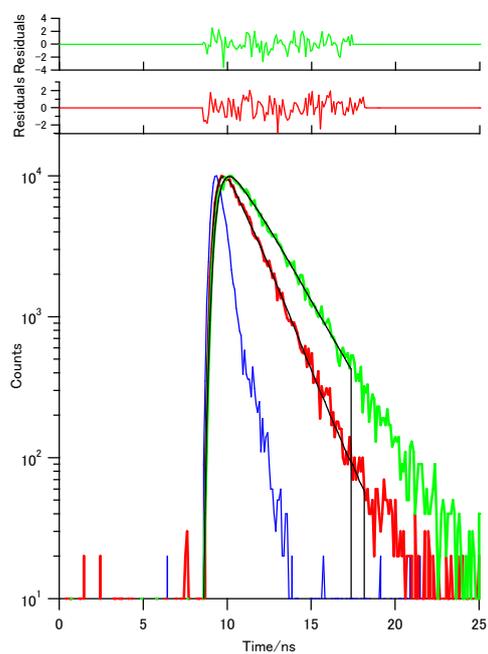


Fig. S6. UV-vis spectra taken in the course of the titration of **1H** DMSO solution ($1.5 \times 10^{-4}\text{M}$) with TBAF.

(a)



(b)



(c)

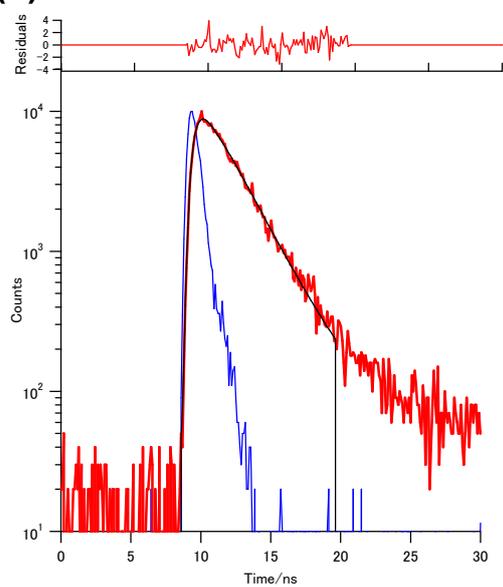


Fig. S7. Fluorescence decay analyses of **1H** in the absence of TBAF at 400 nm (red curve) (a), in the presence of 10 equivalents of TBAF at 400 nm (red curve) and 600 nm (green curve) (b), and in the presence of 200 equivalents of TBAF at 600 nm (red curve) (c).

Table S1. Fluorescence lifetimes of **1H** in the absence and presence of TBAF

	$\tau(\text{A})$	
	400 nm	600 nm
0 eq	1.4 ns (1.0) ^a	-
10 eq	0.14 ns (0.60) ^a	2.1 ns (1.0) ^a
	1.4 ns (0.40) ^a	
200 eq	-	2.3 ns (1.0) ^a

^a Normalized pre-exponential factor.

References

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2. X. H. Sun, W. Li, P. F. Xia, H. B. Luo, Y. Wei, M. S. Wong, Y. K. Cheng, and S. Shuang, *J. Org. Chem.* 2007, **72**, 2419-2426.