Electronic Supplementary Information

for

A New Series of N-H Proton Transfer Molecules; Wide Tautomer Emission Tuning from 590 nm to 770 nm via a Facile, Single Site Amino Derivatization in 10-Aminobenzo[h]quinoline

Huan-Wei Tseng,[a,†] Ta-Chun Lin,[b,†] Chi-Lin Chen,[a,†] Tzu-Chieh Lin,[a] Yi-An Chen,[a]Jun-Qi Liu,[b]Cheng-Hsien Hung,[b] Chi-Min Chao,[b,c,*] Kuan-Miao Liu,[b,c,*] and Pi-Tai Chou[a,*]

[a] *Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan*

[b] *School of Medical Applied Chemistry, Chung Shan Medical University, Taichung 40201, Taiwan*

[c] *Department of Medical Education, Chung Shan Medical University Hospital, Taichung 40201, Taiwan*

Contents

Detailed Synthesis and Characterizations

All reactions were carried out in oven- or flame-dried glassware under a positive pressure of argon. Dichloromethane, pyridine were distilled over calcium hydride. All reagents and solvents were purchased commercially and used without further purification. 10-Nitrobenzo[*h*]quinoline was prepared from benzo[*h*]quinoline (TCI) following published procedures.[1] TLC was performed on Merck 5735 DC-plastikfolien Kieselgel 60 F254 precoated plates. Flash column chromatography was performed on silica gel (Merck 7736 Kieselgel 60H). ^{1}H-NMR (7.24 ppm for residual $CHCl_3$ in the $CDCl_3$ solvent as internal standard) and ^{13}C-NMR (77.0 ppm for $CDCl_3$ as internal standard) spectra were recorded on a Varian Unity-400 MHz instrument. Coupling constants were reported in Hertz. IR spectra were recorded using a Bomen MB-100FT spectrometer. HRMS data was obtained from an FOEL JMS-HX110 spectrometer. Single crystal structure was determined on a Bruker AXS SMART-1000 instrument. Elemental analysis was done on an elementary Vario EL cube instrument.

N-methyl-10-aminobenzo[h]quinoline (**I**). A mixture of **III** (54 mg, 0.278 mmol), methyl iodide (19 uL, 0.306 mmol) and potassium carbonate (38 mg, 0.278 mmol) in CH_3CN (2 mL) was stirred at 80 ^{o}C for 17 h. H_2O (2 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residual crude product was purified on silica gel to give 45 mg (78% yield) of **II** as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 10.72 (brs, 1H), 8.87 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.13 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.61-7.55 (m, 2H), 7.42 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.16 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.85 (dd, *J* = 8.0, 0.4 Hz, 1H), 3.14 (d, *J* = 3.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 150.2, 149.4, 145.8, 135.9, 135.3, 129.5, 129.2, 126.7, 125.0, 119.4, 114.9, 114.5, 106.4, 30.1. IR (KBr, cm^{-1}) 3055, 2923, 2803, 1588, 1559, 1442, 1420, 1388, 833, 728. HRMS (EI, m/z) calcd for $C_{14}H_{12}N_2$, 208.1; found, 208.1003.

N-benzyl-10-aminobenzo[h]quinoline (**II**). A mixture of **III** (50 mg, 0.258 mmol), benzyl bromide (35 uL, 0.284 mmol) and potassium carbonate (36 mg, 0.258 mmol) in CH_3CN (3 mL) was stirred at room temperature for 22 h. H_2O (2 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residual crude product was purified on silica gel to give 43 mg (58% yield) of **II** as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 11.55 (s, 1H), 8.86 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.15 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.56-7.49 (m, 3H), 7.44 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.41-7.35 (m, 2H), 7.33-7.26 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 149.4, 149.1, 145.8, 139.9, 135.9, 135.3, 129.5, 129.1, 128.5, 127.0, 126.7, 125.0, 119.4, 115.1, 114.9, 47.5. IR (KBr, cm^{-1}) 3055, 2924, 2802, 1587, 1559, 1441, 1421, 1389, 832, 727. HRMS (EI, m/z) calcd for $C_{20}H_{16}N_2$,

284.1313; found, 284.1315.

10-Aminobenzo[h]quinoline (**III**). A mixture of 10-nitrobenzo[*h*]quinoline (257 mg, 1.146 mmol), ammonium chloride (37 mg, 0.688 mmol) and iron powder (128 mg, 2.292 mmol) in EtOH/H_2O (15/5 mL) was stirred at 85 ^oC for 2 h. After cooling to room temperature, the solvent was removed under reduced pressure. The crude mixture was purified on silica gel to provide 180 mg (0.927 mmol, 81%) of **III** as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$, ppm) 8.89 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.48-7.41 (m, 2H), 7.37 (brs, 2H), 7.25-7.18 (m, 1H), 6.93 (dd, *J* = 8.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 149.4, 148.3, 146.1, 135.8, 135.2, 129.1, 128.6, 126.6, 125.0, 119.6, 116.1, 115.4, 112.9. IR (KBr, cm^{-1}) 3466, 3290, 3059, 3025, 2925, 2801, 1612, 1560, 1389, 835, 728. HRMS (EI, m/z) calcd for $C_{13}H_{10}N_2$, 194.0844; found, 194.0846. Anal. Calcd for C13H10N2: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.42; H, 5.32; N, 14.25.

N-(benzo[h]quinolin-10-yl)pivalamide (**IV**). To a mixture of **III** (35 mg, 0.178 mmol), pivaloyl chloride (30 uL, 0.214 mmol) and 4-dimethylaminopyridine (3 mg, 0.018 mmol) in CH_2Cl_2 (2 mL) was added triethylamine (40 uL, 0.267 mmol) and stirred at room temperature for 27 h. H_2O (1 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residual crude product was purified on silica gel to give 30 mg (60% yield) of **IV** as an orange solid. ^1H NMR (400 MHz, $CDCl_3$, ppm) 14.91 (s, 1H), 9.22 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.89 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.23 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54 (dd, *J* = 8.0, 4.8 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 178.6, 147.8, 145.5, 139.9, 136.6, 135.0, 129.6, 129.0, 127.5, 124.9, 122.7, 120.7, 118.3, 118.0, 40.7, 27.9. IR (KBr, cm^{-1}) 3053, 2961, 2868, 1729, 1673, 1625, 1591, 1553, 1476, 1404, 1285, 1208, 1165, 834. HRMS (EI, m/z) calcd for $C_{18}H_{18}N_2O$, 278.1419; found, 278.1416.

N-(benzo[h]quinolin-10-yl)acetamide (**V**). A mixture of **III** (60 mg, 0.310 mmol) and acetic anhydride (45 uL, 0.465 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. H_2O was added and the mixture was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residual crude product was purified on silica gel to give 76 mg (96% yield) of **V** as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$, ppm) 14.83 (s, 1H), 9.08 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.88 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.21 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.62-7.57 (m, 2H), 7.52 (dd, *J* = 8.0, 4.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 169.1, 147.4, 145.4, 139.2, 136.3, 134.7, 129.0, 128.6, 127.2, 124.8, 122.7, 120.5, 117.8, 117.0, 25.8. IR (KBr, cm^{-1}) 3047, 2925, 1682, 1611, 1558, 1494, 1405, 1340, 1252, 831, 720. HRMS (EI, m/z) calcd for $C_{15}H_{12}N_2O$, 236.095; found, 236.0953.

N-(benzo[h]quinolin-10-yl)benzamide (**VI**). A mixture of **III** (58 mg, 0.299 mmol) and benzoyl chloride (104 uL, 0.896 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 20 h. H_2O was added and the mixture was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residual crude product was purified on silica gel to give 68 mg (76% yield) of **VI** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 15.67 (s, 1H), 9.32 (d, *J* = 8.0 Hz, 1H), 8.83 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.25-8.21 (m, 2H), 8.16 (dd, *J* = 8.4 Hz, 2.0Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.61-7.54 (m, 5H), 7.48 (dd, *J* = 8.4, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 166.4, 147.6, 145.5, 139.6, 136.7, 136.5, 135.0, 131.4, 129.4, 129.0, 128.6, 127.6, 127.5, 125.0, 123.1, 120.7, 118.4, 117.8. IR (KBr, cm^{-1}) 3049, 2927, 1666, 1626, 1614, 1555, 1490, 1405, 1343, 1261, 832, 705. HRMS (EI, m/z) calcd for $C_{20}H_{14}N_2O$, 298.1106; found, 298.1101.

N-tosylbenzo[h]quinolin-10-amine (**VII**). A mixture of **III** (50 mg, 0.257 mmol), toluenesulfonyl chloride (75 mg, 0.386 mmol) and pyridine (35 uL, 0.386 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 1 h. 1M $HCl_{(aq)}$ was added and the mixture was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residual crude product was purified on silica gel to give 81 mg (90% yield) of **VII** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 15.28 (s, 1H), 8.95 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.88 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.58-7.49 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 147.3, 145.8, 143.1, 138.5, 137.2, 136.7, 135.1, 129.4, 129.0, 128.6, 127.3, 127.2, 125.4, 122.7, 121.2, 117.3, 116.1, 21.4. IR (KBr, cm^{-1}) 3048, 2989, 2925, 2865, 2737, 1626, 1596, 1580, 1529, 1464, 1321, 1152, 1094, 819, 714. HRMS (EI, m/z) calcd for $C_{20}H_{16}N_2O_2S$, 348.0932; found, 348.0935.

N-(benzo[h]quinolin-10-yl)-2,2,2-trifluoroacetamide (**VIII**). A mixture of **III** (72 mg, 0.372 mmol), trifluoroacetic anhydride (60 uL, 0.409 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 2 h. Saturated $NaHCO_{3(aq)}$ was added and the mixture was extracted with EtOAc (3 x 3 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residual crude product was purified on silica gel to give 73 mg (68% yield) of **VIII** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 16.68 (s, 1H), 9.03 (dd, *J* = 6.4, 2.8 Hz, 1H), 8.90 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.30 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.84 (d, *J* = 8.8 Hz, 1H), 7.76-7.69 (m, 3H), 7.61 (dd, *J* = 8.4, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 155.4, 147.0, 145.6, 137.0, 136.9, 134.8, 129.1, 128.8, 127.5, 125.4, 124.9, 121.3, 119.0, 117.9, 115.0. IR (KBr, cm^{-1}) 3053, 2742, 2216, 1713, 1626, 1614, 1566, 1494, 1418, 1403, 1274, 1174, 1164, 1145, 835, 719. HRMS (EI, m/z) calcd for $C_{15}H_9F_3N_2O$, 290.0667; found, 290.0660.

N,N-dimethyl-10-aminobenzo[h]quinoline (**IX**). A mixture of **III** (32 mg, 0.165 mmol), methyl iodide (51 uL, 0.825 mmol) and potassium carbonate (57 mg, 0.415 mmol) in CH_3CN (3 mL) was stirred at 100 ^oC for 20 h. H_2O (2 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 4 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residual crude product was purified on silica gel to give 19 mg (52% yield) of **IX** as a yellow liquid. ^1H NMR (400 MHz, $CDCl_3$, ppm) 9.07 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.09 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.62-7.56 (m, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.41 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.29 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.95 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 152.4, 147.7, 147.3, 136.9, 135.3, 129.0, 128.0, 127.1, 125.8, 122.8, 121.3, 120.0, 115.6, 45.5. IR (KBr, cm^{-1}) 3055, 2924, 1589, 1558, 1442, 1421, 831, 726. HRMS (EI, m/z) calcd for $C_{15}H_{14}N_2$, 222.1157; found, 222.11553.

N,N-dibenzyl-10-aminobenzo[h]quinoline (**X**). A mixture of **III** (50 mg, 0.258 mmol), benzyl bromide (70 uL, 0.568 mmol) and potassium carbonate (71 mg, 0.516 mmol) in CH_3CN (2 mL) was stirred at 60 ^oC for 3 h. H_2O (2 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residual crude product was purified on silica gel to give 44 mg (46% yield) of **X** as a red liquid. ^1H NMR (400 MHz, $CDCl_3$, ppm) 9.14 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.17 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.52-7.47 (m, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.31-7.18 (m, 4H), 4.45 (brs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 150.4, 148.1, 147.8, 139.4, 137.2, 135.5, 129.4, 129.0, 128.2, 127.9, 127.4, 126.8, 126.1, 124.7, 122.6, 121.2, 120.7, 57.5. IR (KBr, cm^{-1}) 3059, 3025, 2803, 1587, 1560, 1440, 1421, 1389, 833, 728, 699. HRMS (EI, m/z) calcd for $C_{20}H_{16}N_2$, 374.1783; found, 374.1786.

Computational Methodology

The geometries of the singlet ground states were optimized by the density functional theory (DFT) method, and the excited state structures and related optical properties of all molecules were calculated with time dependent density functional theory (TDDFT) methodology with a B3LYP hybrid function in combination with a polarizable continuum model (PCM) in cyclohexane. The 6-311+G(d,p) basis set was employed for all atoms. All calculations were carried out using the Gaussian 09 program.[2]

Spectroscopic Measurements

Steady-state absorption spectra were recorded using a Hitachi U-3310 Spectrophotometer, and emission spectra were obtained using an Edinburgh FS920 Fluorometer. Detailed time-resolved spectroscopic measurements have been reported previously.[3] In brief, nanosecond time-resolved experiments were performed by using an Edinburgh FLS920 time-correlated single photon-counting

(TCSPC) system with a pulsed hydrogen-filled lamp as the excitation source. Data were fitted with the sum of exponential functions using a non-linear least-squares procedure in combination with a convolution method.

Sub-nanosecond to nanosecond time-resolved studies were performed using another TCSPC system (OB-900 L lifetime spectrometer, Edinburgh) with an excitation light source from the second harmonic generation (SHG, 370 nm) of pulse-selected femtosecond laser pulses at 740 nm (Tsunami, Spectra-Physics). The fluorescence was collected at a right angle with respect to the pump beam path and passed through a polarizer, which was located in front of the detector. The polarization was set at a magic angle (54.7º) with respect to the pump polarization direction to eliminate anisotropy. Similar data analysis and fitting procedures were applied. The temporal resolution, after partial removal of the instrumental time broadening, was ~20 ps.

Ultrafast spectroscopic study of the titled compounds was performed by a femtosecond photoluminescence up-conversion (uPL) system pumped at 370 nm (for compounds **III, VII** and **VIII**). The femtosecond oscillator (Tsunami, Spectra-Physics) mentioned in the previous paragraph was used with the central output wavelength at 740 nm. In this measurement, fluorescence from a rotating sample cell was focused in a BBO crystal and its frequency was summed along with an interrogation gate pulse at a designated delay time with respect to the pump pulse. A half-wave plate was used to set the pump polarization at a magic angle (54.7º) with respect to the gate pulse to prevent the fluorescence anisotropy contributed by solute reorientation. The IRF was determined from the Raman scattering signal and its profile was fitted to a Gaussian function with a full width at half maximum of ~150 fs.

References:

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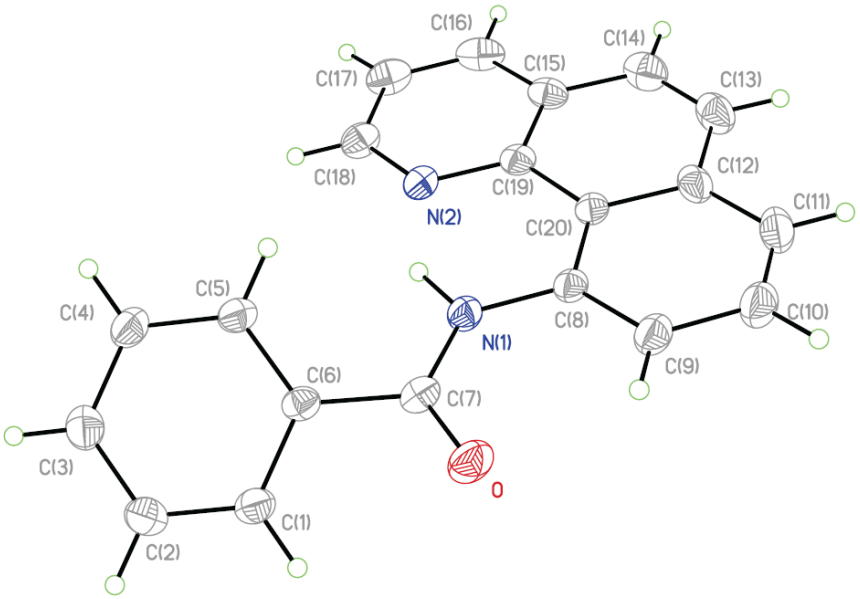

Figure S1. The X-ray crystal structure of compound **VI**.

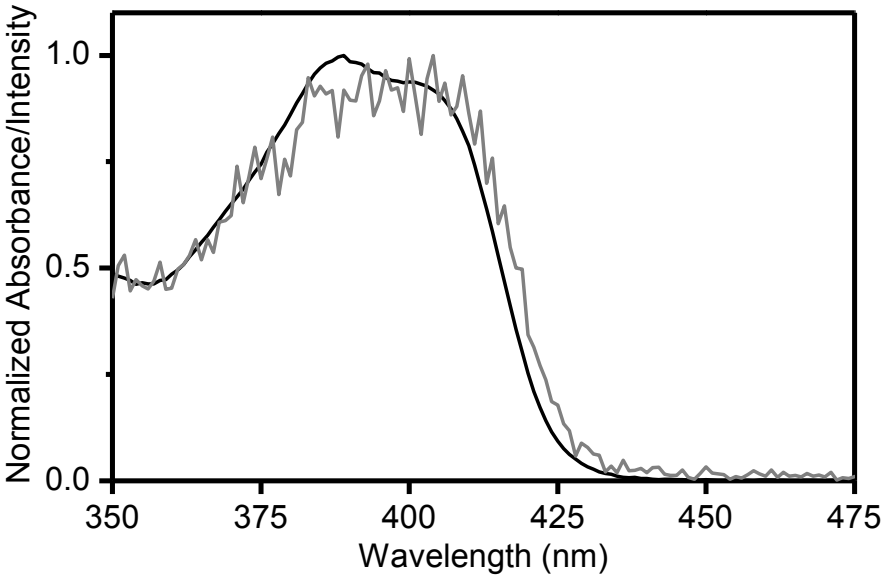

Figure S2. UV-Vis absorption spectrum (black) and excitation spectrum (gray) monitored at 730 nm of compound **III** in cyclohexane.

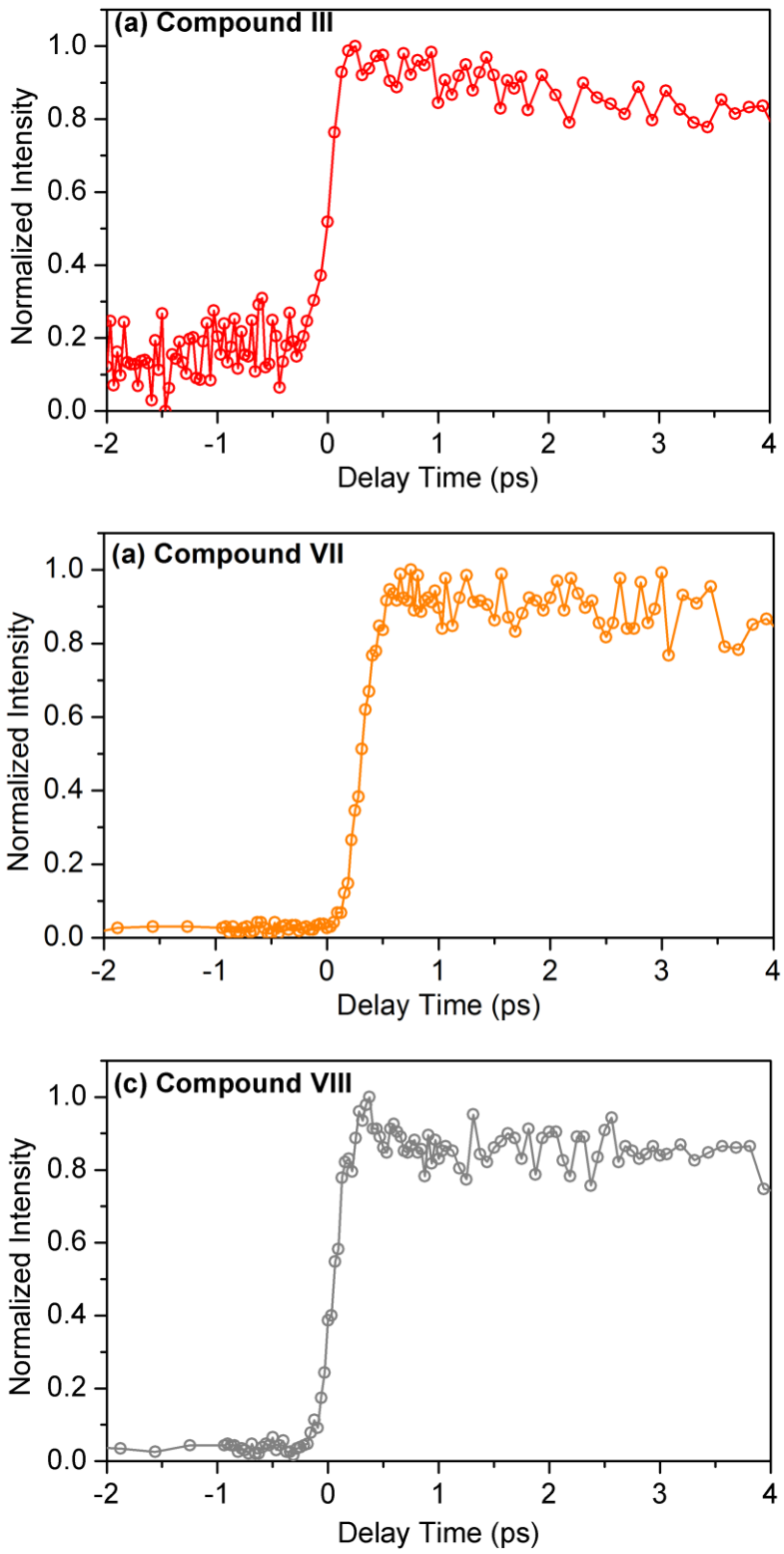

Figure S3. The early reaction dynamics for compound **III** (370 nm excitation; 680 nm emission), compound **VII** (370 nm excitation; 640 nm emission) and **VIII** (370 nm excitation; 600 nm emission).

Table S1. X-ray single crystal data and structure refinements for compound **VI**

CCDC NO.	1421361
Identification code	nbqbz3
Empirical formula	C20 H14 N2 O
Formula weight	298.33
Temperature	297(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 10.9292(8) Å
	b = 16.0839(11) Å
	c = 8.7040(8) Å
	α = 90°
	β = 103.591(8)°
	γ = 90°
Volume	1487.2(2) $Å^3$
Z	4
Density (calculated)	1.332 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	624
Crystal size	0.32 x 0.30 x 0.03 mm^3
Theta range for data collection	2.72 to 28.92°
Index ranges	$-14 \leq h \leq 14$, $-21 \leq k \leq 11$, $-5 \leq l \leq 11$
Reflections collected	6356
Independent reflections	3423 [R(int) = 0.0590]
Completeness to theta = 25.00°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.84517
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3423 / 0 / 212
Goodness-of-fit on F^2	0.990
Final R indices [I>2sigma(I)]	R1 = 0.0637, wR2 = 0.1013
R indices (all data)	R1 = 0.1655, wR2 = 0.1395
Largest diff. peak and hole	0.166 and -0.178 $e.Å^{-3}$

Table S2 Bond lengths and angles in the crystal structure of compound **VI**

Bond Lengths (Å)					
O-C(7)	1.226(3)	C(4)-H(4A)	0.9300	C(12)-C(13)	1.431(4)
N(1)-C(7)	1.358(3)	C(5)-C(6)	1.379(3)	C(13)-C(14)	1.336(4)
N(1)-C(8)	1.406(3)	C(5)-H(5A)	0.9300	C(13)-H(13A)	0.9300
N(1)-H(1A)	1.03(2)	C(6)-C(7)	1.496(3)	C(14)-C(15)	1.417(4)
N(2)-C(18)	1.321(3)	C(8)-C(9)	1.381(3)	C(14)-H(14A)	0.9300
N(2)-C(19)	1.362(3)	C(8)-C(20)	1.436(3)	C(15)-C(16)	1.391(4)
C(1)-C(2)	1.383(3)	C(9)-C(10)	1.386(4)	C(15)-C(19)	1.410(3)
C(1)-C(6)	1.386(3)	C(9)-H(9A)	0.9300	C(16)-C(17)	1.363(4)
C(1)-H(1B)	0.9300	C(10)-C(11)	1.364(4)	C(16)-H(16A)	0.9300
C(2)-C(3)	1.369(4)	C(10)-H(10A)	0.9300	C(17)-C(18)	1.384(3)
C(2)-H(2A)	0.9300	C(11)-C(12)	1.398(4)	C(17)-H(17A)	0.9300
C(3)-C(4)	1.375(4)	C(11)-H(11A)	0.9300	C(18)-H(18A)	0.9300
C(3)-H(3A)	0.9300	C(12)-C(20)	1.421(3)	C(19)-C(20)	1.453(3)
C(4)-C(5)	1.383(3)				

Bond Angles (°)			
C(7)-N(1)-C(8)	129.0(2)	C(11)-C(10)-H(10A)	119.5
C(7)-N(1)-H(1A)	119.2(13)	C(9)-C(10)-H(10A)	119.5
C(8)-N(1)-H(1A)	111.4(13)	C(10)-C(11)-C(12)	120.6(3)
C(18)-N(2)-C(19)	119.0(2)	C(10)-C(11)-H(11A)	119.7
C(2)-C(1)-C(6)	119.5(3)	C(12)-C(11)-H(11A)	119.7
C(2)-C(1)-H(1B)	120.2	C(11)-C(12)-C(20)	120.5(3)
C(6)-C(1)-H(1B)	120.2	C(11)-C(12)-C(13)	120.3(3)
C(3)-C(2)-C(1)	120.7(3)	C(20)-C(12)-C(13)	119.2(3)
C(3)-C(2)-H(2A)	119.6	C(14)-C(13)-C(12)	122.5(3)
C(1)-C(2)-H(2A)	119.6	C(14)-C(13)-H(13A)	118.7
C(2)-C(3)-C(4)	120.0(3)	C(12)-C(13)-H(13A)	118.7
C(2)-C(3)-H(3A)	120.0	C(13)-C(14)-C(15)	120.3(3)
C(4)-C(3)-H(3A)	120.0	C(13)-C(14)-H(14A)	119.8
C(5)-C(4)-C(3)	119.8(3)	C(15)-C(14)-H(14A)	119.8
C(5)-C(4)-H(4A)	120.1	C(16)-C(15)-C(19)	118.2(3)
C(3)-C(4)-H(4A)	120.1	C(16)-C(15)-C(14)	121.7(3)
C(6)-C(5)-C(4)	120.5(3)	C(19)-C(15)-C(14)	120.1(3)
C(6)-C(5)-H(5A)	119.8	C(17)-C(16)-C(15)	120.3(3)

C(4)-C(5)-H(5A)	119.8	C(17)-C(16)-H(16A)	119.8
C(5)-C(6)-C(1)	119.5(2)	C(15)-C(16)-H(16A)	119.8
C(5)-C(6)-C(7)	122.5(2)	C(16)-C(17)-C(18)	118.3(3)
C(1)-C(6)-C(7)	118.0(2)	C(16)-C(17)-H(17A)	120.8
O-C(7)-N(1)	125.3(2)	C(18)-C(17)-H(17A)	120.8
O-C(7)-C(6)	121.0(2)	N(2)-C(18)-C(17)	123.5(3)
N(1)-C(7)-C(6)	113.7(2)	N(2)-C(18)-H(18A)	118.3
C(9)-C(8)-N(1)	121.3(2)	C(17)-C(18)-H(18A)	118.3
C(9)-C(8)-C(20)	120.9(2)	N(2)-C(19)-C(15)	120.6(2)
N(1)-C(8)-C(20)	117.8(2)	N(2)-C(19)-C(20)	119.5(2)
C(8)-C(9)-C(10)	120.1(3)	C(15)-C(19)-C(20)	119.9(3)
C(8)-C(9)-H(9A)	120.0	C(12)-C(20)-C(8)	116.8(2)
C(10)-C(9)-H(9A)	120.0	C(12)-C(20)-C(19)	118.0(3)
C(11)-C(10)-C(9)	121.0(3)	C(8)-C(20)-C(19)	125.2(2)

Table S3. The computed corresponding energy differences (ΔE and ΔE^*, in kcal/mol) between the normal form and tautomer form species in the ground (S_0) and the lowest excited state (S_1) for the proton-transfer compounds **I-VIII**

S_0			
Compound	Normal Form (hartree)	Tautomer Form (hartree)	Computed ΔE (kcal/mol)
I	-650.410692	[#]	
II	-881.517891	[#]	
III	-611.095528	[#]	
IV	-881.770571	[#]	
V	-763.801422	[#]	
VI	-955.582840	[#]	
VII	-1430.169404	-1430.156679	7.98
VIII	-1061.612728	[#]	
S_1			
Compound	Normal Form (hartree)	Tautomer Form (hartree)	Computed ΔE^* (kcal/mol)
I	-650.307054	-650.310359	-2.07
II	-881.413056	-881.418583	-3.47
III	-610.987652	-610.992928	-3.31
IV	-881.653068	-881.661723	-5.43
V	-763.682646	-763.691959	-5.84
VI	-955.465672	-955.477064	-7.15
VII	[#]	-1430.072435	
VIII	[#]	-1061.508657	

[#] Failure of locating energy minimum of the excited normal state.