Supporting Information

Near-infrared Fluorescent Probes Based on TBET and FRET Rhodamine Acceptors with different pK_a values for Sensitive Ratiometric Visualization of pH changes in Live Cells

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1. INSTRUMENTS AND MATERIALS

Solvents and reagents were obtained from Sigma-Aldrich or Fisher scientific. Column chromatographic purification was conducted on silica gel (200-300 mesh) obtained from Sigma-Aldrich while thin-layer chromatography (TLC) analysis was conducted in silica gel plates obtained from Sigma-Aldrich. Compound **1**, **6**, and **7** were prepared according to the reported procedures[1, 2]. Intermediates and the fluorescent probes were characterized by Varian Unity Inova NMR spectrophotometer at 400 MHz and 100 MHz to record ^1H NMR and ^{13}C NMR spectra in $CDCl_3$ or CD_3OD solutions, respectively. Double focusing magnetic mass spectrometer or fast atom bombardment (FAB) ionization mass spectrometer was used to determine high-resolution mass spectrometer data (HRMS). Absorption spectra were collected by employing Per-kin Elmer Lambda 35 UV/VIS spectrometer while fluorescence spectra were performed on Jobin Yvon Fluoromax-4 spectrofluorometer.

Synthesis of compound 3: Compound **2** (0.35 g, 2.2 mmol) was slowly put to solution of compound **1** (0.8 g, 2.2 mmol) in H_2SO_4 (10 ml) at 0 °C. The reaction was stirred for 3 h at 100 °C. After reaction completed, the mixture was poured into the ice-water and $HClO_4$ (1 ml) was added. The precipitate was formed, filtrated and purified by column chromatography employing methanol/dichloromethane/ (1:10, v/v) to afford compound **3** as blue solid (1.0 g, 79%). ^1H NMR ($CD_3OD/CDCl_3$, 400 MHz) δ: 8.32 (s, 1H), 8.03 (d, *J* = 6.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 6.96 – 6.93 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.50 (s, 1H), 3.21 (s, 3H), 3.20 (s, 3H), 2.82 (m, 2H), 2.57 (m, 2H); HRMS:calculated for $C_{26}H_{22}BrN_2O_3^+$ $[M-ClO_4]^+$ 489.0808, found 489.0813.

Synthesis of compound 8: The procedure for compound **8** was the same as synthesis of compound **3** using compound **1** (0.8 g, 2.2 mmol) and compound **2** (0.42 g, 2.2 mmol) as starting materials. The produce was obtained as blue solid (1.1 g, 82%).^1H NMR ($CD_3OD/CDCl_3$, 400 MHz) δ: 8.22 (s, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.76 – 6.74 (m, 2H), 6.66 (d, *J* = 9.2 Hz, 1H), 6.42 (s, 1H), 3.11 (s, 3H), 3.10 (s, 3H), 3.10 (s, 3H), 3.09 (s, 3H), 2.84 – 2.75 (m, 2H), 2.52 – 2.45 (m, 2H); HRMS:calculated for $C_{28}H_{26}BrN_2O_3^+$ $[M-ClO_4]^+$ 517.1127, found 517.1130.

Synthesis of compound 5: Compound **3** (0.36 g, 0.6 mmol) and BOP reagent (0.33 g, 0.75 mmol) was put to dry dichloromethane (15 ml). After the mixture was stirred for 30 min, compound **4** (0.1 g, 0.75 mmol) and Et_3N (0.5 ml) were further added to the mixture, and the reaction was conducted overnight. When the mixture was washed with water (10 ml *2), the organic layer was collected, dried over Na_2SO_4, and filtered. After the filtrate was concentrated under reduced pressure, the residue was purified by column chromatography using hexane /ethyl acetate (1:1, v/v) to yield the product as grey yellow solid (0.18 g, 50%). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 1.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.59 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.44 – 6.38 (m, 3H), 6.32 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 3.78 (s, 2H), 3.55 (t, *J* = 4.8 Hz, 4H), 3.49 – 3.41 (m, 1H), 3.31 – 3.23 (m, 1H), 2.94 (s, 6H), 2.62 – 2.50 (m, 2H), 2.42 – 2.38 (m, 1H), 2.34 – 2.23 (m, 4H), 2.17 – 2.11 (m, 1H), 1.81– 1.75 (m, 1H), 1.65 – 1.59 (m, 1H);

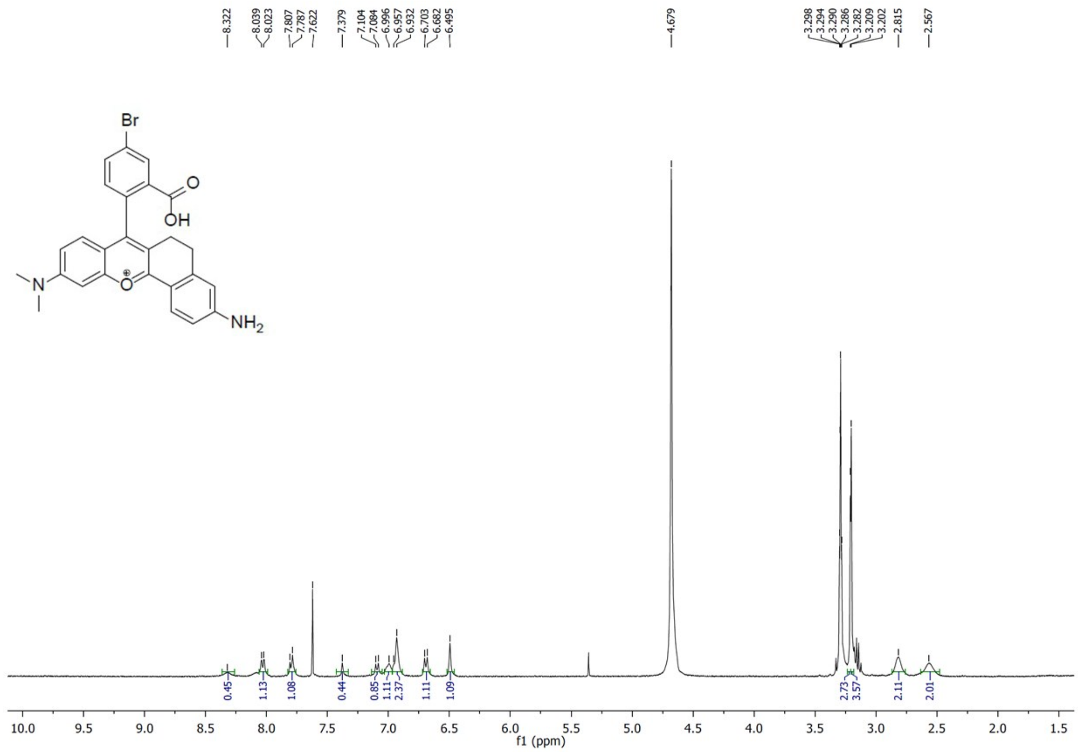
^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.9, 152.8, 151.5, 150.2, 147.3, 138.4, 135.4, 134.1, 128.8, 126.2, 125.3, 123.7, 122.6, 120.4, 114.3, 112.7, 109.3, 105.7, 100.6, 98.9, 67.1, 66.5, 56.6, 53.7, 40.5, 37.3, 28.4, 21.3. HRMS (ESI): calculated for $C_{32}H_{24}BrN_4O_3$ $[M+H]^+$ 600.1814, found 600.1807.

Synthesis of compound 9: A mixture of 1, 2-diaminobenzene (1.0 g, 9.25 mmol), 1-chloro-2-[2-(2-methoxyethoxy)ethoxy]ethane (2.0 g, 11 mmol), KI (0.46 g, 2.8 mmol) and K_2CO_3 (2.56 g, 18.5 mmol) in dry DMF (15 ml) was heated for 24 h at 100 °C. After the reaction was filtered, the solvent was removed from the filtrate. The residue was purified by column chromatography employing methanol /dichloromethane (1:20, v/v) to afford the product as colorless oil (0.5 g, 21%). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.79 – 6.75 (m, 1H), 6.70 – 6.64 (m, 4H), 3.72 (t, J = 5.2 Hz, 2H), 3.66 – 3.65 (m, 4H), 3.64 – 3.63 (m, 2H), 3.55 – 3.52 (m, 2H), 3.36 (s, 3H), 3.27 (t, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 135.2, 120.4, 119.2, 116.4, 112.7, 72.2, 70.9, 70.8, 70.6, 70.0, 59.3, 44.3. HRMS (ESI): calculated for $C_{13}H_{22}N_2NaO_3$ $[M+Na]^+$ 277.1528, found 277.1536.

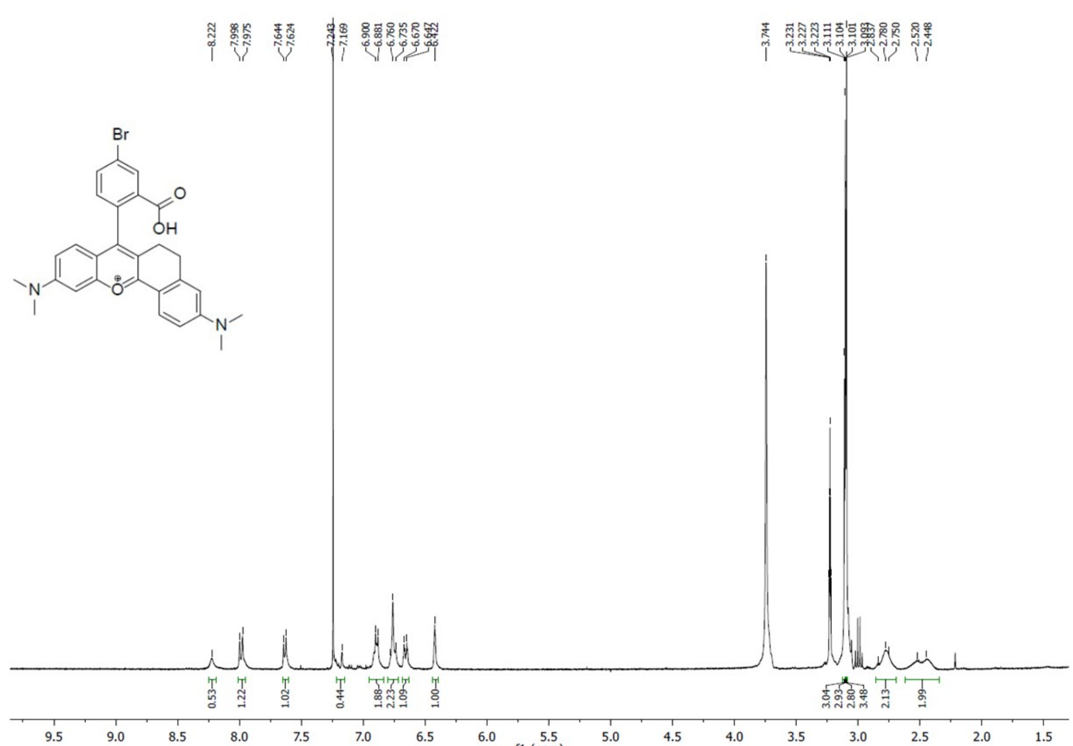
Synthesis of compound 10: The procedure for compound **10** was the same as synthesis of compound **5** using compound **8** (0.31 g, 0.5 mmol) and compound **9** (0.15 g, 0.6 mmol) as starting materials. The product was obtained as grey yellow solid (0.17 g, 45%). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.06 (s, 1H), 7.62 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.64 – 6.54 (m, 4H), 6.45 – 6.39 (m, 4H), 3.60 – 3.59 (m, 8H), 3.53 – 3.51 (m, 2H), 3.39 (s, 3H), 3.17 – 3.16 (m, 2H), 2.95 (s, 12H), 2.58 – 2.51 (m, 2H), 2.20 – 1.96 (m, 1H), 1.89 – 1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.7, 153.4, 151.4, 150.8, 150.2, 145.1, 135.7, 133.8, 129.1, 128.7, 126.8, 126.0, 125.7, 125.3, 123.4, 122.7, 118.4, 117.9, 117.5, 112.4, 111.4, 111.1, 109.8, 109.3, 99.6, 99.1, 71.9, 70.7, 70.5, 70.3, 69.9, 59.4, 43.5, 40.7, 40.6, 29.0, 22.7. HRMS (ESI): calculated for $C_{41}H_{45}BrN_4NaO_5$ $[M+Na]^+$ 775.2471, found 775.2461.

Synthesis of compound 12: The procedure for compound **12** was the same as synthesis of compound **5** using compound **8** (0.31 g, 0.5 mmol) and 1,2-diaminobenzene (65 mg, 0.6 mmol) as starting material. The product was obtained as grey yellow solid (0.12 g, 40%). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.14 (s, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.33 (dd, J = 6.0 Hz, 2.8 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.92 (t, J = 8.0 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 6.48 – 6.40 (m, 4H), 3.85 (s, 2H), 2.95 (s, 6H), 2.94 (s, 6H), 2.77 – 2.71 (m, 1H), 2.59 – 2.53 (m, 1H), 2.11 – 2.08 (m, 1H), 1.87 – 1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 153.1, 151.4, 150.8, 147.5, 144.0, 138.4, 135.7, 133.6, 128.8, 126.7, 125.7, 123.4, 123.1, 122.7, 119.0, 118.4, 118.3, 111.4, 109.8, 109.3, 100.0, 99.1, 70.7, 40.7, 40.6, 29.0, 22.3. HRMS (ESI): calculated for $C_{34}H_{32}BrN_4O_2$ $[M+H]^+$ 607.1709, found 607.1701.

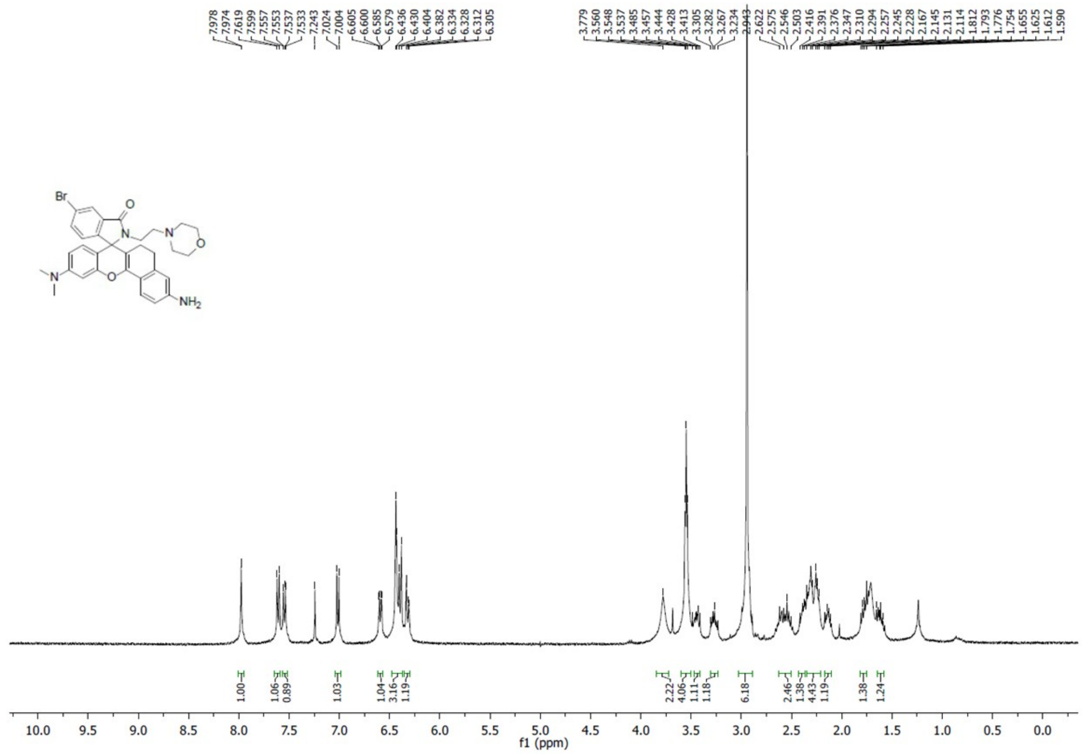
2. ^{1}H AND ^{13}C NMR SPECTRA OF INTERMEDIATES AND THE PROBES



- **Figure S1**. ^{1}H NMR spectrum of compound **3** in $CD_3OD/CDCl_3$ solution.



- **Figure S2**. ^{1}H NMR spectrum of compound **8** in $CD_3OD/CDCl_3$ solution.



- **Figure S3**. ^{1}H NMR spectrum of compound **5** in $CDCl_3$ solution.

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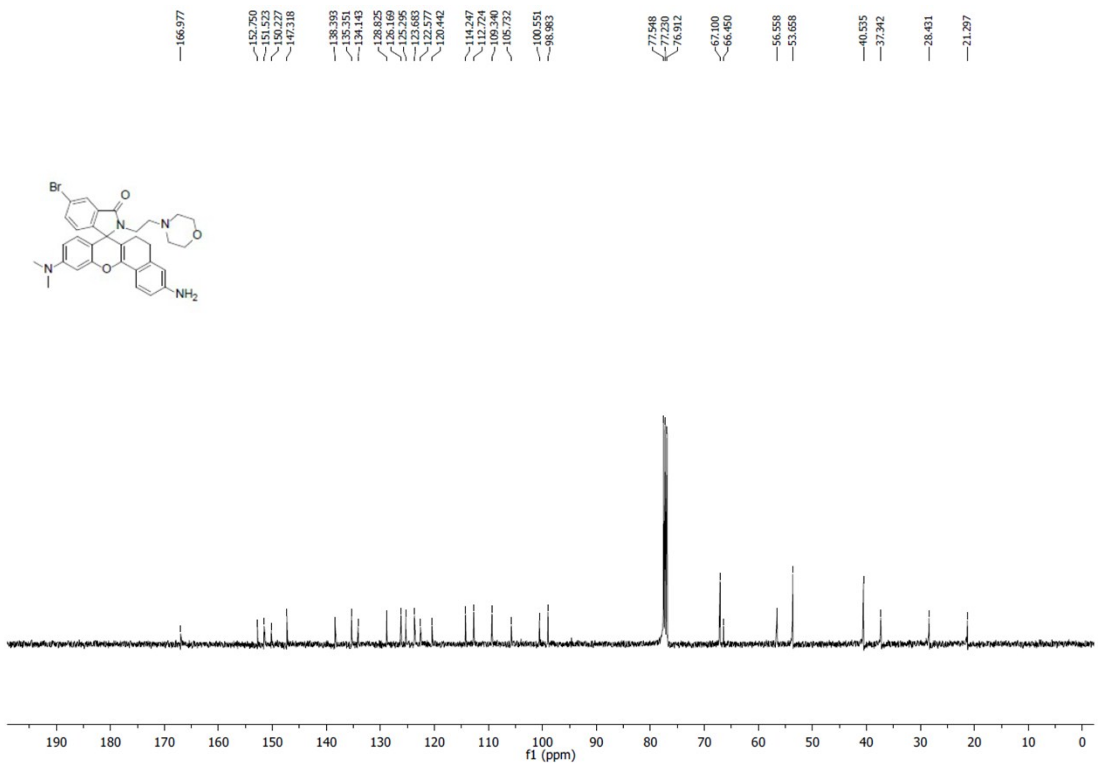
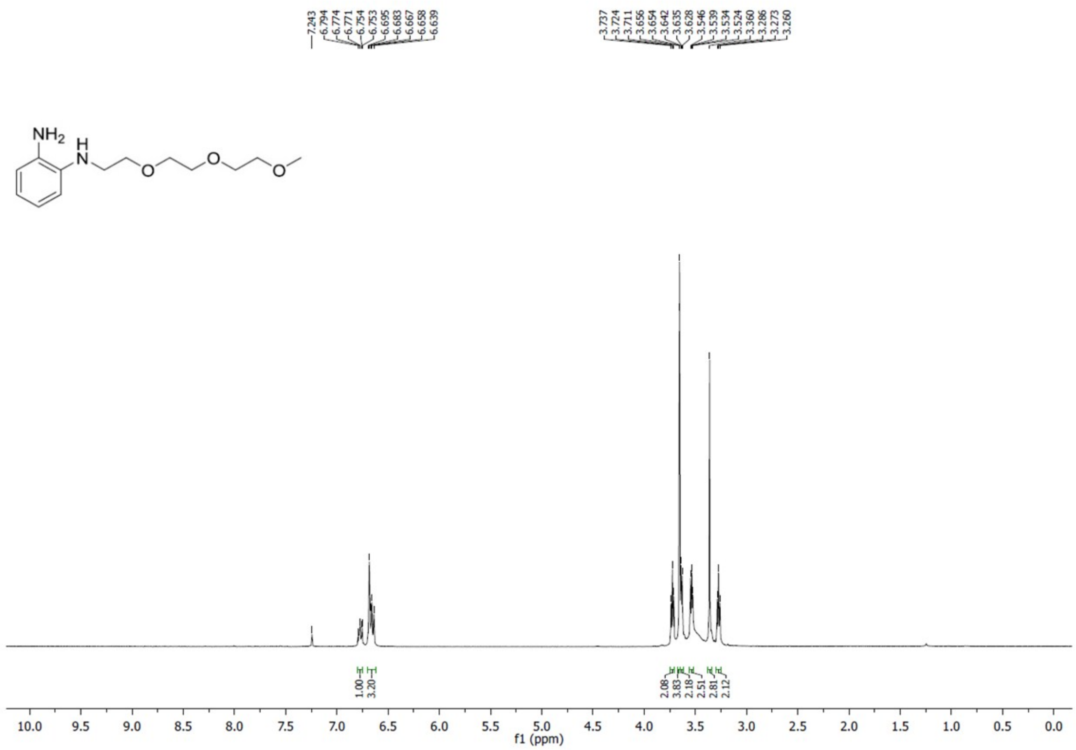
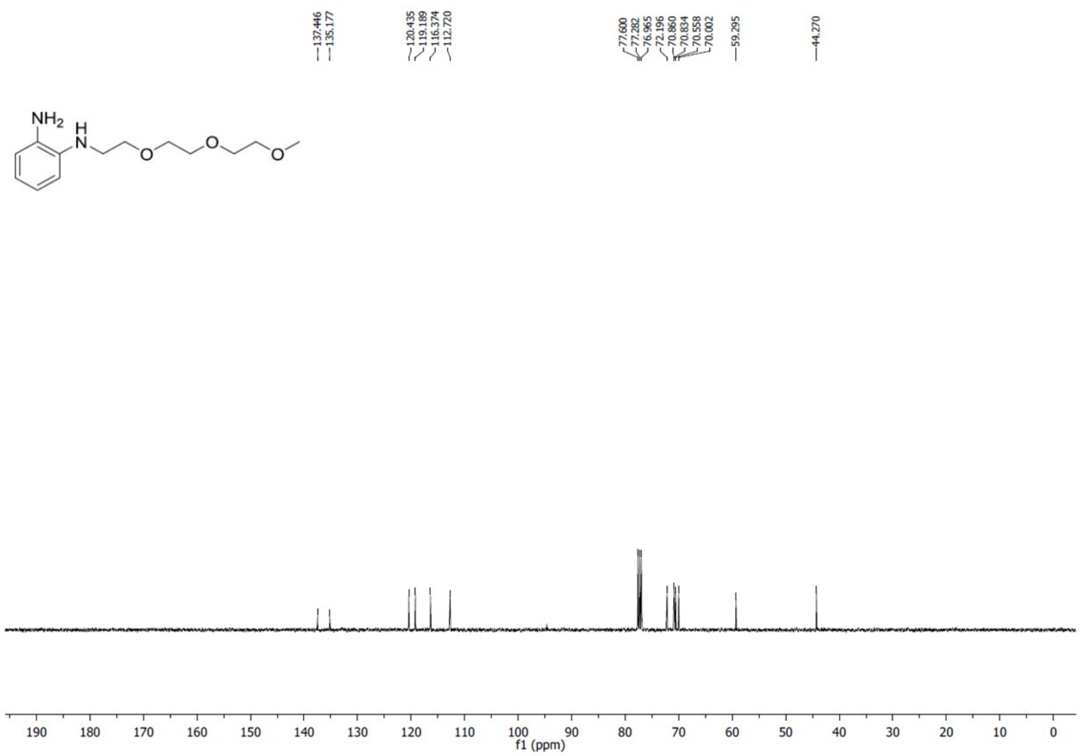


- **Figure S4**. ^{13}C NMR spectrum of compound **5** in $CDCl_3$ solution.



- **Figure S5**. [1]H NMR spectrum of compound **9** in $CDCl_3$ solution.



- **Figure S6**. [13]C NMR spectrum of compound **9** in $CDCl_3$ solution.

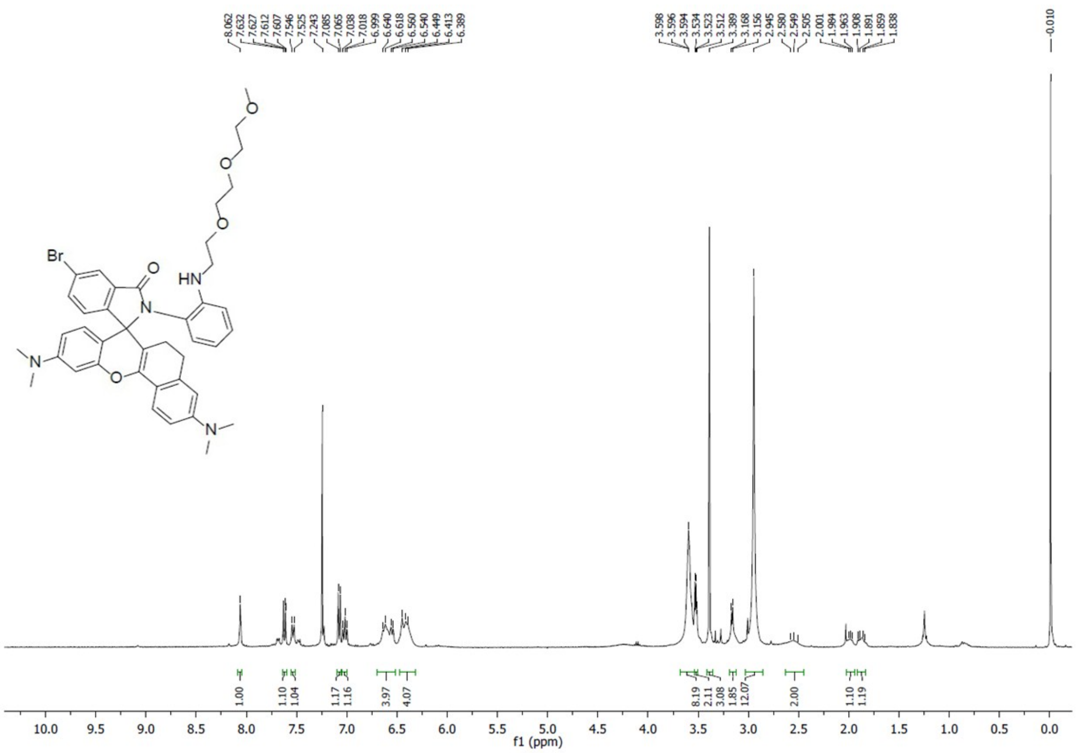


Figure S7. ^{1}H NMR spectrum of compound **10** in $CDCl_3$ solution.

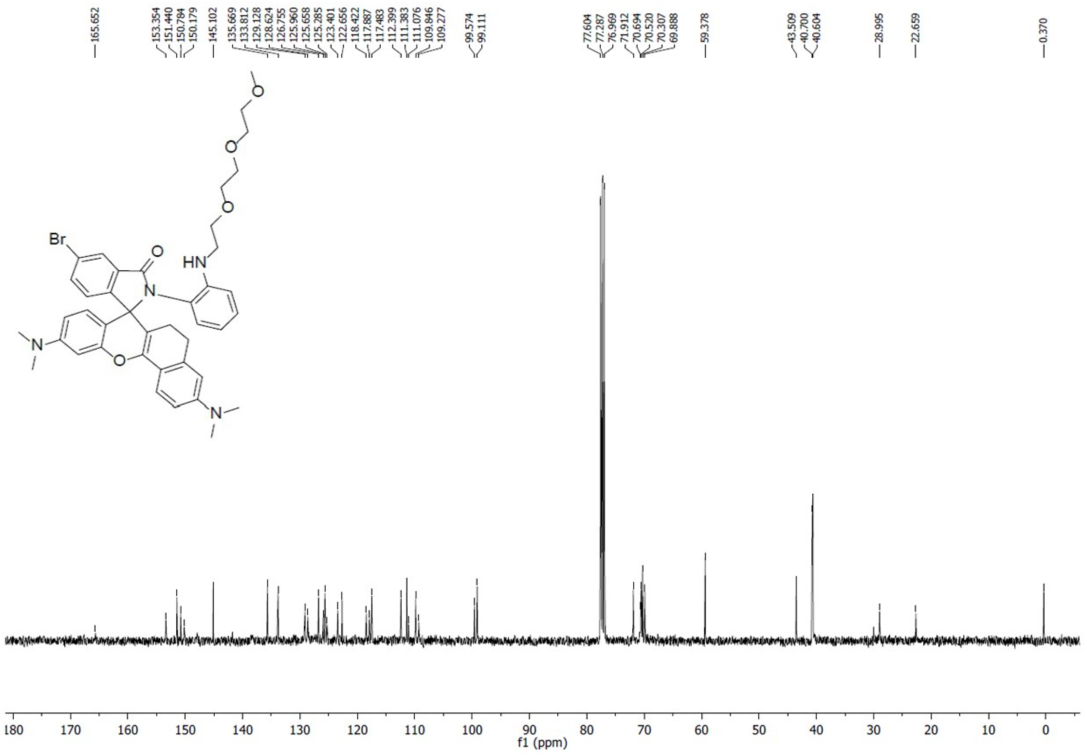


Figure S8. ^{13}C NMR spectrum of compound **10** in $CDCl_3$ solution.

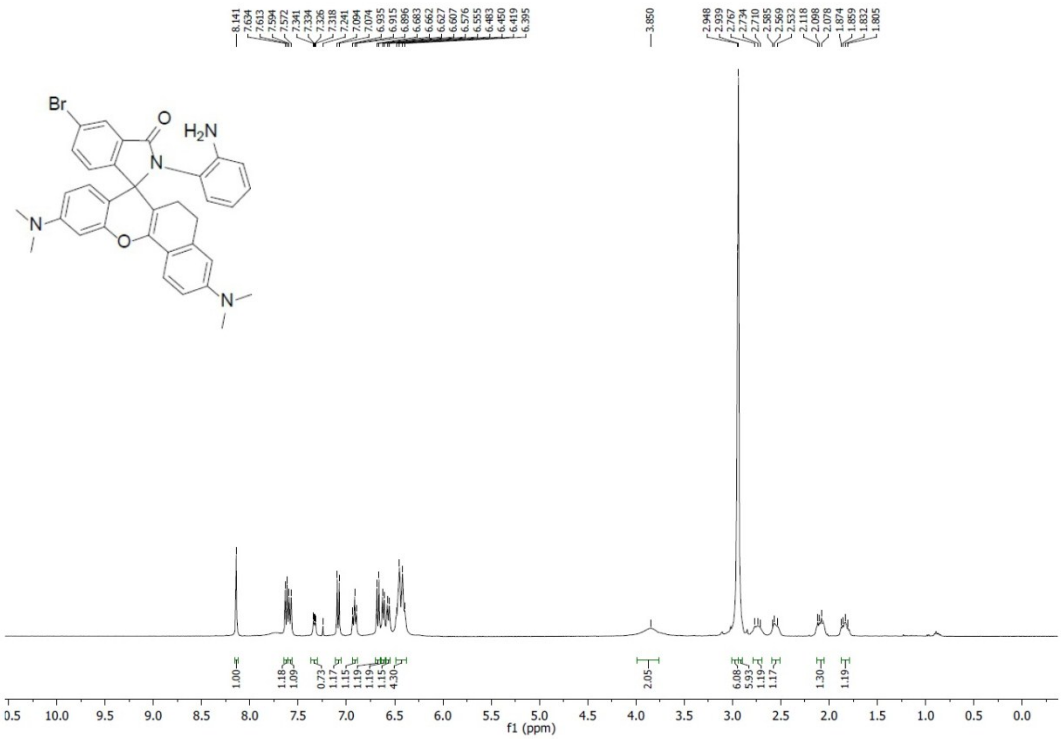


Figure S9. ^{1}H NMR spectrum of probe **12** in $CDCl_3$ solution.

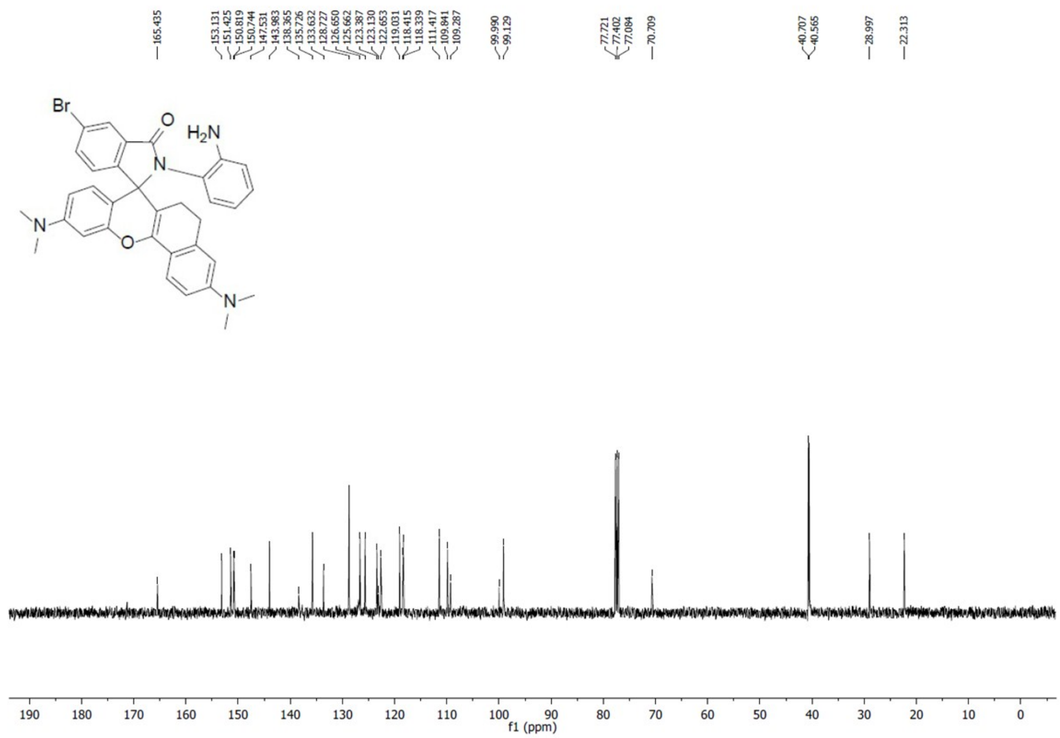


Figure S10. ^{13}C NMR spectrum of probe **12** in $CDCl_3$ solution.

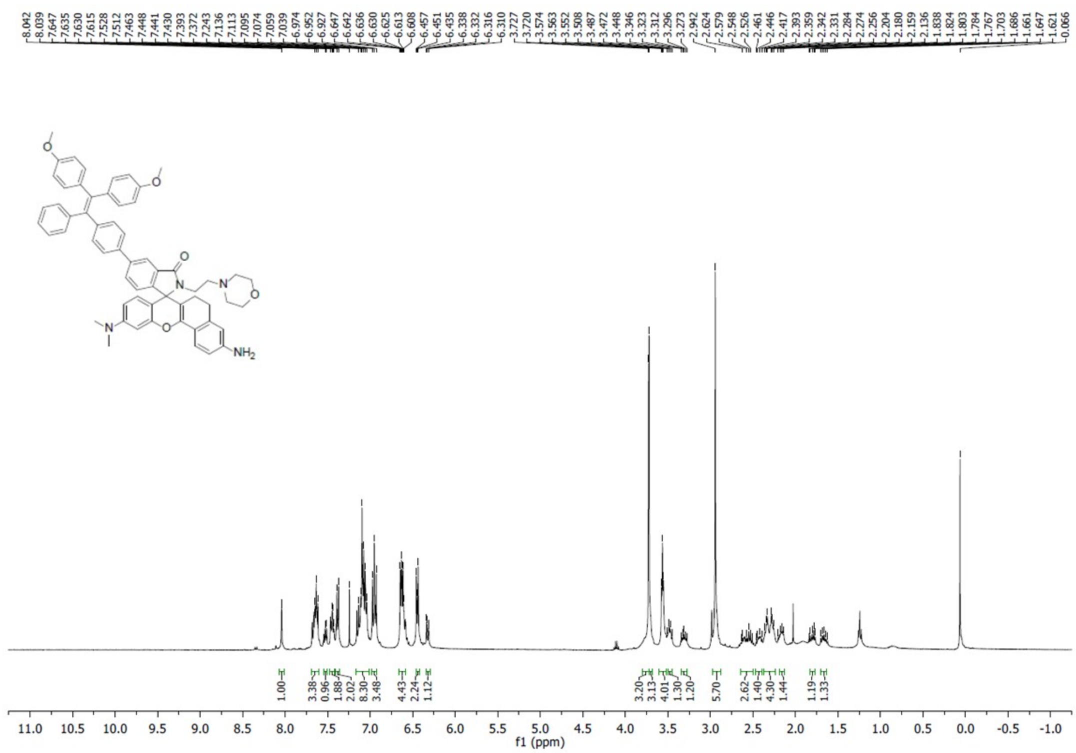


Figure S11. ^{1}H NMR spectrum of probe **A** in $CDCl_3$ solution.

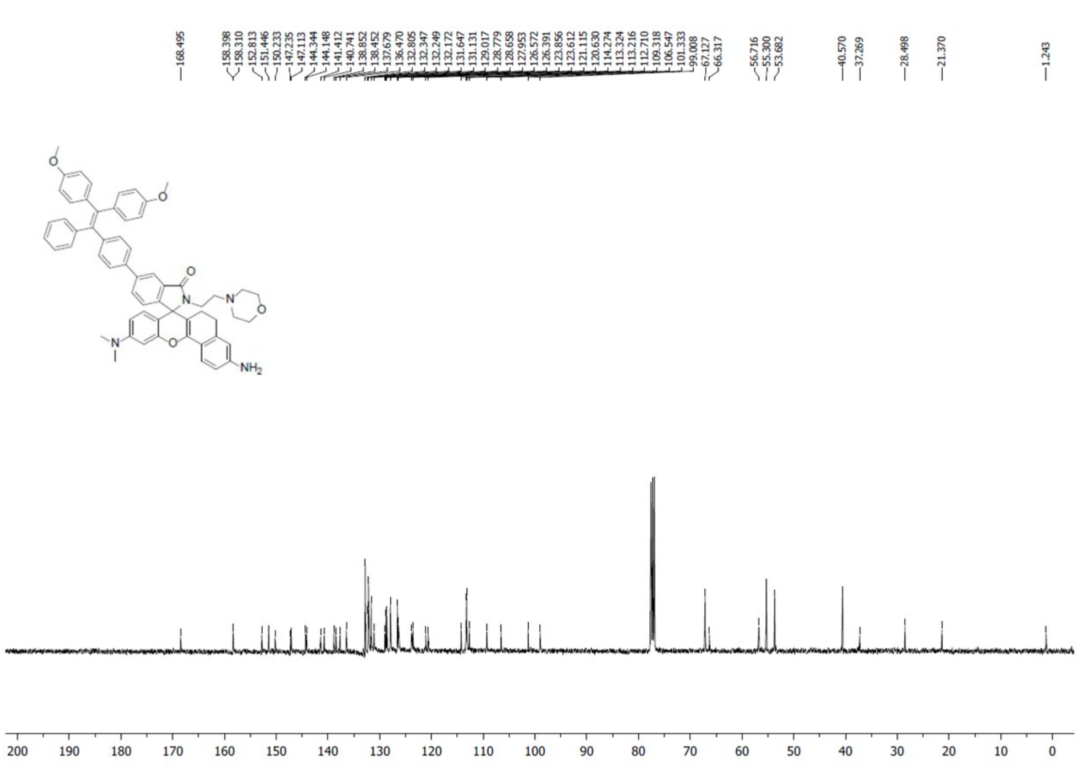


Figure S12. ^{13}C NMR spectrum of probe **A** in $CDCl_3$ solution.

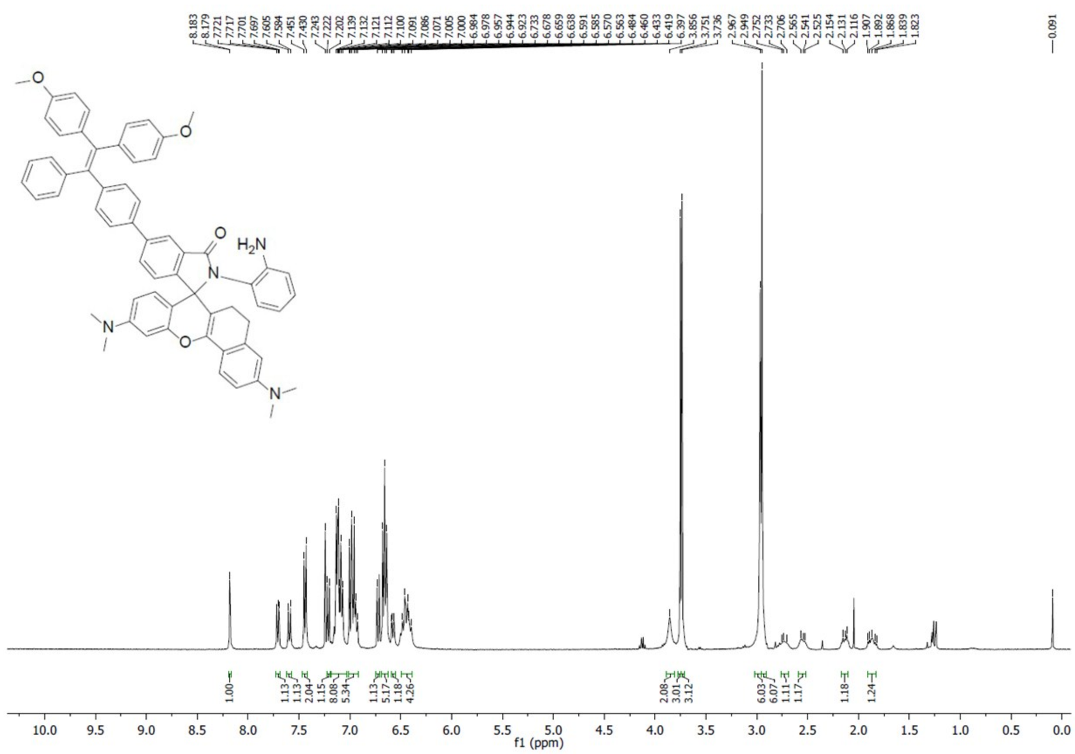


Figure S13. ^{1}H NMR spectrum of probe **B** in $CDCl_3$ solution.

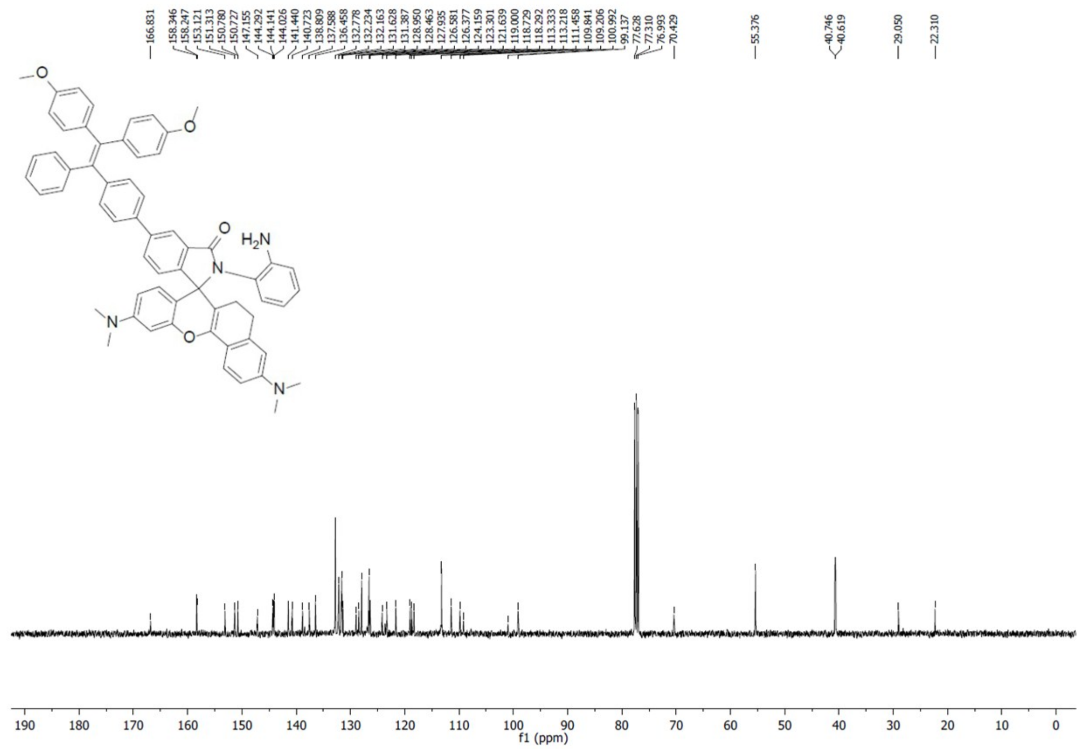


Figure S14. ^{13}C NMR spectrum of probe **B** in $CDCl_3$ solution.

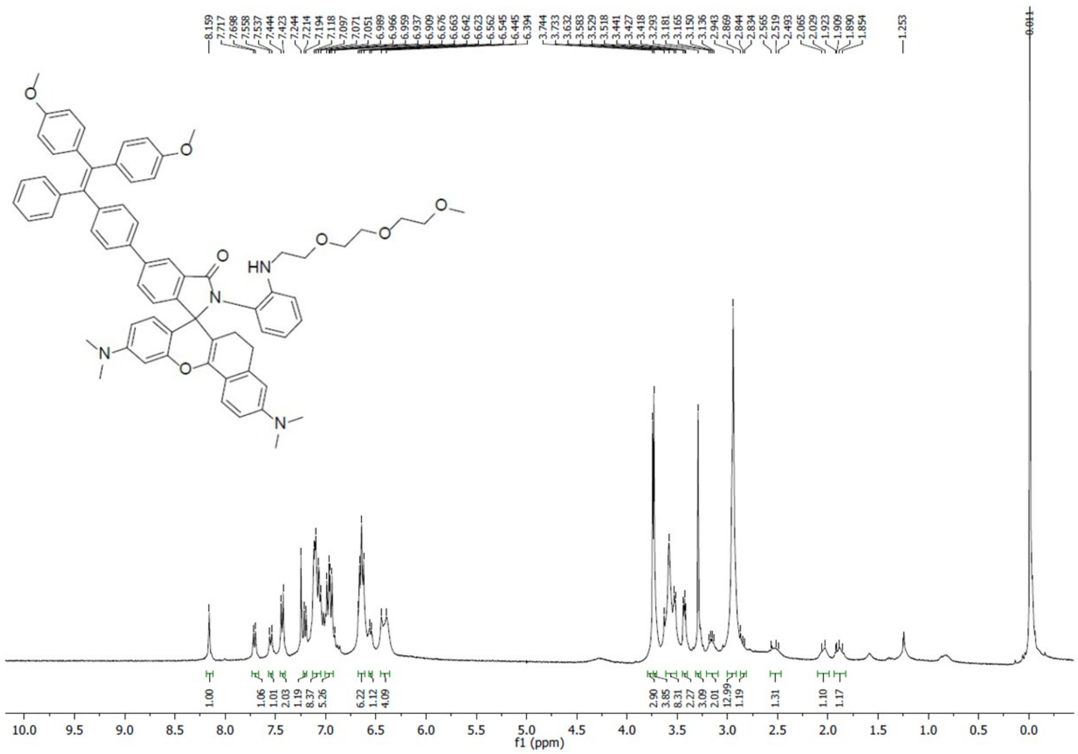


Figure S15. ^{1}H NMR spectrum of probe **C** in $CDCl_3$ solution.

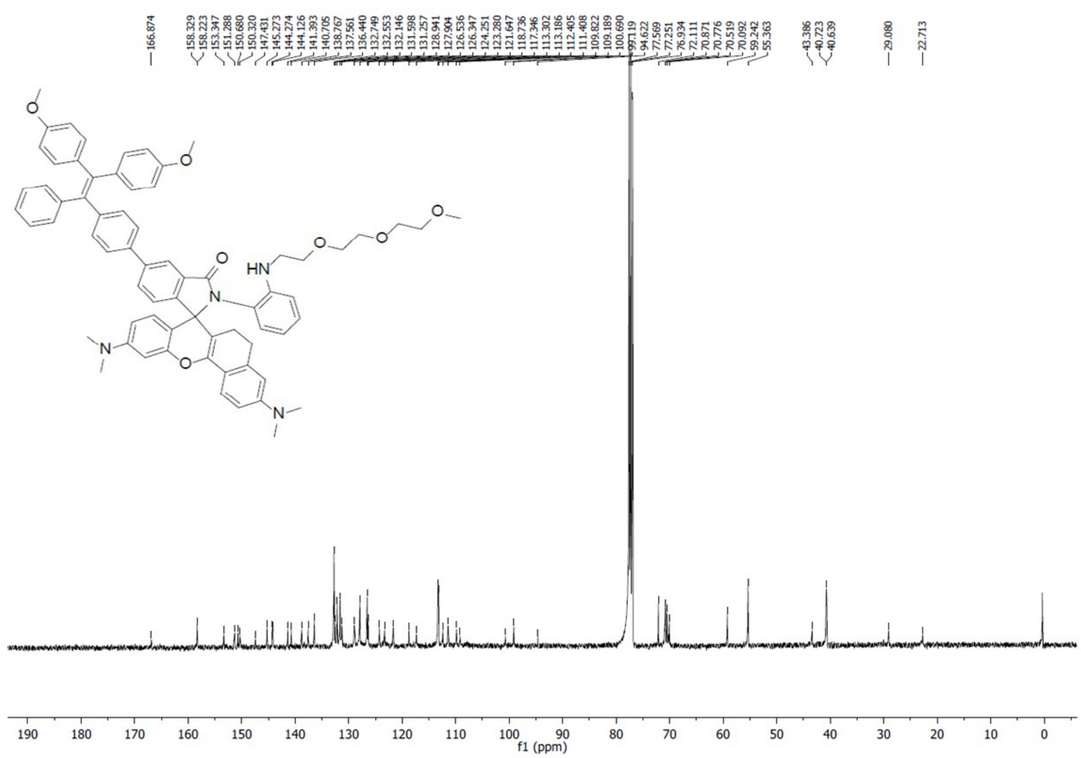


Figure S16. ^{13}C NMR spectrum of probe **C** in $CDCl_3$ solution.

3. INVESTIGATE AGGREGATION-INDUCED EMISSION OF THE PROBES.

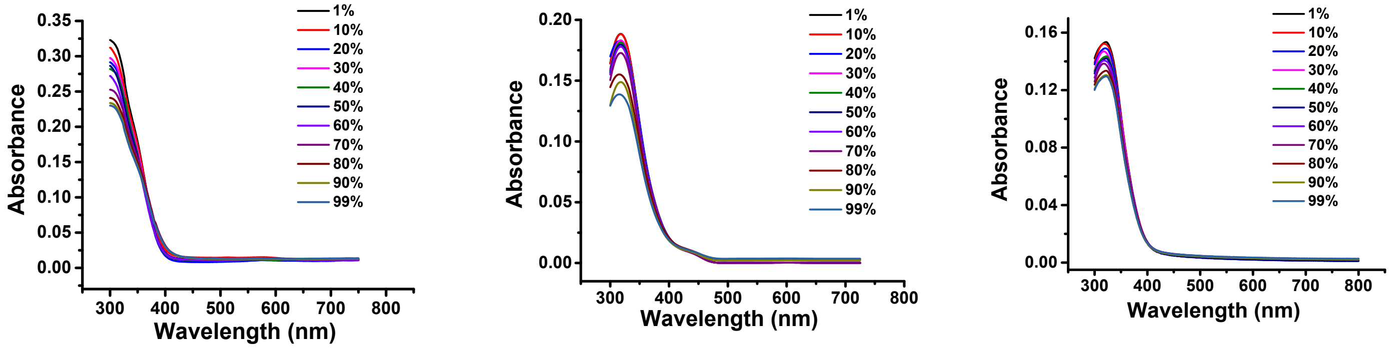


Figure S17. Absorption spectra of probes **A**, **B**, and **C** with water percentages from 1% to 99% in ethanol and water mixtures.

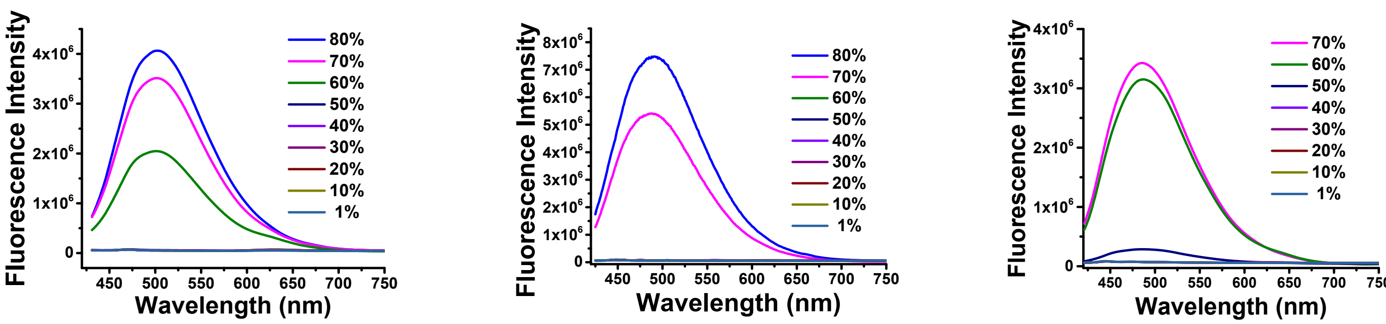


Figure S18. Fluorescence spectra of 10 μM probes **A**, **B**, and **C** with different water percentages from 1% to 80% in ethanol and water mixtures.

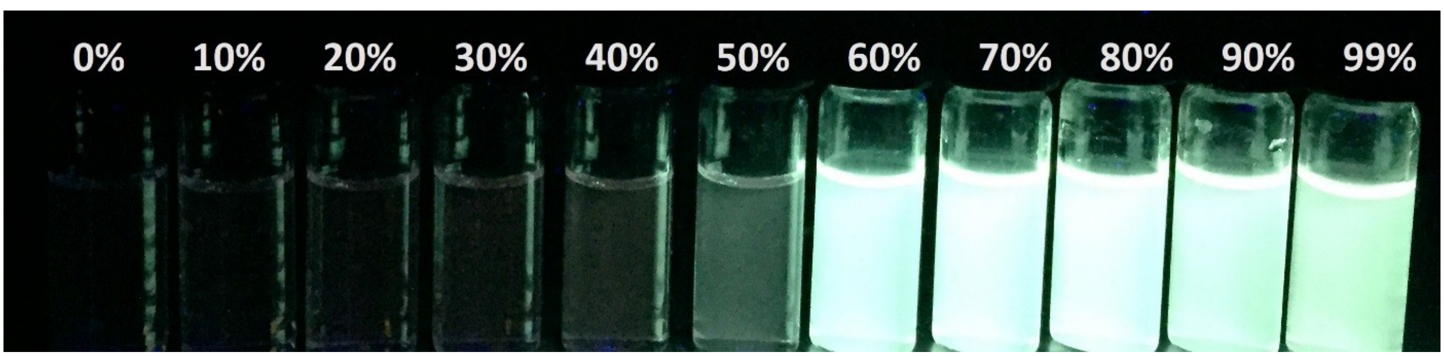


Figure S19. A photo of probe **A** with different water percentages from 0% to 99% in water and ethanol mixed solutions under UV radiation (365 nm).

4. Dynamic Light Scattering Measurement

We investigate nanoparticles sizes of probe **A** in mixed ethanol and water solutions with different water percentages by conducting dynamic light scattering measurement through Coulter NP4plus, Beckman Coulter, Fllerton, CA. The measurements are carried out with scattering angles of 90 degree at room temperature of 25 ^{o}C.   There is not obvious dynamic light scattering peak related to formation of nanoparticles of probe **A** in ethanol solution (Figure S20). However, increase of water percentage to 80% causes aggregation of probe A in the solution as dynamic light scattering peaks were observed with large nanoparticles of 7422 nm (Figure S21).

Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coef (m^2/s)	Counts/s	Baseline Error	Overflow
Rept.1	744.3	-2.512	4.81e-13	1.17e+05	0.38%	0
Rept.2	0.0	-203.628	-1.74e-13	1.42e+05	0.40%	0
Rept.3	127.6	1.305	2.80e-12	1.55e+05	0.08%	0
Average	290.6 ± 325.02	-68.278 ± 95.720				

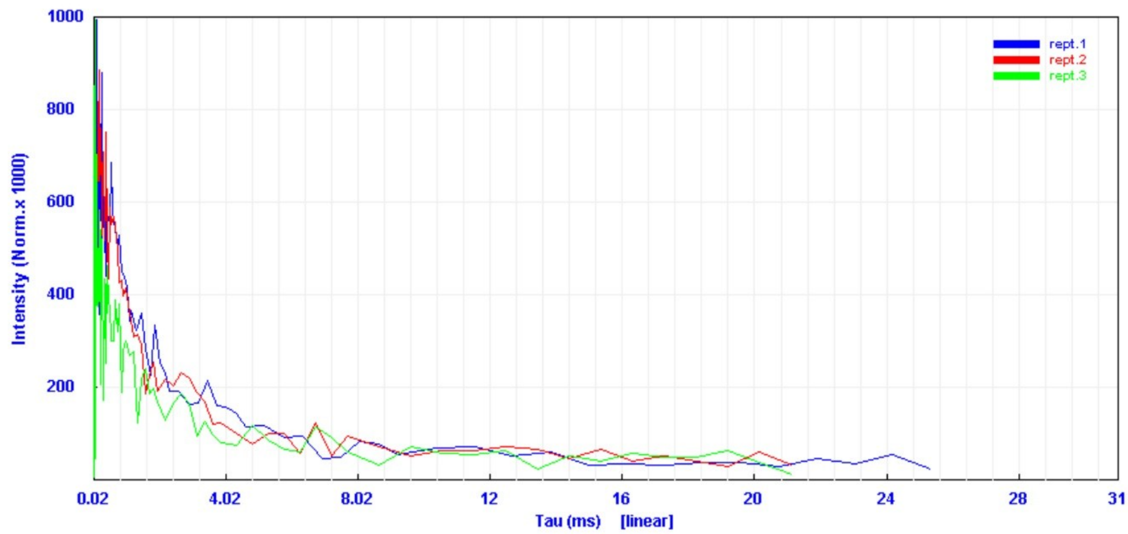


Figure S20. Dynamic light scattering measurement data of 5 µM in ethanol solution.

Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coef (m^2/s)	Counts/s	Baseline Error	Overflow
Rept.1	6306.2	0.473	5.14e-14	1.56e+06	8.79%	0
Rept.2	8145.1	-0.152	3.98e-14	1.48e+06	2.95%	0
Rept.3	7816.0	-0.194	4.15e-14	1.47e+06	1.23%	0
Average	7422.4 ± 800.65	0.042 ± 0.305				

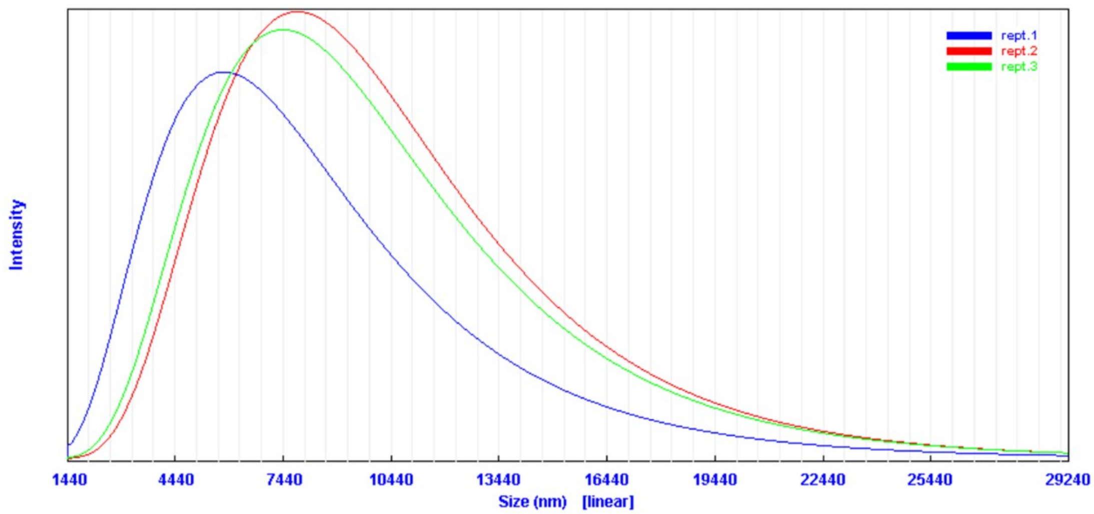


Figure S21. Dynamic light scattering measurement data of 5 μM in ethanol solution containing 80% water.

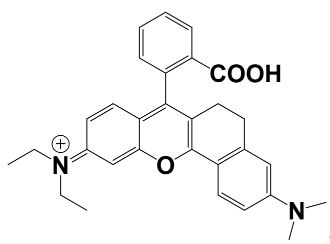
5. CALCULATION OF FLUORESCENCE QUANTUM YIELDS OF THE PROBES

Fluorescence quantum yields of the probes were calculated according to literature[3] using the equation below.

$$\phi_x = \phi_{st}\frac{\eta_x^2 A_{st} I_x}{\eta_{st}^2 A_x I_{st}}$$

ϕ represents fluorescence quantum yield. I_x is integration of sample's fluorescence spectra at specific excitation wavelength. A is the absorbance at the specific excited wavelength while the absorbances at the wavelength of excitation is optimally kept in between 0.02 and 0.05. η is the refractive index of solvents which were used for optical measurements, and the subscripts x and st stand for the probe and a reference compound of known fluorescence quantum yield, respectively.

Fluorescence quantum yields of the probe rhodamine acceptors were calculated at pH 2.8 using a near-infrared rhodamine dye (Standard)[4] as a standard with a fluorescence quantum yield 37% in pH 7.4 PBS buffer with 10% ethanol. Rhodamine 6G[3] with fluorescence quantum yield of 95% in ethanol was used as standard to calculate quantum yields of TPE donor parts.



Standard

6. DETERMINATION OF pKa BY FLUOROMETRIC TITRATION

The constant $K_{\mathbf{a}}$ of probes was obtained by fluorometric titration as a function of pH using the fluorescence spectra. The expression of the steady-state fluorescence intensity *F* as a function of the proton concentration has been extended for the case of a n: 1 complex between H^+ and a fluorescent probe, which is expressed by the equation below:[5]

$$F = \frac{F_{min}[\mathrm{H}^+]^n + F_{max}K_a}{K_a + [\mathrm{H}^+]^n}$$

F_{min} and F_{max} are the fluorescence intensities at maximal and minimal H^+ concentrations, respectively, and *n* is apparent stoichiometry of H^+ binding to the probe which affects the fluorescent change. Nonlinear fitting of equation expressed above to the fluorescence titration data recoded as a function of H^+ concentration with $K_{\mathbf{a}}$ and n as free adjustable parameters yields the estimated apparent constant of $K_{\mathbf{a}}$.

7. TPE DONOR EMISSION SPECTRA AT pH 7.6, AND RHODAMINE ACCEPTOR ABSORPTION SPECTRA AT pH 3.2

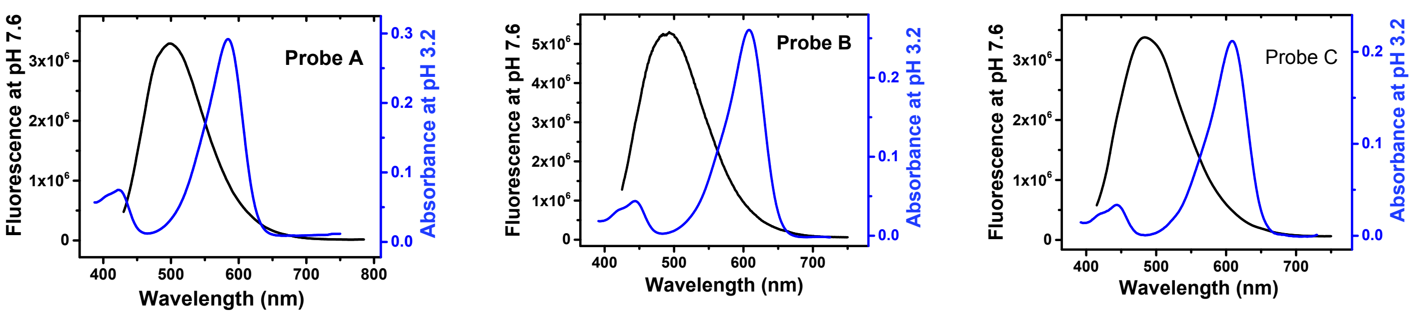


Figure S22. TPE donor fluorescence spectra of probes **A** (left), **B** (middle) and **C** (right) in 10 mM pH 7.6 citrate buffers and rhodamine acceptor absorption spectra of probes **A** (left), **B** (middle) and **C** (right) in 10 mM pH 3.2 citrate buffers.

8. PROBE OPTICAL RESPONSES TO PH CHANGES.

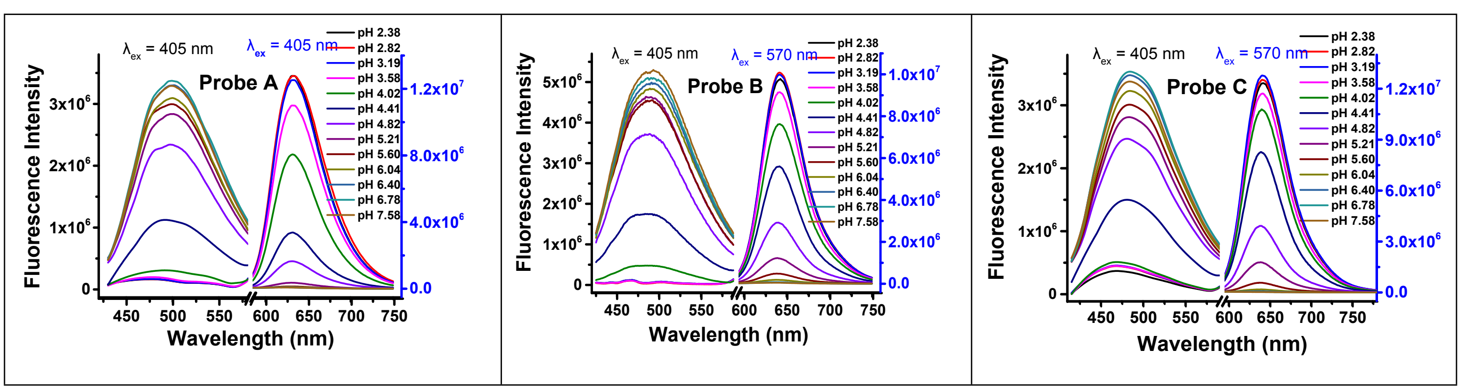


Figure S23. Fluorescence spectra (left) of probes **A** (left), **B** (middle) and **C** (right) in 10 mM citrate buffers under TPE excitation at 405 nm and rhodamine excitation at 570 nm.

9. FLUORESCENCE SPECTRA OF THE PROBES UNDER RHODAMINE EXCITATION

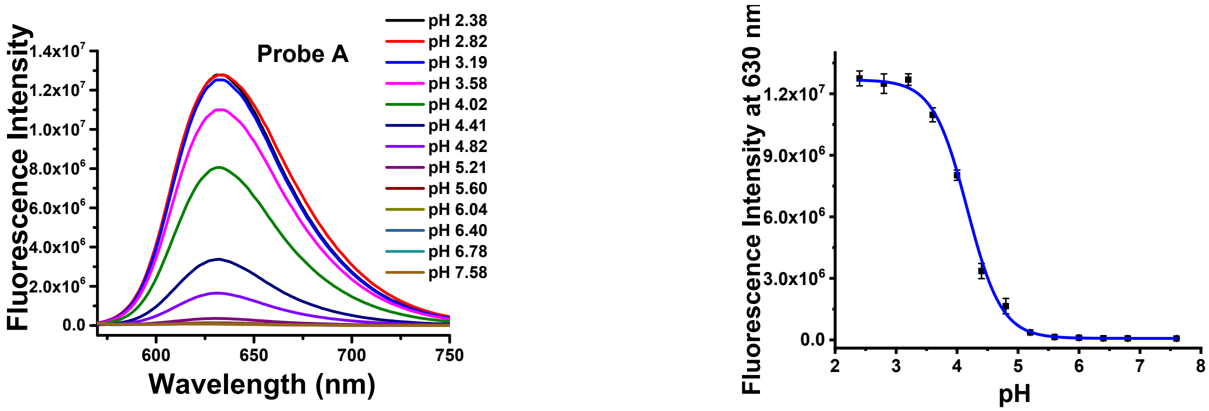


Figure S24. Fluorescence spectra (left) of probe **A** in 10 mM citrate buffers under rhodamine excitation of 550 nm, and plot (right) of fluorescence intensity versus pH.

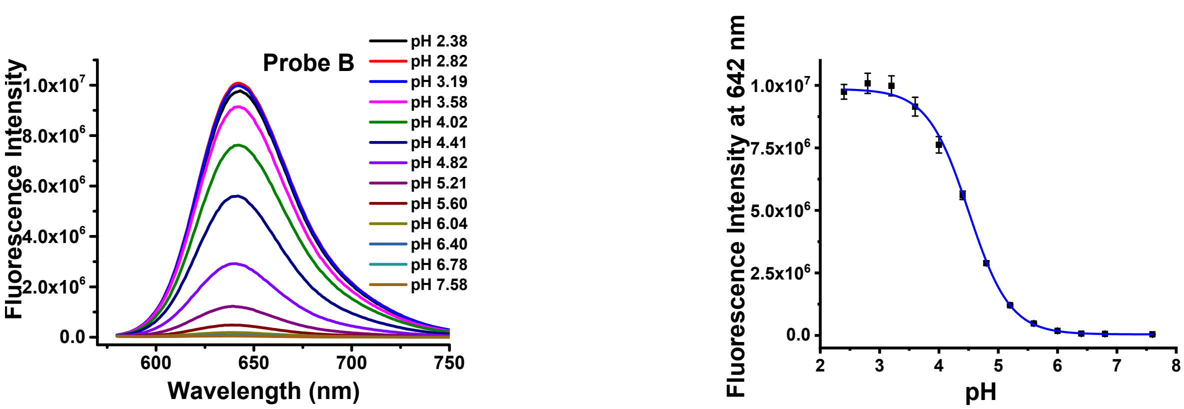


Figure S25. Fluorescence spectra (left) of probe **B** in 10 mM citrate buffers under rhodamine excitation of 570 nm, and plot (right) of fluorescence intensity versus pH.

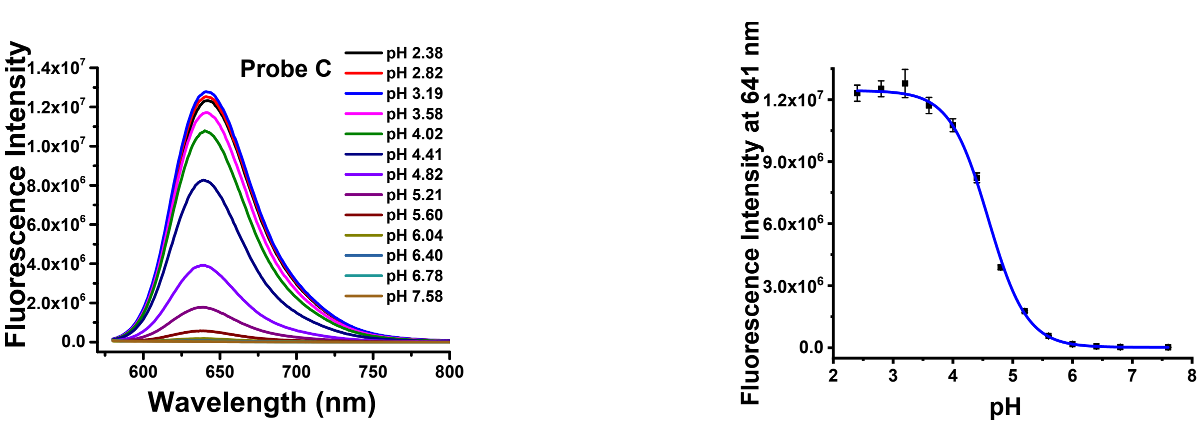


Figure S26. Fluorescence spectra (left) of probe **C** in 10 mM citrate buffers under rhodamine excitation at 570 nm, and plot (right) of fluorescence intensity versus pH.

10. PROBE SELECTIVITY TO pH OVER CATIONS, ANIONS, AND AMINO ACIDS

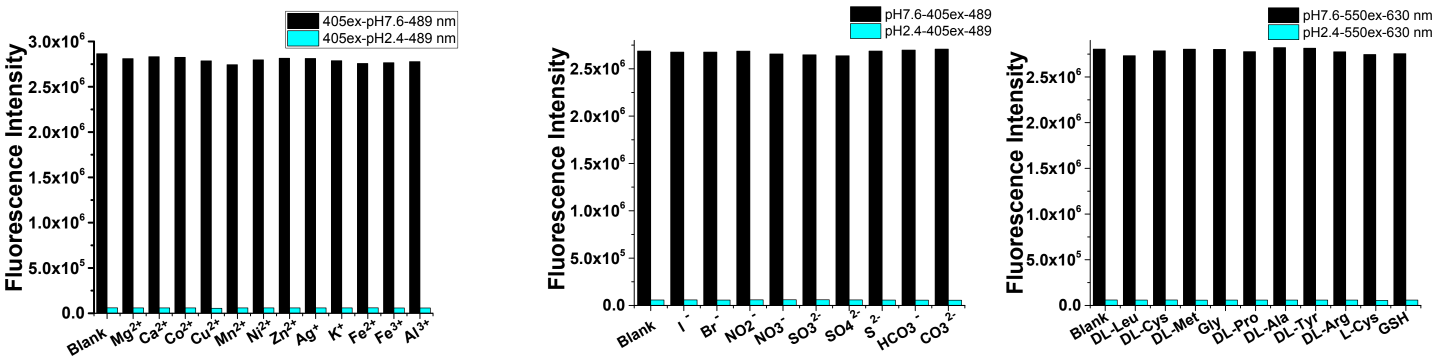


Figure S27. TPE donor fluorescence intensity of probe **A** at 489 nm in 10 mM citrate buffers with pH 7.58 or 2.38 containing 50 µM different cations, anions, amino acids or biothiols under excitation at 405 nm

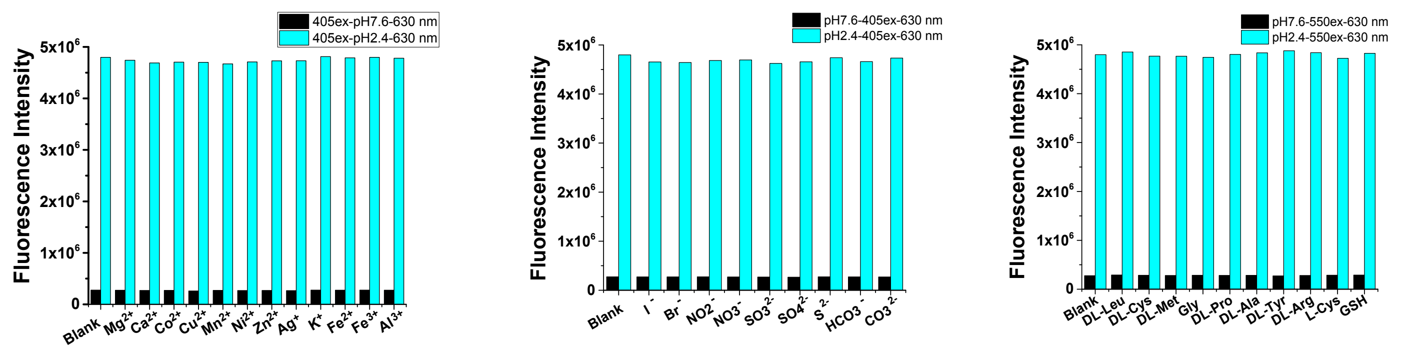


Figure S28. Rhodamine fluorescence intensity of probe **A** at 630 nm in 10 mM citrate buffers with pH 7.58 or 2.38 containing 50 µM different cations, anions, amino acids or biothiols under excitation at 405 nm.

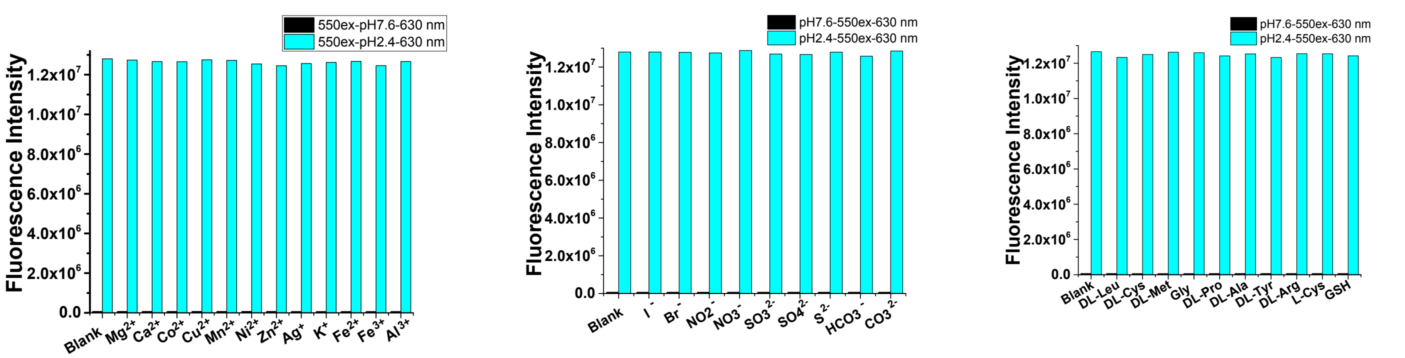


Figure S29. Rhodamine acceptor fluorescence intensity of probe **A** at 630 nm in buffers with pH 7.58 or 2.38 containing 50 µM different cations, anions, amino acids or biothiols under excitation at 555 nm.

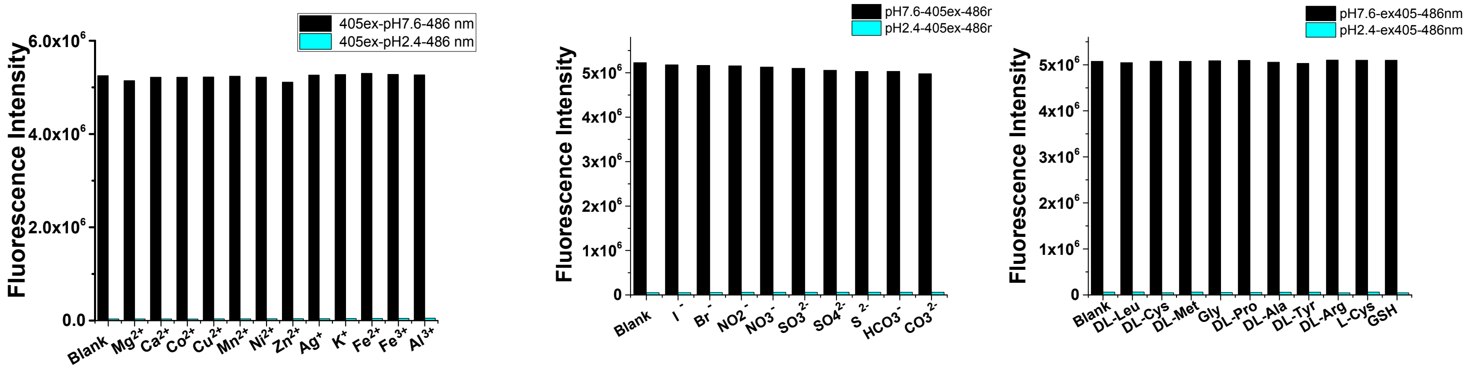


Figure S30. TPE donor fluorescence intensity of probe **B** at 486 nm in 10 mM citrate buffers with pH 7.58 or 2.38 containing 50 μM different cations, anions, amino acids, or biothiols under excitation at 405 nm.

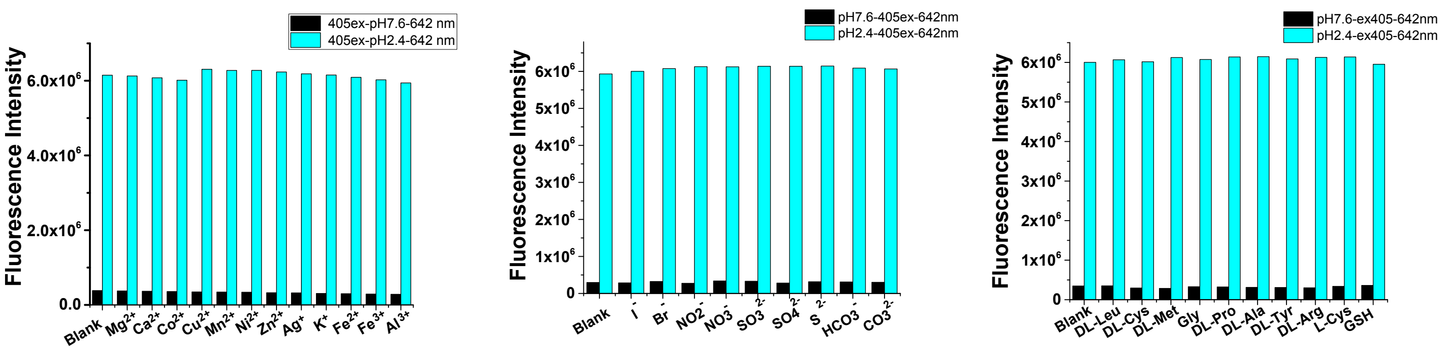


Figure S31. Rhodamine acceptor fluorescence intensity of probe **B** at 642 nm in 10 mM citrate buffers with pH 7.58 or 2.38 containing 50 μM different cations, anions, amino acids, or biothiols under excitation at 405 nm.

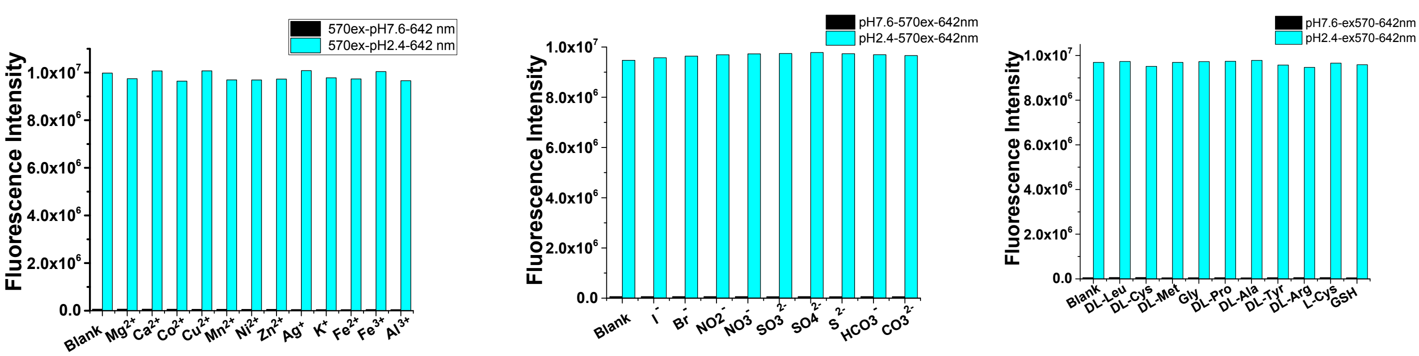


Figure S32. Rhodamine acceptor fluorescence intensity of probe **B** at 642 nm in buffers with pH 7.58 or 2.38 containing 50 μM different cations, anions, amino acids or biothiols under excitation at 570 nm.

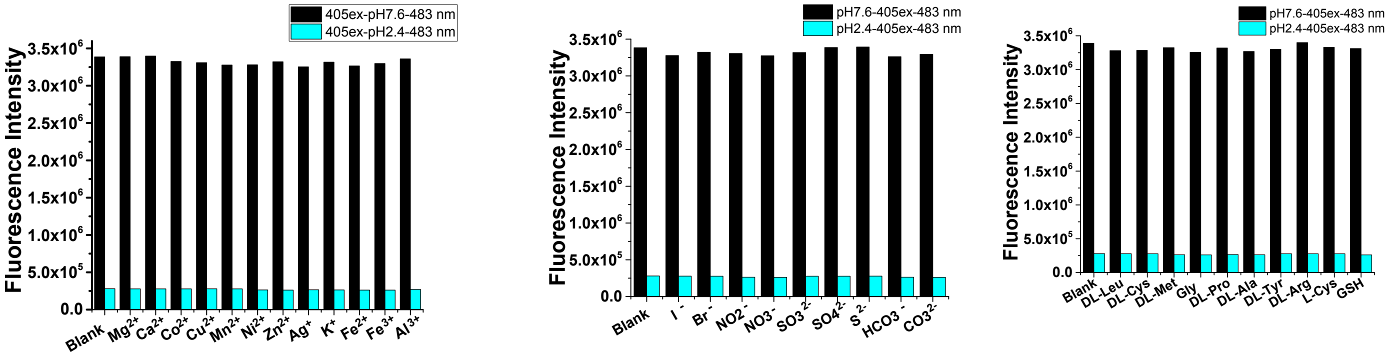


Figure S33. TPE donor fluorescence intensity of probe **C** at 483 nm in 10 mM citrate buffers with pH 7.58 or 2.38 containing 50 μM different cations, anions, amino acids or biothiols under excitation at 405 nm.

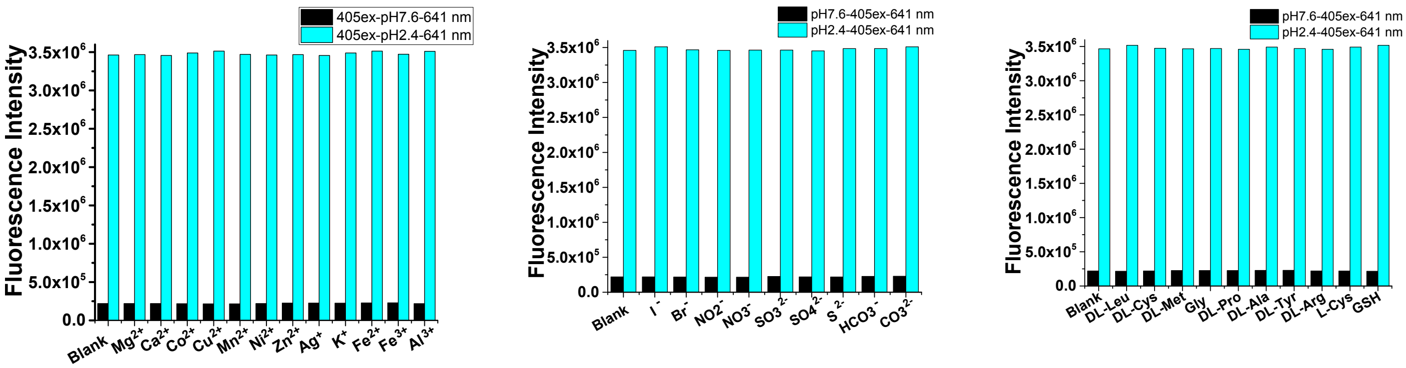


Figure S34. Rhodamine fluorescence intensity of probe **C** at 641 nm in 10 mM citrate buffers with pH 7.58 or 2.38 containing 50 μM different cations, anions, amino acids or biothiols under excitation at 405 nm.

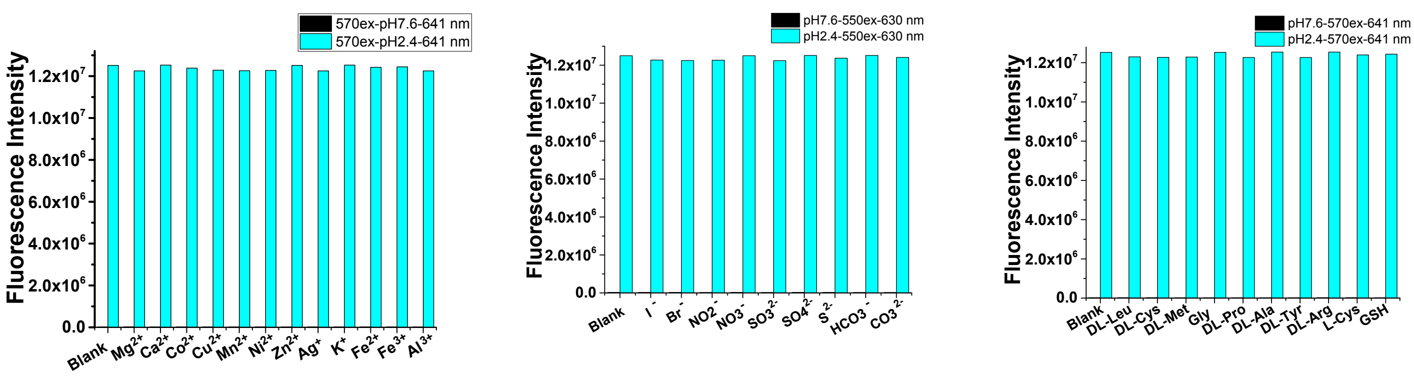


Figure S35. Rhodamine acceptor fluorescence intensity of probe **C** at 641 nm in buffers with pH 7.58 or 2.38 containing 50 μM different cations, anions, amino acids or biothiols under excitation at 570 nm.

11. REVERSIBILITY OF PROBE FLUORESCENCE RESPONSES TO pH CHANGES

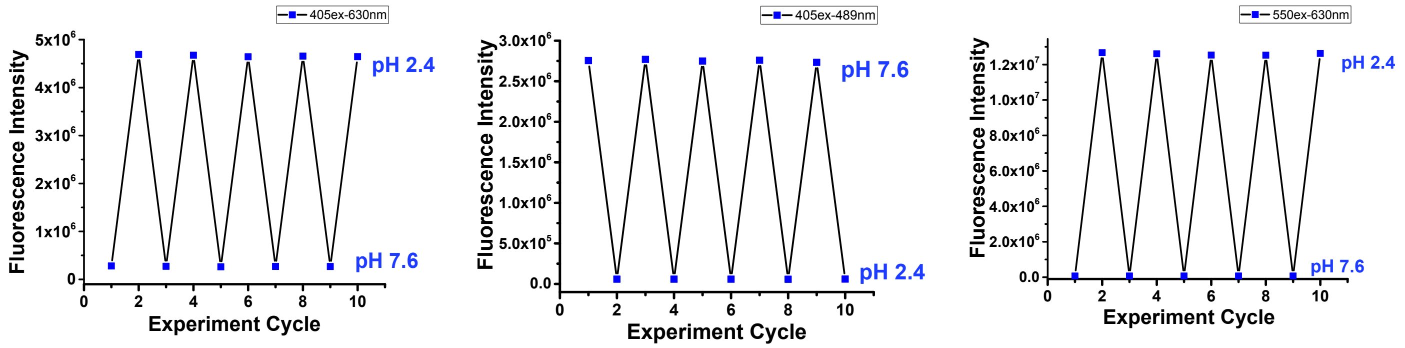


Figure S36. TPE donor (left) and rhodamine acceptor (middle and right) fluorescence responses of probes **A** to pH changes in 10 mM citrate buffers 2.4 and 7.6 under TPE excitation at 405 nm (left and middle) or rhodamine excitation at 550 nm (right).

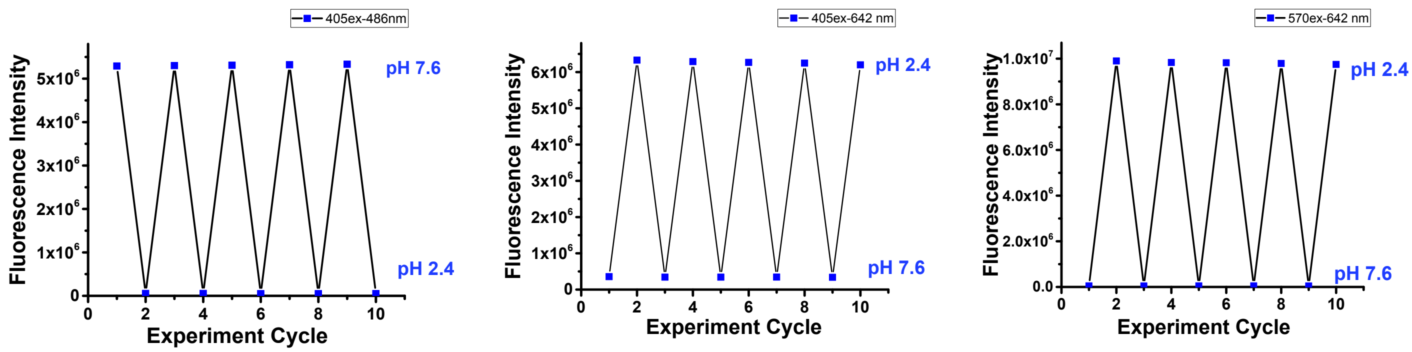


Figure S37. TPE donor (left) and rhodamine acceptor (middle and right) fluorescence responses of probe **B** to pH changes in 10 mM citrate buffers with pH 2.4 and 7.6 under TPE excitation at 405 nm (left and middle) or rhodamine excitation at 570 nm (right).

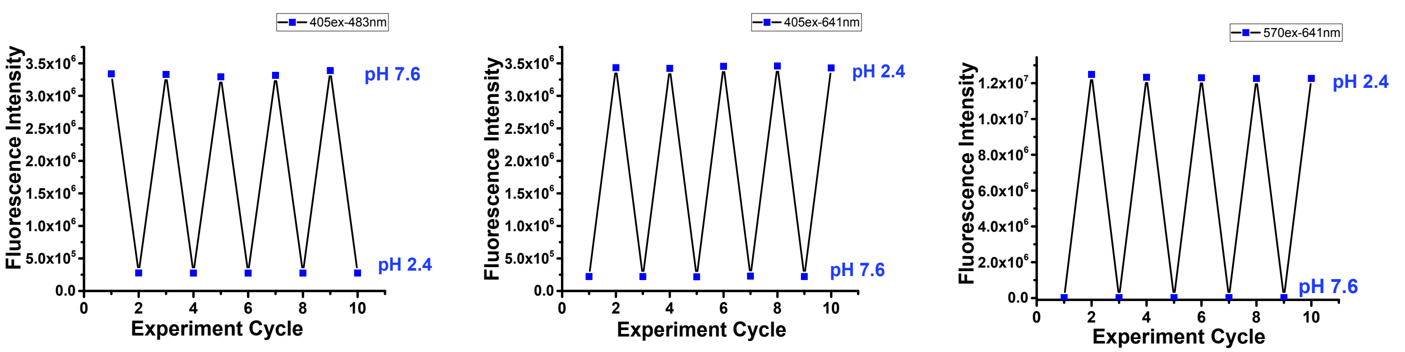


Figure S38. TPE donor (left) and rhodamine acceptor (middle and right) fluorescence responses of probe **C** to pH changes in 10 mM citrate buffers with pH 2.4 and 7.6 under TPE donor excitation at 405 nm (left and middle) or rhodamine excitation at 570 nm (right).

12. PHOTOSTABILITY OF THE PROBES TO PH CHANGES

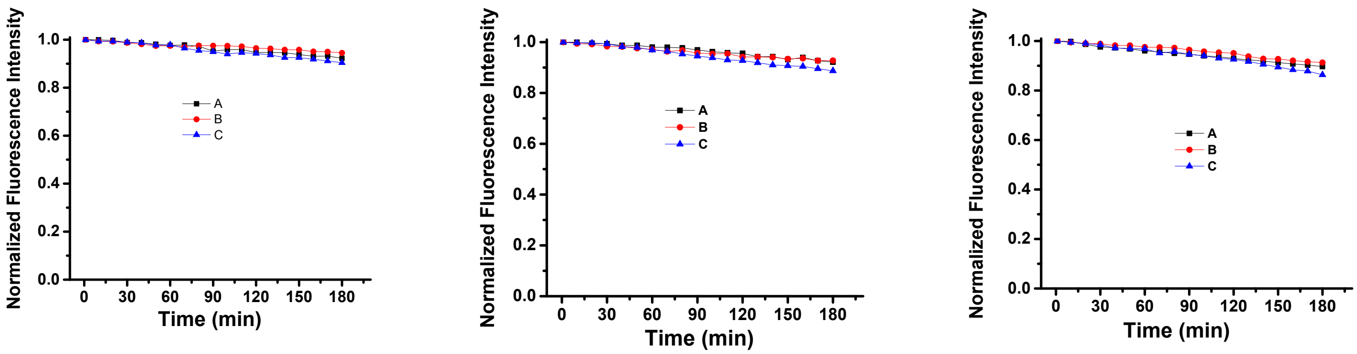


Figure S39. TPE donor fluorescence intensities at 489 nm, 486 nm and 483 nm (left) for probes **A**, **B**, and **C** under excitation at 405 nm versus time in a 10 mM citrate buffer with pH 7.6, respectively. Rhodamine fluorescence intensities at 630 nm, 642 nm, and 641 nm for probes **A**, **B** and **C** under TPE donor excitation at 405 nm (middle), and under rhodamine acceptor excitation at 550 nm, 570 nm and 570 nm (right) for probes **A**, **B,** and **C** versus time in a 10 mM citrate buffer with pH 2.4, respectively.

13. Cytotoxicity of the fluorescent probe.

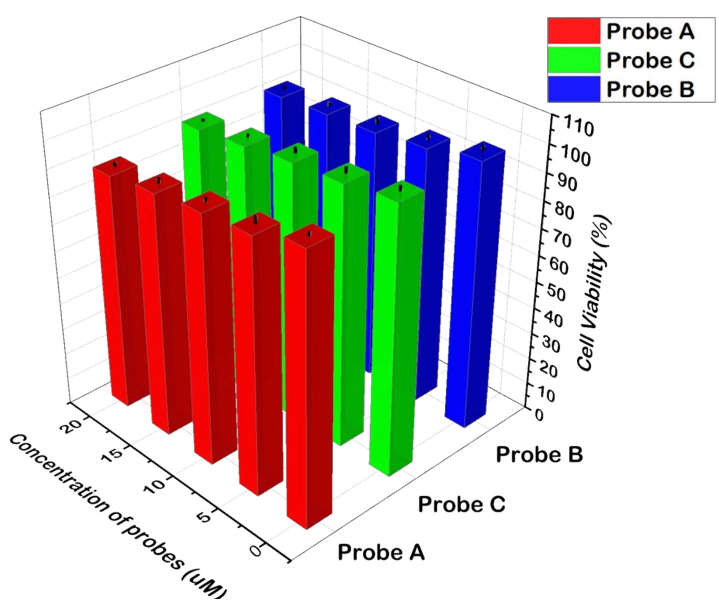


Figure S40. Cytotoxicity of probes **A**, **B**, and **C** determined by MTS assay. The HeLa cells were incubated with 0, 5, 10, 15, and 20 µM of probes **A**, **B**, and **C** for 48 h. The relative cell viability was normalized to untreated cells and the cell viability was obtained by measuring the absorbance at 490 nm, which has a linear relationship with the cell viability. The error bars indicate ± SD.

14. CELLULAR IMAGING OF THE PROBES

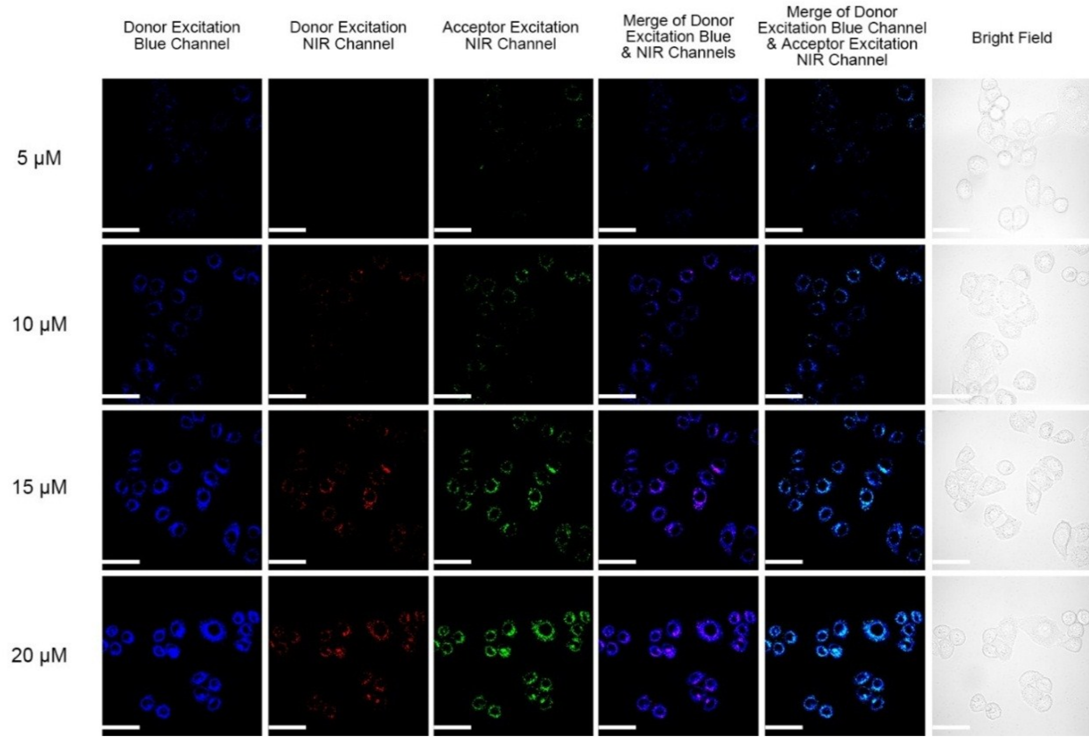


Figure S41. Cellular images of HeLa cells in 10 mM citrate pH 7.4 buffers containing probe **A** with different concentrations. The confocal fluorescence microscope was employed to obtain cellular images at 60× magnification. The blue channel of TPE donor fluorescence was collected from 475 to 525 nm, and the NIR channel (pseudo-colored as red for clarity) of rhodamine acceptor fluorescence in the second column was collected from 650 to 700 nm under excitation of TPE donor at 405 nm. The NIR channel (pseudo-colored as green for clarity) of rhodamine acceptor in the third column was collected from 650 to 700 nm under excitation of Rhodamine acceptor at 559 nm. Scale bar: 50 μM.

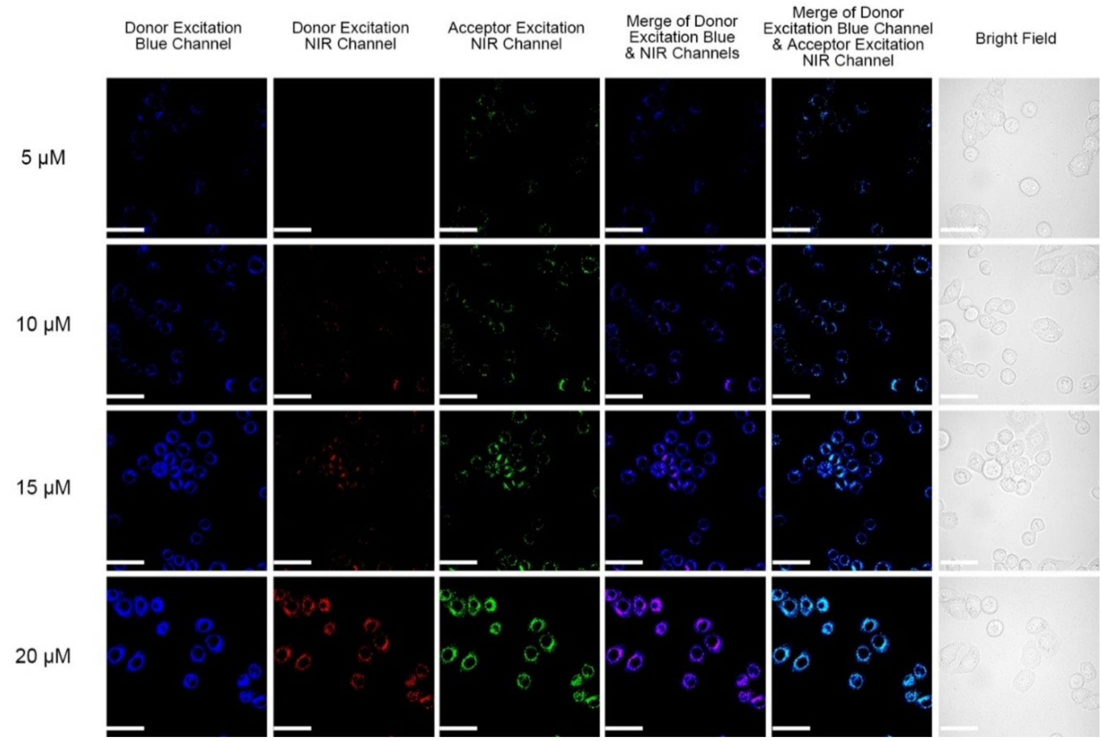


Figure S42. Cellular images of HeLa cells in 10 mM citrate pH 7.4 buffers containing probe **B** with different concentrations. The confocal fluorescence microscope was employed to obtain cellular images at 60× magnification. The blue channel of TPE donor fluorescence was collected from 475 to 525 nm, and the NIR channel (pseudo-colored as red for clarity) of rhodamine acceptor fluorescence in the second column was collected from 650 to 700 nm under excitation of TPE donor at 405 nm. The NIR channel (pseudo-colored as green for clarity) of rhodamine acceptor in the third column was collected from 650 to 700 nm under excitation of Rhodamine acceptor at 559 nm. Scale bar: 50 μM.

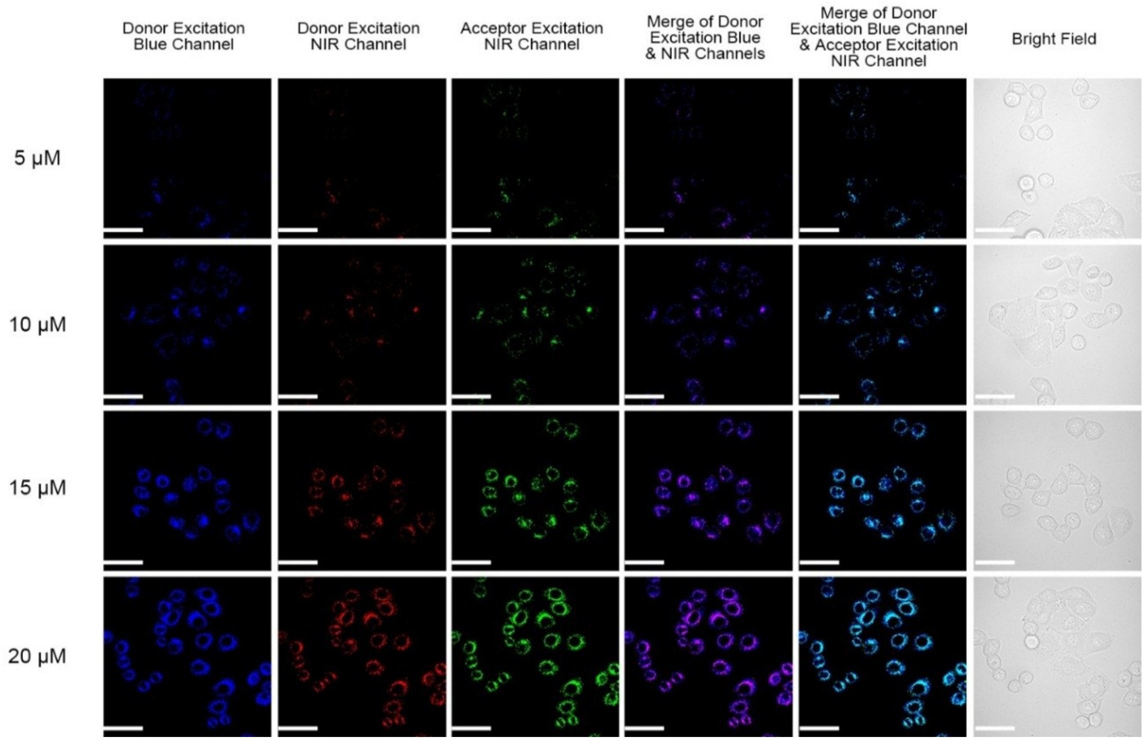
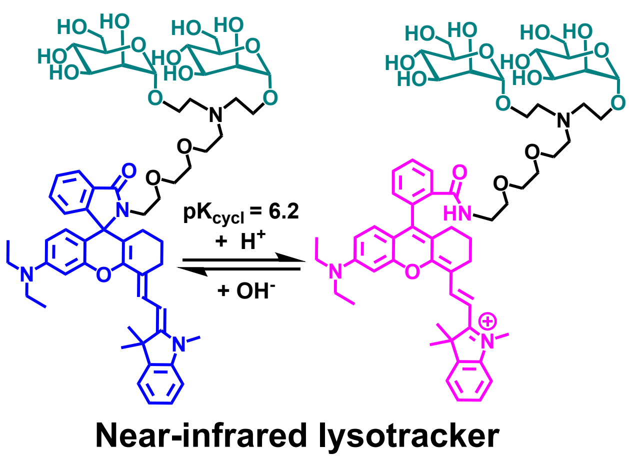


Figure S43. Cellular images of HeLa cells in 10 mM citrate pH 7.4 buffers containing probe **C** with different concentrations. The confocal fluorescence microscope was employed to obtain cellular images at 60× magnification. The blue channel of TPE donor fluorescence was collected from 475 to 525 nm, and the NIR channel (pseudo-colored as red for clarity) of rhodamine acceptor fluorescence in the second column was collected from 650 to 700 nm under excitation of TPE donor at 405 nm. The NIR channel (pseudo-colored as green for clarity) of rhodamine acceptor in the third column was collected from 650 to 700 nm under excitation of Rhodamine acceptor at 559 nm. Scale bar: 50 μM.



In order to investigate whether our probes as weak bases can be used to target lysosomes in live cells, we used a near-infrared fluorescent lysotacker[6] to conduct collocalization correlation analysis. The pearson's coefficients between donor excitation blue channel and near-infrared Lysotracker channel for probes **A**, **B** and **C** are 0.917, 0.896 and 0.934 respectively, indicating that our probes stay with near-infrared lysotracker together in lysosomes in live cells.

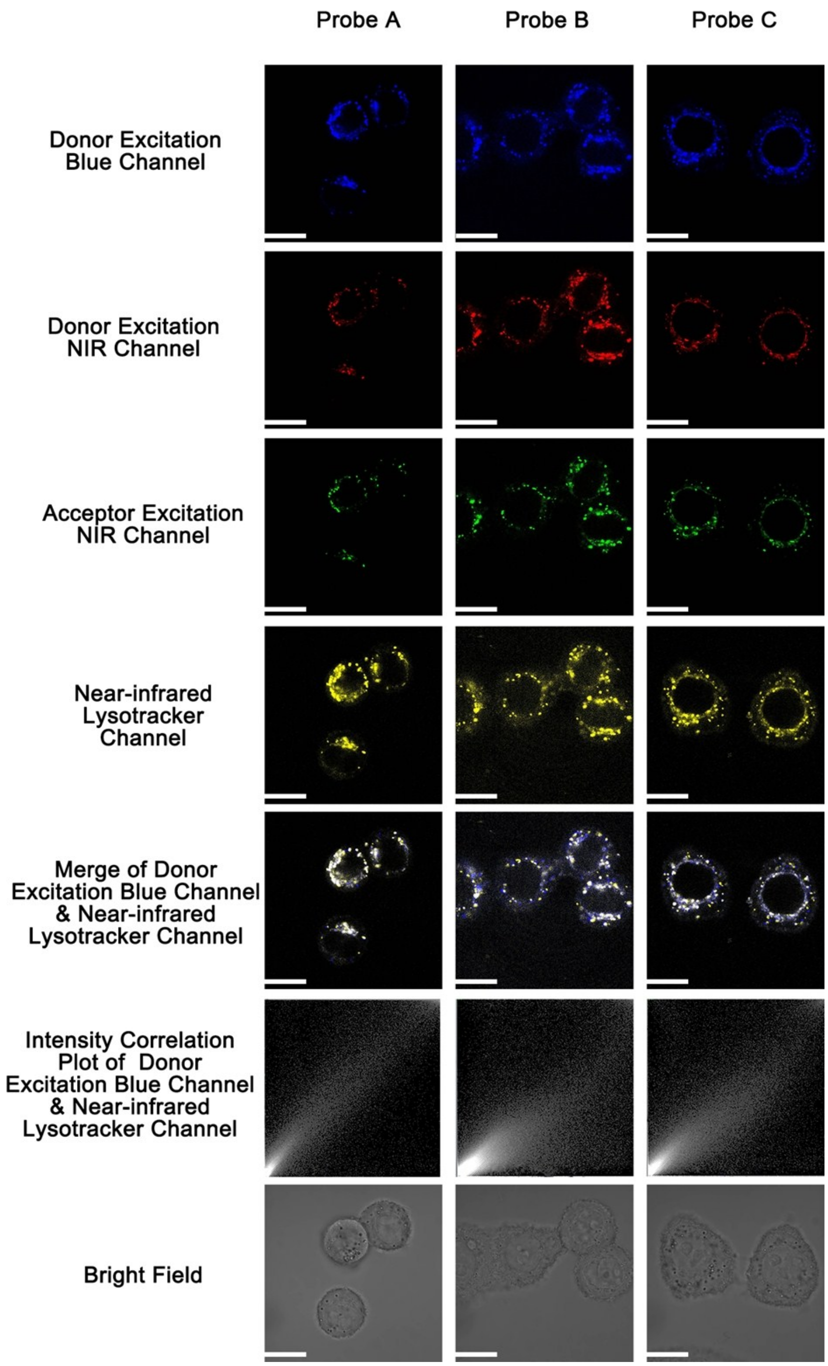


Figure S44. Fluorescence cellular images of HeLa Cells incubated with 10 μM near-infrared lysotracker and 15 μM probes **A**, **B** and **C**, respectively. The excitation of near-infrared lysotracker is at 635 nm and the fluorescence (pseudo-colored as yellow for clarity) was collect at the range of 725-775 nm. The blue channel of TPE donor fluorescence was collected from 475 to 525 nm, and the NIR channel (pseudo-colored as red for clarity) of rhodamine acceptor fluorescence in the second column was collected from 650 to 700 nm under excitation of TPE donor at 405 nm. The NIR channel (pseudo-colored as green for clarity) of rhodamine acceptor in the third column was collected from 650 to 700 nm under excitation of Rhodamine acceptor at 559 nm. Scale bar: 20 μM.

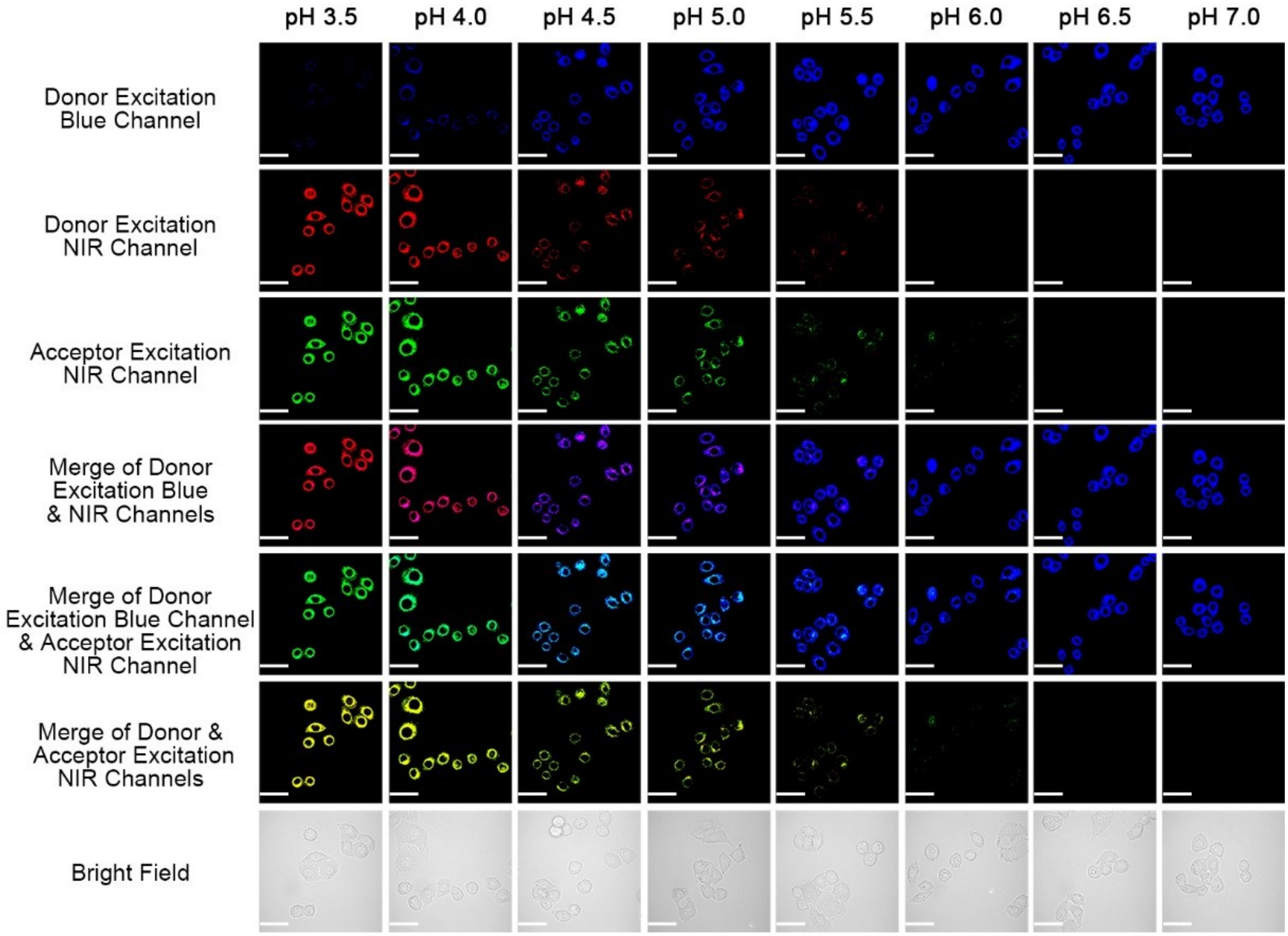


Figure S45: Cellular fluorescence images of 15 µM probes **A** incubated with HeLa cells in 10 mM citrate buffers having pH from 3.5 to 7.0 in the presence of 5 µg/mL nigericin. The blue channel in the first row was obtained from 475 to 525 nm, and two NIR channels (pseudo-colored as red and green for clarity) in the second and third rows were obtained from 650 to 700 nm under excitation of TPE donor and rhodamine acceptor at 405 nm and 559 nm, respectively. Confocal fluorescence microscope was employed to obtain fluorescence images at 60× magnification with scale bars of 50 µM.

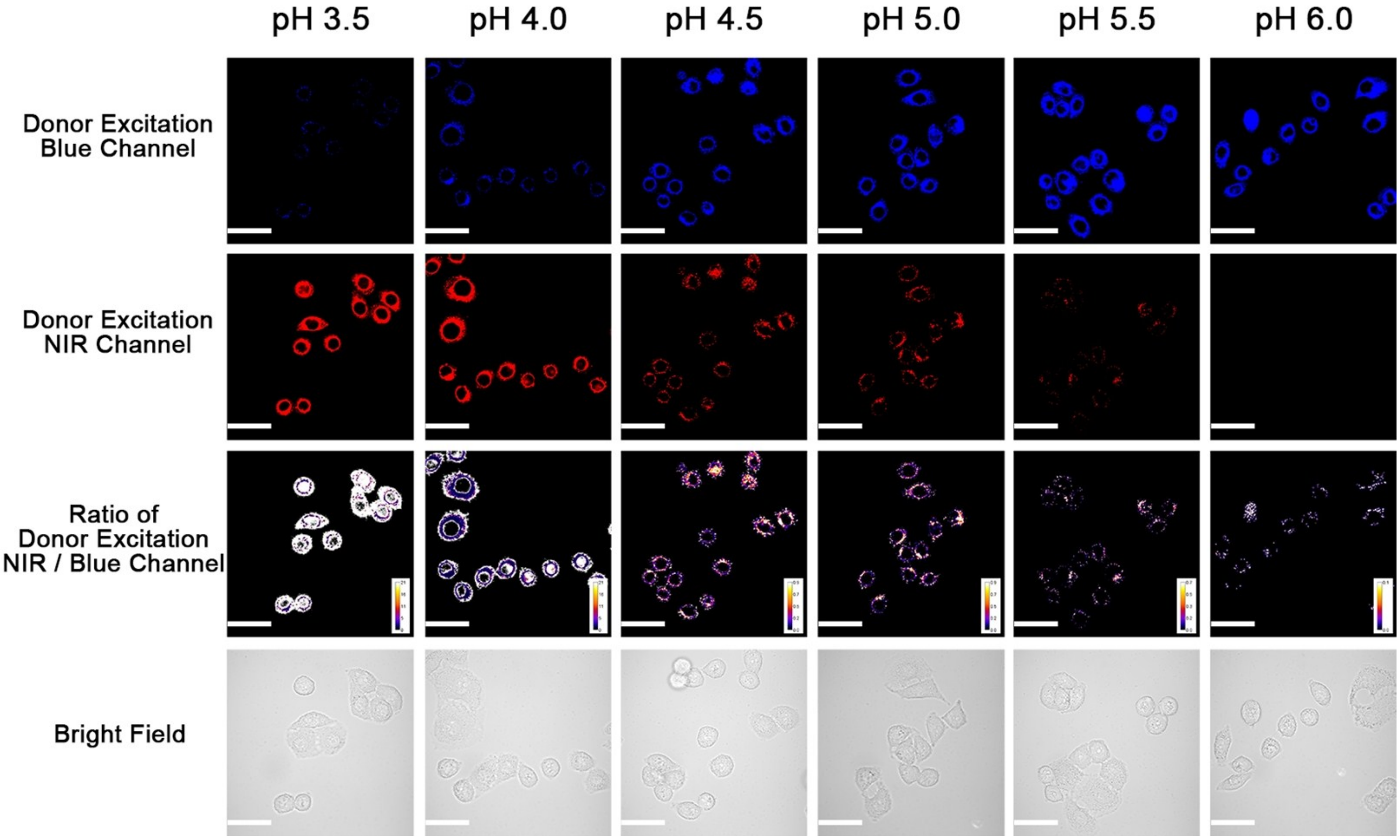


Figure S46: Cellular fluorescence images of 15 μM probes **A** incubated with HeLa cells in 10 mM citrate buffers having pH from 3.5 to 7.0 in the presence of 5 μg/mL nigericin. The blue channel in the first row was obtained from 475 to 525 nm, and NIR channel (pseudo-colored as red for clarity) in the second row were obtained from 650 to 700 nm under excitation of TPE donor at 405 nm. Confocal fluorescence microscope was employed to obtain fluorescence images at 60× magnification with scale bars of 50 μM. Ratiometric images (red channel/blue channel) in the third row.

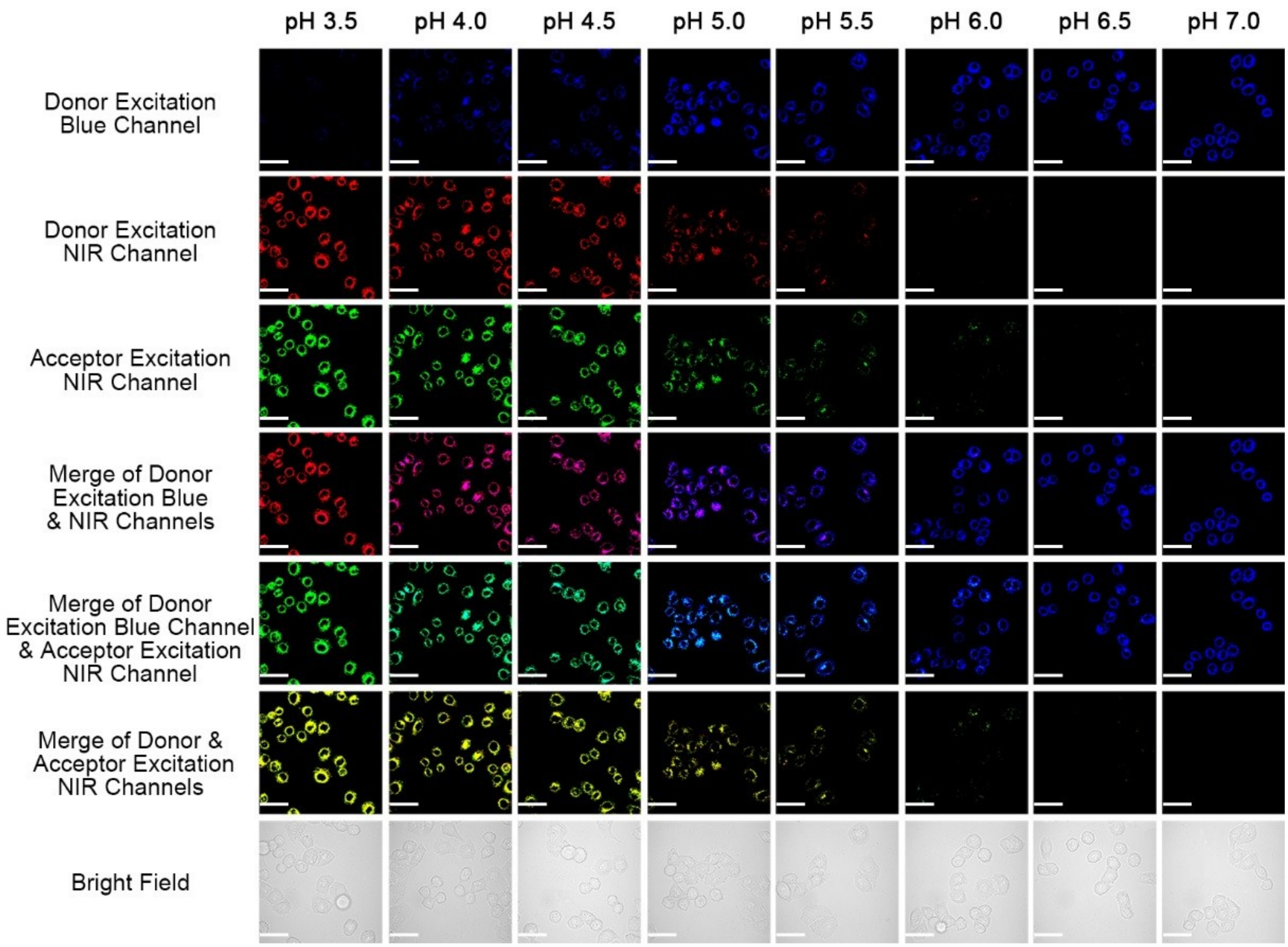


Figure S47: Cellular fluorescence images of 15 µM probes **B** incubated with HeLa cells in 10 mM citrate buffers having pH from 3.5 to 7.0 in the presence of 5 µg/mL nigericin. The blue channel in the first row was obtained from 475 to 525 nm, and two NIR channels (pseudo-colored as red and green for clarity) in the second and third rows were obtained from 650 to 700 nm under excitation of TPE donor and rhodamine acceptor at 405 nm and 559 nm, respectively. Confocal fluorescence microscope was employed to obtain fluorescence images at 60× magnification with scale bars of 50 µM.

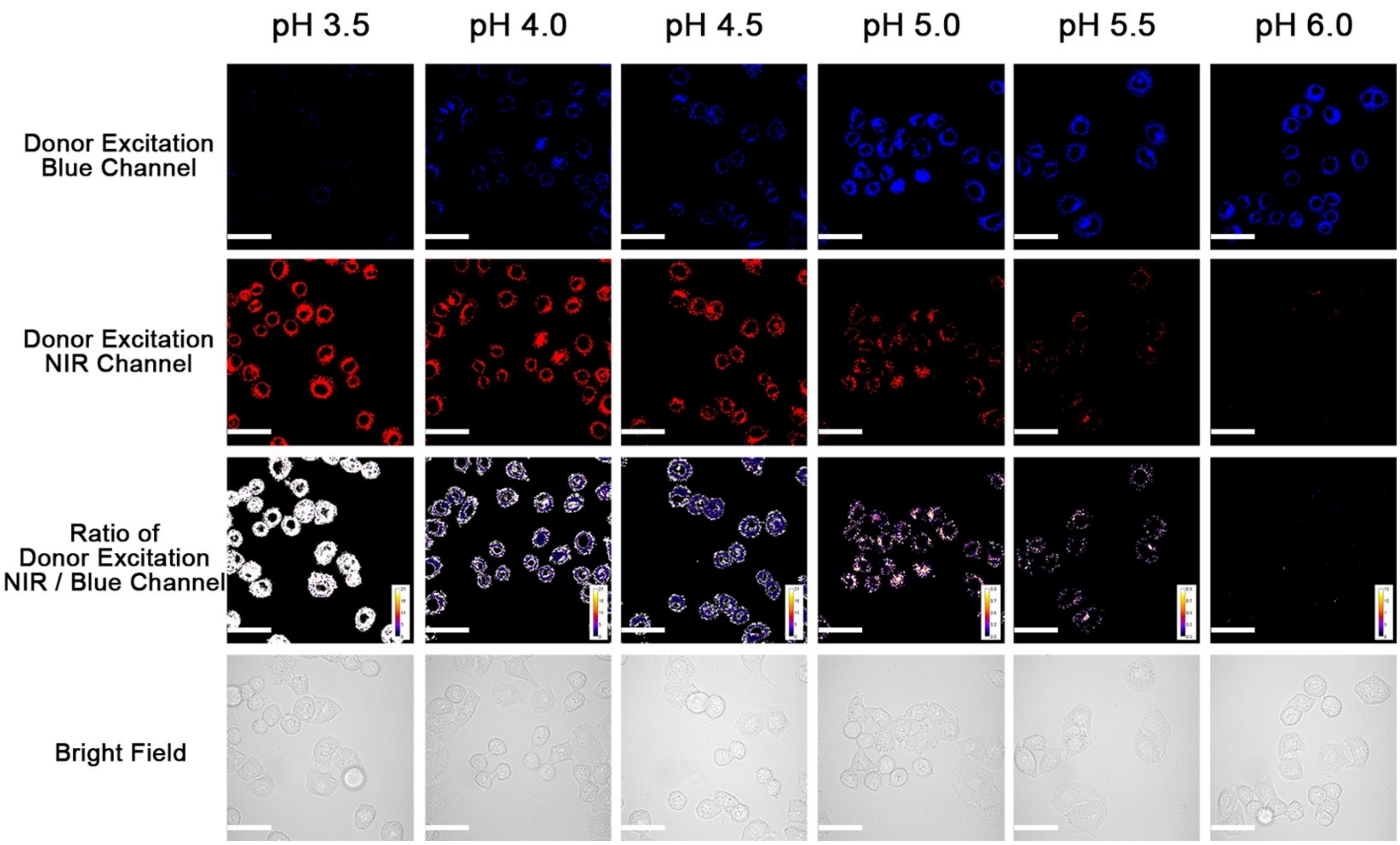


Figure S48: Cellular fluorescence images of 15 μM probes **B** incubated with HeLa cells in 10 mM citrate buffers having pH from 3.5 to 7.0 in the presence of 5 μg/mL nigericin. The blue channel in the first row was obtained from 475 to 525 nm, and NIR channel (pseudo-colored as red for clarity) in the second row were obtained from 650 to 700 nm under excitation of TPE donor at 405 nm. Confocal fluorescence microscope was employed to obtain fluorescence images at 60× magnification with scale bars of 50 μM. Ratiometric images (red channel/blue channel) in the third row.

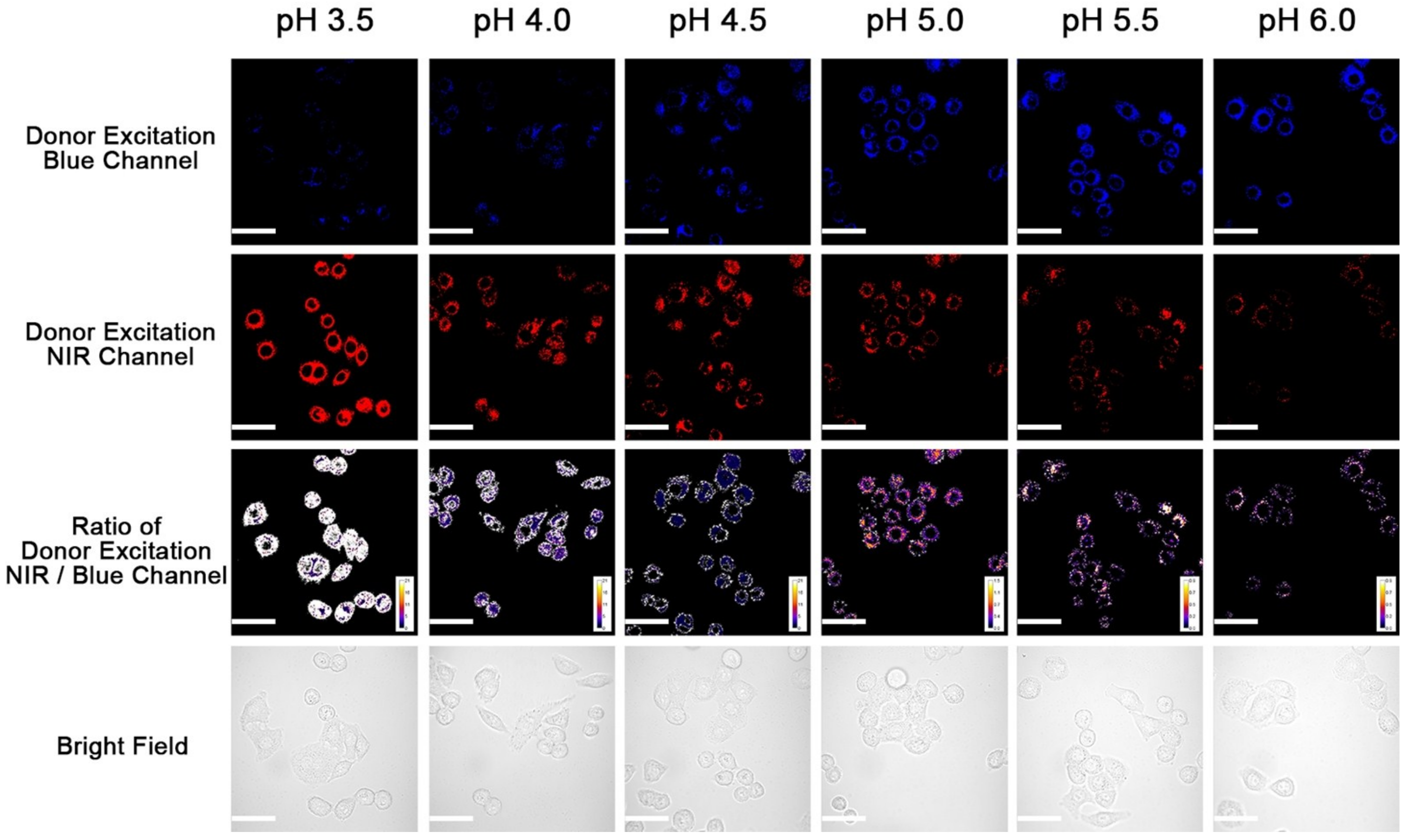


Figure S49: Cellular fluorescence images of 15 µM probes **C** incubated with HeLa cells in 10 mM citrate buffers having pH from 3.5 to 7.0 in the presence of 5 µg/mL nigericin. The blue channel in the first row was obtained from 475 to 525 nm, and NIR channel (pseudo-colored as red for clarity) in the second row were obtained from 650 to 700 nm under excitation of TPE donor at 405 nm. Confocal fluorescence microscope was employed to obtain fluorescence images at 60× magnification with scale bars of 50 µM. Ratiometric images (red channel/blue channel) in the third row.

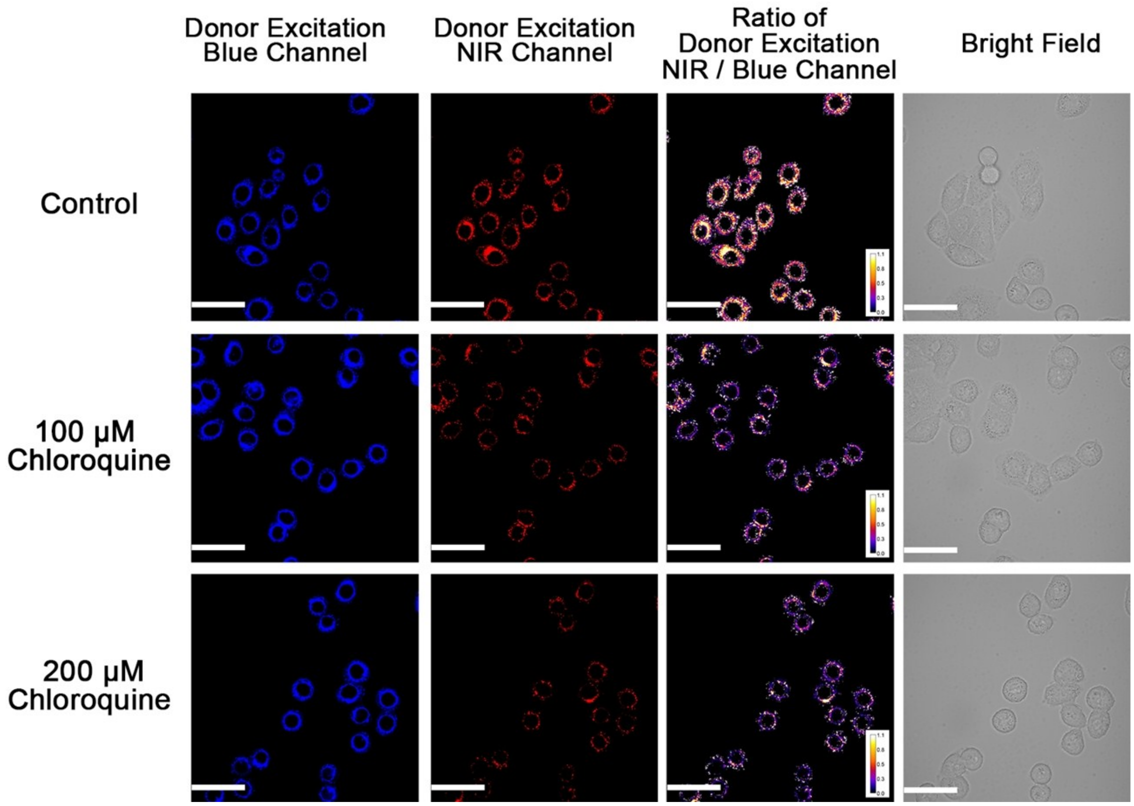


Figure S50: Cellular fluorescence images of 20 μM probes **C** incubated with HeLa cells in 10 mM citrate buffers with pH 7.4 in the absence and in the presence of 100 and 200 μM chloroquine. The blue channel in the first column was obtained from 475 to 525 nm, and NIR channel (pseudo-colored as red for clarity) in the second column was got from 650 to 700 nm under excitation of TPE donor at 405 nm. Confocal fluorescence microscope was used to acquire the images at 60× magnification with scale bars of 50 μM. Ratiometric images (red channel/blue channel) in the third row.

15. PROBE RATIOMETRIC FLUORESCENCE RESPONSES TO INTRACELLULAR pH CHANGES

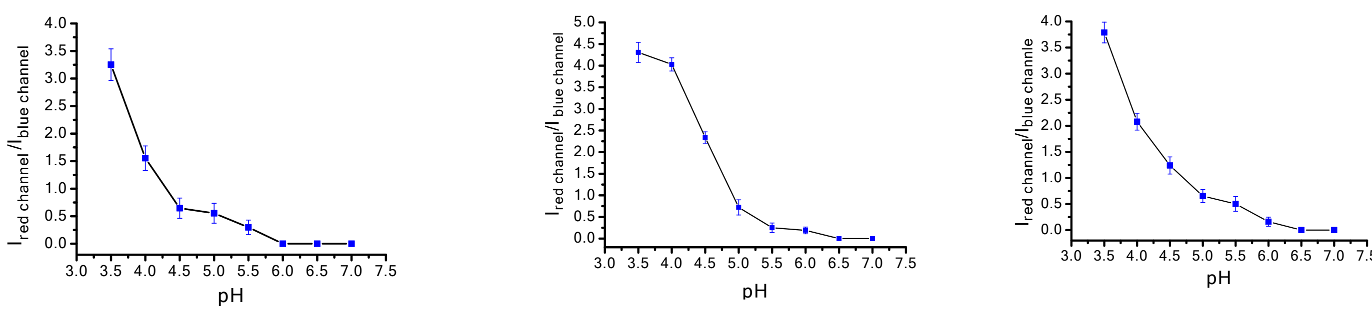


Figure S51. Cellular fluorescence ratio responses of TPE donor to rhodamine acceptor in probes **A** (left), **B** (middle), and **C** (left) to pH changes in 10 mM citrate buffers with pH ranging from 3.5 to 7.0 containing 5 μg/mL nigericin under TPE excitation at 405 nm. The fluorescence ratios of probes **A**, **B**, and **C** in HeLa live cells were obtained through statistical analysis of the confocal imaging data in Figures $45, S47, and 6.

16. RESULTS OF THEORETICAL CALCULATIONS

Probe A

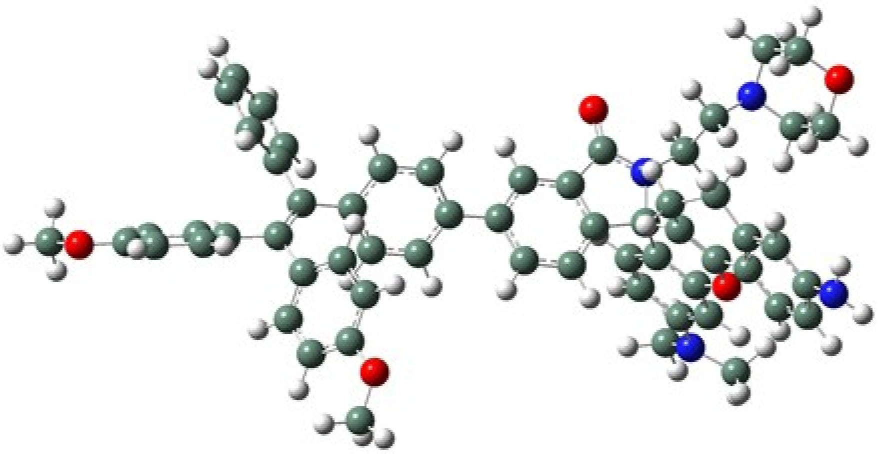


Figure S52. GaussView representation of Probe A**.**

Table S1. Computational results for Probe A.

a (Optimization completed)		
/home/rluck/calculation/liu/tbt/superior/a.log		
File Type	.log	
Calculation Type	FREQ	
Calculation Method	RTPSSh	
Basis Set	TZVP	
Charge	0	
Spin	Singlet	
Solvation	scrf=solvent=water	
E(RTPSSh)	-2916.356993	Hartree
RMS Gradient Norm	0.000002	Hartree/Bohr
Imaginary Freq		
Dipole Moment	9.117061	Debye
Point Group	C1	
Job cpu time:	10 days 21 hours 41 minutes 5...	

Table S2. Calculated atomic coordinates for Probe A.

Row	Symbol	X	Y	Z
1	C	4.3909	-1.20242	4.159996
2	C	5.461523	-0.3412	4.515407
3	C	5.990225	0.483428	3.506905
4	C	5.451107	0.462108	2.223026
5	C	4.392679	-0.36943	1.866113
6	C	3.883864	-1.19819	2.875052
7	N	5.952318	-0.30237	5.802477
8	C	5.55878	-1.33593	6.752717
9	C	7.183815	0.427679	6.072388
10	C	3.849439	-0.41155	0.453747
11	C	2.333162	-0.26581	0.402523
12	C	1.746559	-1.40707	-0.13031
13	C	0.371738	-1.52688	-0.27984
14	C	-0.44694	-0.45864	0.113484
15	C	0.161361	0.696302	0.646306
16	C	1.541581	0.804812	0.795139
17	C	2.811739	-2.39177	-0.44306
18	O	6.045239	1.323736	1.329598
19	C	5.530349	1.402334	0.054623
20	C	4.530809	0.625429	-0.4065
21	C	6.150071	2.464787	-0.73862
22	C	5.900914	2.506155	-2.12507
23	C	5.096266	1.388615	-2.74304
24	C	4.004331	0.87707	-1.80077
25	O	2.681624	-3.5363	-0.88504
26	N	3.996241	-1.7904	-0.12772
27	C	-1.91904	-0.538	-0.02502
28	C	6.962147	3.453873	-0.16885
29	C	7.511411	4.464888	-0.94393
30	C	7.261104	4.516969	-2.32485
31	C	6.448747	3.521084	-2.89607
32	C	-2.77078	0.077594	0.905373
33	C	-4.15058	0.003102	0.774988
34	C	-4.74454	-0.69122	-0.28976
35	C	-3.89234	-1.32616	-1.20617
36	C	-2.51164	-1.24233	-1.08389
37	C	-6.22173	-0.80948	-0.41063
38	C	-6.71997	-2.18126	-0.71071
39	C	-7.06048	0.258573	-0.25931
40	C	-8.52689	0.098809	-0.07901
41	C	-6.57265	1.662382	-0.26736
42	C	-7.63876	-2.40677	-1.74651
43	C	-8.07448	-3.69344	-2.04842
44	C	-7.60212	-4.78459	-1.31943
45	C	-6.68009	-4.57705	-0.29418
46	C	-6.23569	-3.29078	-0.00139
47	C	-9.4352	0.906448	-0.78572
48	C	-10.8034	0.774979	-0.61494
49	C	-11.3111	-0.16008	0.296424
50	C	-10.4273	-0.95557	1.031127
51	C	-9.05498	-0.81974	0.834556
52	C	-5.67377	2.120361	-1.24622
53	C	-5.24317	3.436114	-1.27238
54	C	-5.69739	4.3442	-0.30699
55	C	-6.60096	3.916383	0.669828
56	C	-7.03527	2.592616	0.670368
57	O	-5.21519	5.61707	-0.40792
58	O	-12.6707	-0.21418	0.405009
59	C	-13.228	-1.15995	1.325917
60	C	-5.66313	6.577275	0.556751
61	N	7.745245	5.563783	-3.09856
62	C	5.262894	-2.5066	-0.16234
63	C	5.913755	-2.51658	-1.55253
64	N	7.149781	-3.30738	-1.52378
65	C	7.491947	-3.93555	-2.80898
66	C	8.096711	-2.95703	-3.81167
67	O	9.259826	-2.32496	-3.25612
68	C	8.919984	-1.62063	-2.05281
69	C	8.32028	-2.5696	-1.01715
70	H	3.960278	-1.87265	4.890981
71	H	6.817958	1.153094	3.694727
72	H	3.066669	-1.87096	2.634545
73	H	5.887127	-2.33714	6.443441

74	H	6.007815	-1.10543	7.717076	100	H	-10.7911	-1.67077	1.757394
75	H	4.474305	-1.35014	6.882732	101	H	-8.3802	-1.43821	1.415124
76	H	7.079592	1.477599	5.787597	102	H	-5.31852	1.432026	-2.00439
77	H	7.383187	0.388347	7.141735	103	H	-4.55967	3.782396	-2.03937
78	H	8.046042	0.00599	5.538082	104	H	-6.9726	4.597832	1.424056
79	H	-0.05533	-2.44262	-0.67279	105	H	-7.74179	2.276173	1.429996
80	H	-0.46373	1.534809	0.93193	106	H	-14.3063	-1.042	1.246631
81	H	1.978595	1.709402	1.20385	107	H	-12.9472	-2.18173	1.055394
82	H	5.781751	0.562838	-2.97458	108	H	-12.9077	-0.94549	2.349393
83	H	4.661043	1.711767	-3.69153	109	H	-5.16278	7.506952	0.295408
84	H	3.182253	1.604106	-1.75462	110	H	-6.74688	6.712634	0.500198
85	H	3.578695	-0.04596	-2.20424	111	H	-5.37867	6.276824	1.56908
86	H	7.162191	3.431784	0.895482	112	H	7.824235	5.379021	-4.08925
87	H	8.135261	5.223242	-0.48212	113	H	8.558183	6.040653	-2.73322
88	H	6.251973	3.544008	-3.96423	114	H	5.92023	-2.04042	0.574591
89	H	-2.3495	0.595482	1.760177	115	H	5.080071	-3.53781	0.147355
90	H	-4.7826	0.474062	1.518864	116	H	5.224101	-2.99251	-2.25251
91	H	-4.31938	-1.87729	-2.03694	117	H	6.061091	-1.4816	-1.8901
92	H	-1.8857	-1.71463	-1.83324	118	H	8.224739	-4.72528	-2.60893
93	H	-8.00543	-1.5636	-2.3208	119	H	6.596976	-4.40378	-3.22635
94	H	-8.7792	-3.84548	-2.85902	120	H	8.431005	-3.4748	-4.7126
95	H	-7.94292	-5.78716	-1.55339	121	H	7.365231	-2.18798	-4.09892
96	H	-6.30355	-5.41905	0.276788	122	H	9.847502	-1.17949	-1.68353
97	H	-5.51301	-3.13971	0.793374	123	H	8.220379	-0.80804	-2.29407
98	H	-9.0593	1.639778	-1.49077	124	H	9.080558	-3.30378	-0.73001
99	H	-11.4963	1.391193	-1.17661	125	H	8.041502	-2.01347	-0.11903

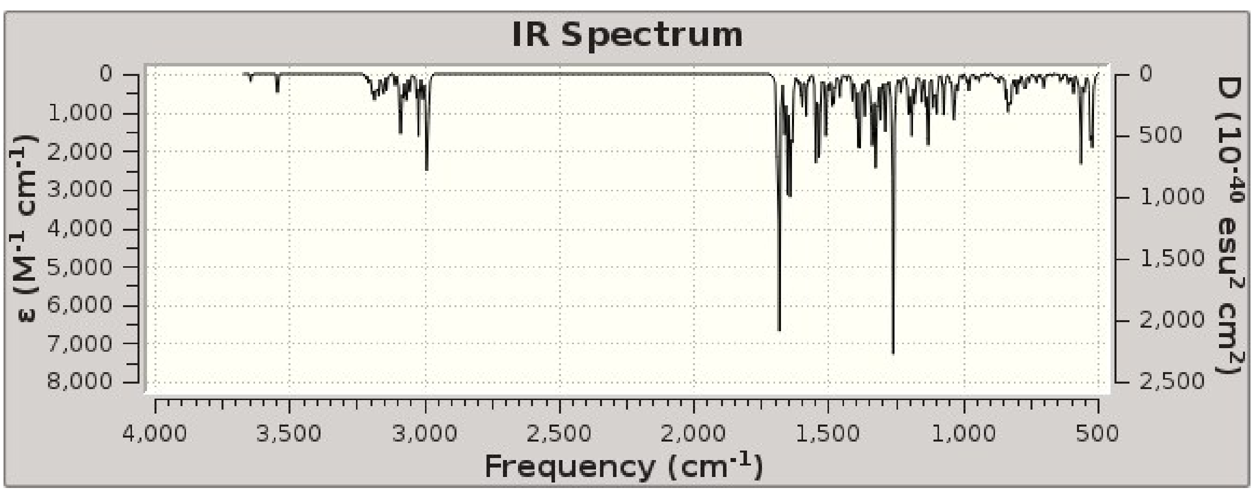


Figure S53. **Calculated IR spectrum for probe** A.

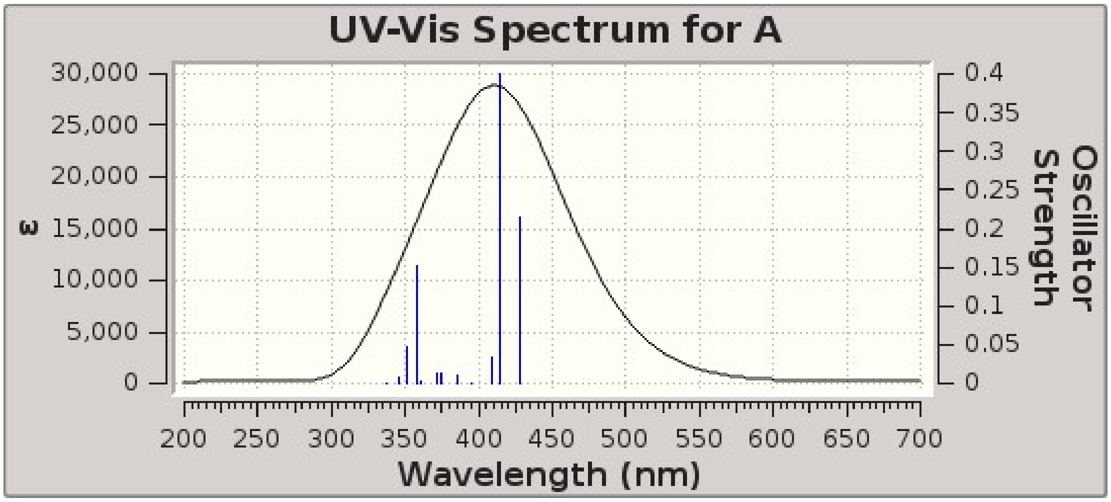


Figure S54. Calculated UV-Vis spectrum for probe **A**.

Table S3. Excitation energies and oscillator strengths listing for probe A.

Excitation energies and oscillator strengths:

```
 Excited State   1:      Singlet-A      2.8945 eV  428.35 nm  f=0.2150  <S**2>=0.000
     241 -> 243        -0.12251
     242 -> 243         0.69228
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -2916.25062318
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      2.9948 eV  414.00 nm  f=0.3996  <S**2>=0.000
     240 -> 243         0.13591
     241 -> 243         0.67602
     242 -> 243         0.11861

 Excited State   3:      Singlet-A      3.0338 eV  408.67 nm  f=0.0350  <S**2>=0.000
     240 -> 243         0.68595
     241 -> 243        -0.13329

 Excited State   4:      Singlet-A      3.1332 eV  395.72 nm  f=0.0006  <S**2>=0.000
     239 -> 243         0.70267

 Excited State   5:      Singlet-A      3.2140 eV  385.77 nm  f=0.0100  <S**2>=0.000
     241 -> 244        -0.20476
     242 -> 244         0.66972

 Excited State   6:      Singlet-A      3.3123 eV  374.31 nm  f=0.0136  <S**2>=0.000
     240 -> 244         0.44997
     241 -> 244         0.50511
```

242 -> 244 0.16993

Excited State 7: Singlet-A 3.3399 eV 371.22 nm f=0.0141 <S**2>=0.000
240 -> 244 0.53082
241 -> 244 -0.44007
242 -> 244 -0.11705

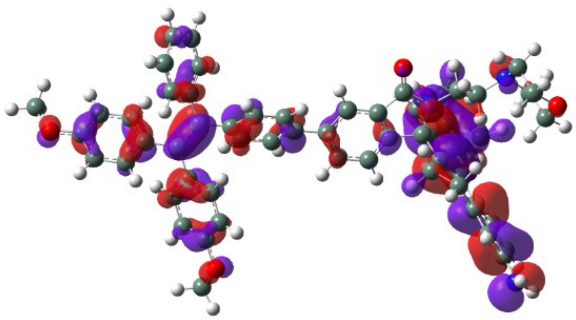
Excited State 8: Singlet-A 3.4400 eV 360.42 nm f=0.0035 <S**2>=0.000
239 -> 244 0.70041

Excited State 9: Singlet-A 3.4600 eV 358.33 nm f=0.1515 <S**2>=0.000
242 -> 245 0.68980

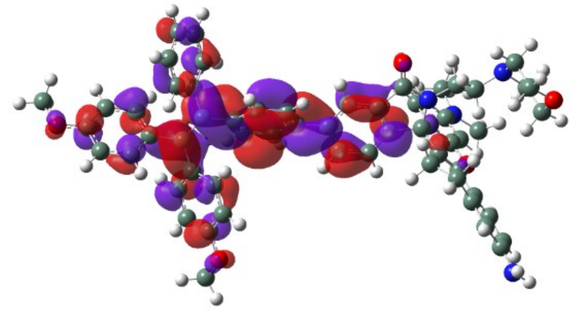
Excited State 10: Singlet-A 3.5332 eV 350.91 nm f=0.0466 <S**2>=0.000
241 -> 245 0.68529

Excited State 11: Singlet-A 3.5891 eV 345.44 nm f=0.0076 <S**2>=0.000
240 -> 245 0.67766
242 -> 246 0.13444

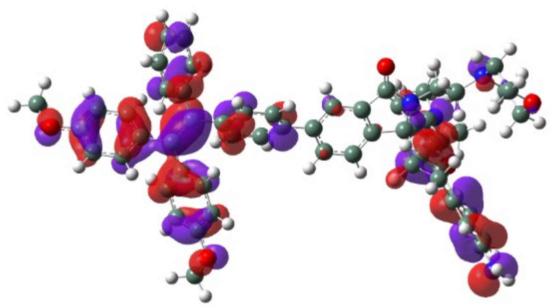
Excited State 12: Singlet-A 3.6731 eV 337.55 nm f=0.0007 <S**2>=0.000
239 -> 245 0.67299
239 -> 246 0.12757
242 -> 246 0.14200



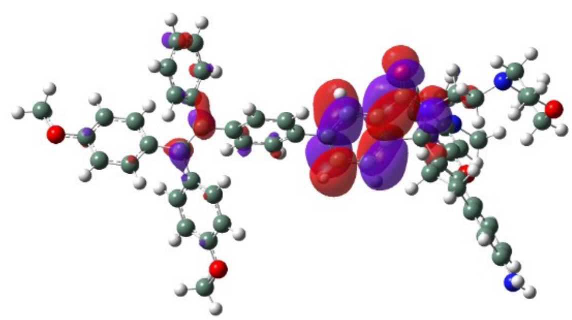
a-242 HOMO



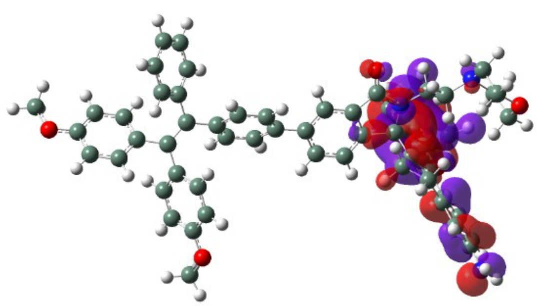
a-243 LUMO



a-241 HOMO-1



a-244 LUMO+1



a-240 HOMO-2

Figure S55. Drawings of the highest occupied and lowest unoccupied orbitals for probe **A**.

Probe AH⁺

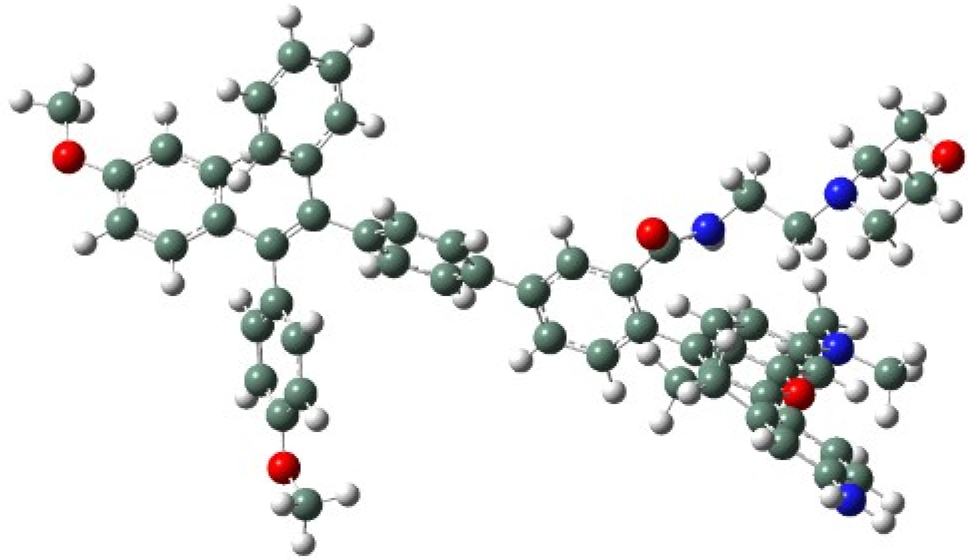


Figure S56. GaussView representation of probe AH⁺.

Table S4. Computational results for Probe AH⁺.

ah (Optimization completed)		
/home/rluck/calculation/liu/tbt/superior/ah.log		
File Type	.log	
Calculation Type	SP	
Calculation Method	RTPSSh	
Basis Set	TZVP	
Charge	1	
Spin	Singlet	
Solvation	scrf=solvent=water	
E(RTPSSh)	-2916.822560	Hartree
RMS Gradient Norm	0.000002	Hartree/Bohr
Imaginary Freq		
Dipole Moment	31.332553	Debye
Point Group	C1	
Job cpu time:	11 days 12 hours 43 minutes 1...	

Table S5. Calculated atomic coordinates for Probe AH+.

Row	Symbol	X	Y	Z
1	C	-4.33857	-1.1402	4.072765
2	C	-5.71452	-1.53456	4.088447
3	C	-6.35422	-1.75287	2.847251
4	C	-5.63934	-1.58576	1.682004
5	C	-4.2753	-1.21235	1.641254
6	C	-3.656	-0.98536	2.896357
7	N	-6.37906	-1.68965	5.257679
8	C	-7.78325	-2.09427	5.255152
9	C	-5.71174	-1.44702	6.537021
10	C	-3.64076	-1.06699	0.380845
11	C	-2.19223	-0.72501	0.320362
12	C	-1.72034	0.513319	-0.1502
13	C	-0.34802	0.736609	-0.25967
14	C	0.590273	-0.23212	0.113602
15	C	0.106695	-1.4576	0.595122
16	C	-1.25616	-1.69839	0.691428
17	C	-2.62757	1.643318	-0.56602
18	O	-6.32098	-1.78903	0.512723
19	C	-5.71614	-1.66974	-0.68653
20	C	-4.36389	-1.31188	-0.7866
21	C	-6.54078	-1.95987	-1.81298
22	C	-6.0728	-1.61305	-3.10969
23	C	-4.76274	-0.87872	-3.23309
24	C	-3.76039	-1.33416	-2.17173
25	O	-2.49439	2.191709	-1.66422
26	N	-3.54544	2.024953	0.351055
27	C	2.042035	0.030597	0.00528
28	C	-7.81088	-2.56789	-1.68102
29	C	-8.58187	-2.84267	-2.78218
30	C	-8.1155	-2.51058	-4.08034
31	C	-6.85109	-1.88937	-4.21238
32	C	2.947383	-0.51536	0.92836
33	C	4.30944	-0.26951	0.827555
34	C	4.829936	0.531132	-0.2008
35	C	3.920682	1.09314	-1.11021
36	C	2.558625	0.841438	-1.01611
37	C	6.282604	0.834103	-0.29132
38	C	6.61001	2.265564	-0.54554
39	C	7.246375	-0.12481	-0.157
40	C	8.679865	0.209668	0.045927
41	C	6.93823	-1.57764	-0.20882
42	C	7.495358	2.6336	-1.56932
43	C	7.771323	3.972762	-1.8286
44	C	7.169055	4.974464	-1.06777
45	C	6.278433	4.623848	-0.05372
46	C	5.993813	3.284454	0.19642
47	C	9.686599	-0.46688	-0.66514
48	C	11.02694	-0.17474	-0.47412
49	C	11.408	0.794865	0.462447
50	C	10.42674	1.461817	1.201622
51	C	9.083224	1.165582	0.984619
52	C	7.495411	-2.4678	0.726005
53	C	7.225707	-3.82548	0.680025
54	C	6.403092	-4.34448	-0.32827
55	C	5.860452	-3.48324	-1.28634
56	C	6.130467	-2.11865	-1.21482
57	O	6.199555	-5.69368	-0.29973
58	O	12.74969	1.010123	0.589982
59	C	13.17891	1.995534	1.537642
60	C	5.362723	-6.26265	-1.31425
61	N	-8.86518	-2.7862	-5.16991
62	C	-4.4933	3.113553	0.136515
63	C	-5.90721	2.588958	-0.14269
64	N	-6.8576	3.685667	-0.33513
65	C	-7.26851	4.299554	0.93405
66	C	-8.21934	5.455725	0.664775
67	O	-9.37737	5.021708	-0.0558
68	C	-8.98484	4.418283	-1.29368
69	C	-8.05252	3.239529	-1.06195
70	H	-3.82258	-0.95741	5.004657
71	H	-7.39362	-2.04007	2.782022
72	H	-2.61469	-0.68867	2.92002
73	H	-8.12205	-2.17785	6.284174
74	H	-8.40467	-1.35458	4.741346
75	H	-7.90947	-3.06463	4.766174
76	H	-6.42758	-1.62483	7.334966
77	H	-5.36054	-0.41404	6.609549
78	H	-0.01389	1.703686	-0.61676
79	H	0.801148	-2.24328	0.868791
80	H	-1.6057	-2.6658	1.034118
81	H	-4.95439	0.194852	-3.11472

82	H	-4.34353	-1.01912	-4.23078	105	H	5.709457	-1.46221	-1.96776
83	H	-3.44436	-2.36258	-2.3876	106	H	14.26443	2.008931	1.471521
84	H	-2.86687	-0.7127	-2.20908	107	H	12.78096	2.981954	1.283508
85	H	-3.53935	1.569151	1.252528	108	H	12.87431	1.72218	2.551803
86	H	-8.17289	-2.83431	-0.69592	109	H	5.329942	-7.32845	-1.09992
87	H	-9.54775	-3.32149	-2.66893	110	H	4.352998	-5.84513	-1.26802
88	H	-6.49602	-1.62064	-5.20195	111	H	5.78713	-6.0992	-2.30881
89	H	2.579129	-1.11353	1.75477	112	H	-8.54977	-2.54542	-6.09587
90	H	4.982797	-0.68854	1.566072	113	H	-9.77195	-3.21683	-5.08552
91	H	4.290126	1.722133	-1.91263	114	H	-4.47765	3.752585	1.020975
92	H	1.891165	1.26416	-1.75914	115	H	-4.13887	3.691322	-0.71585
93	H	7.962468	1.859886	-2.16802	116	H	-6.2236	1.91381	0.670894
94	H	8.453082	4.235178	-2.63055	117	H	-5.88116	2.001063	-1.06311
95	H	7.385455	6.017985	-1.26838	118	H	-7.76389	3.560185	1.588497
96	H	5.80206	5.395195	0.541933	119	H	-6.39085	4.681419	1.46015
97	H	5.294703	3.021403	0.98308	120	H	-7.70126	6.236783	0.091398
98	H	9.409409	-1.22507	-1.38937	121	H	-8.58072	5.880882	1.601844
99	H	11.79525	-0.69051	-1.0389	122	H	-8.48713	5.167158	-1.92514
100	H	10.69387	2.200089	1.946648	123	H	-9.90336	4.0917	-1.78278
101	H	8.332648	1.685348	1.568829	124	H	-8.59214	2.451501	-0.50724
102	H	8.139393	-2.08337	1.509408	125	H	-7.74531	2.826732	-2.02662
103	H	7.646745	-4.50211	1.414991	126	H	-4.86359	-2.12338	6.674356
104	H	5.239874	-3.86018	-2.08899					

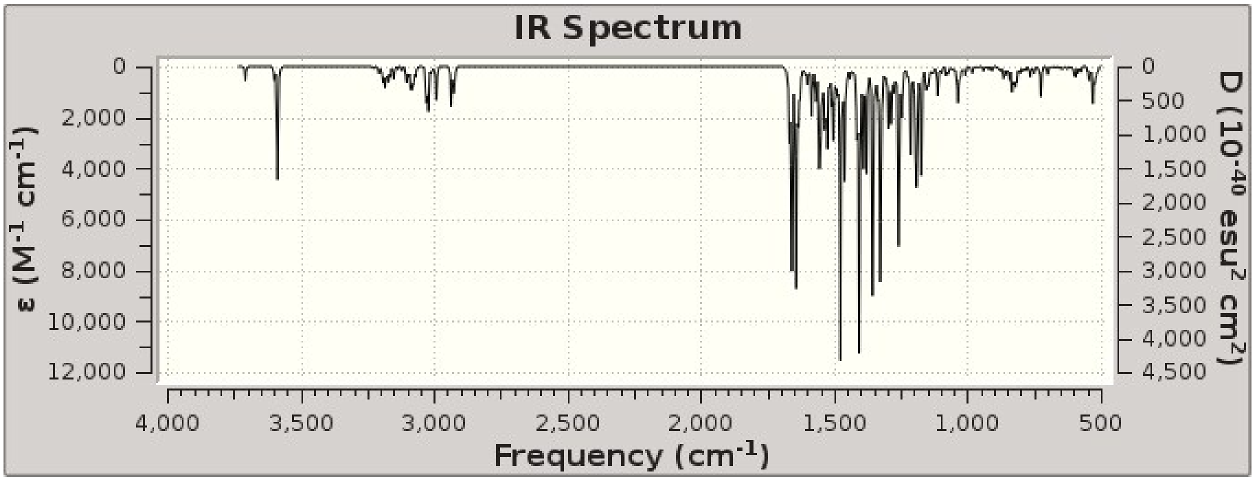


Figure S56. Calculated IR spectrum for probe AH⁺.

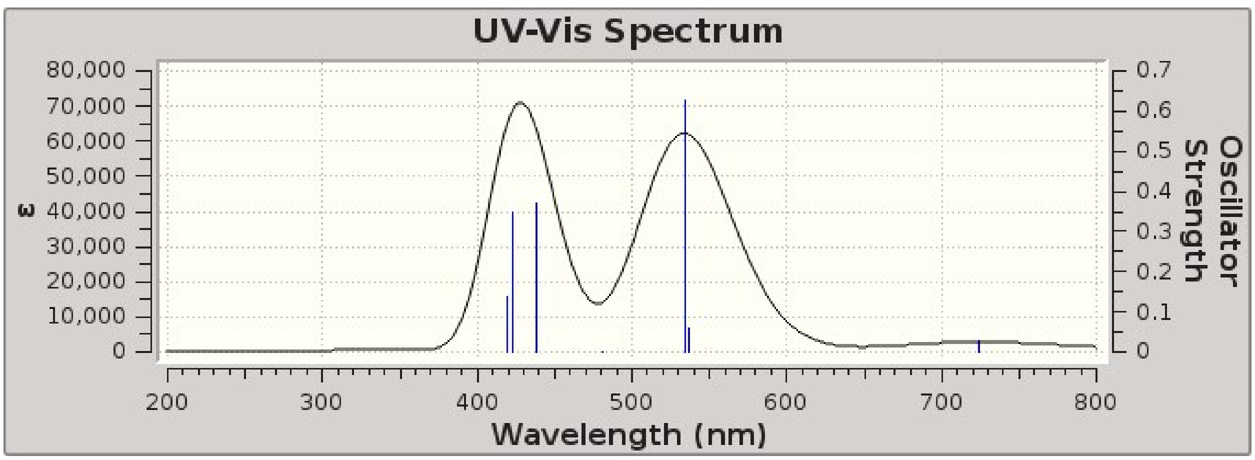
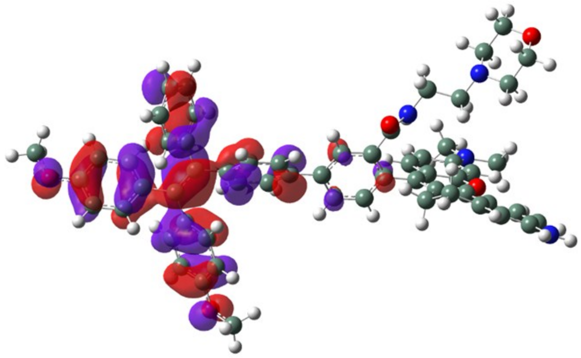
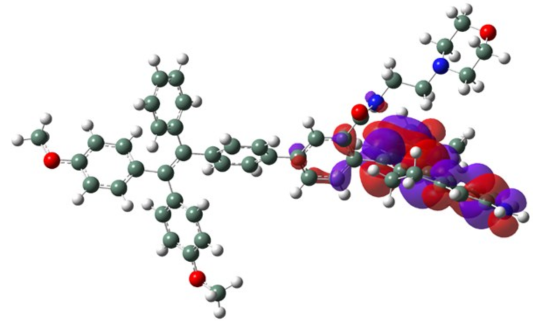
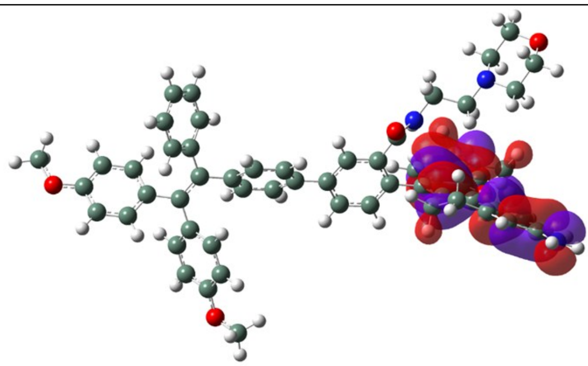
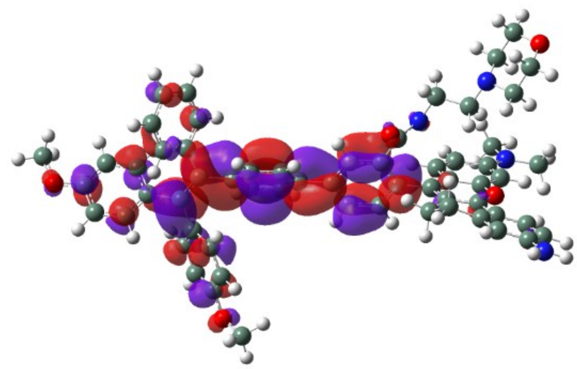
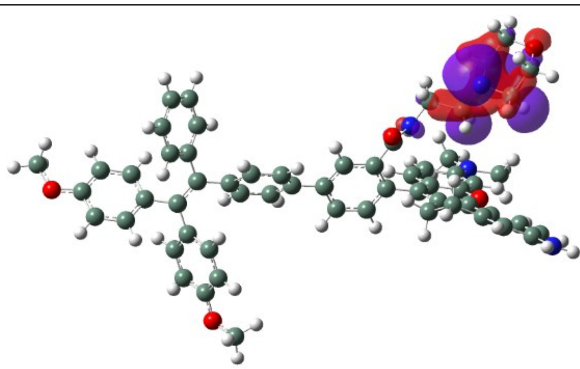
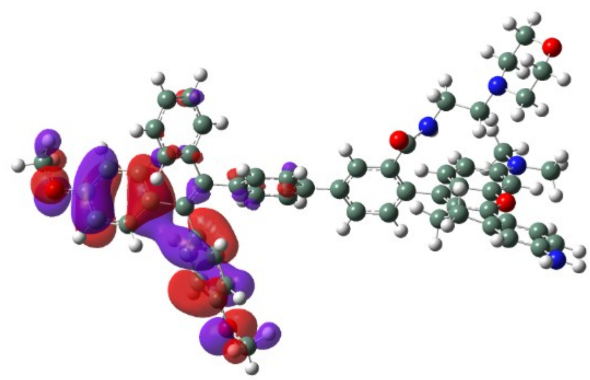


Figure S58. Calculated UV-Vis spectrum for probe AH⁺.

Table S6. Excitation energies and oscillator strengths listing for Probe AH^+.

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      1.7116 eV  724.39 nm  f=0.0259  <S**2>=0.000
    242 -> 243         0.70674
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -2916.75966126
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      2.3081 eV  537.17 nm  f=0.0593  <S**2>=0.000
    240 -> 243         0.67418
    241 -> 243         0.21064

 Excited State   3:      Singlet-A      2.3219 eV  533.98 nm  f=0.6285  <S**2>=0.000
    240 -> 243        -0.21284
    241 -> 243         0.66653

 Excited State   4:      Singlet-A      2.5764 eV  481.23 nm  f=0.0013  <S**2>=0.000
    239 -> 243         0.70672

 Excited State   5:      Singlet-A      2.8321 eV  437.78 nm  f=0.3725  <S**2>=0.000
    237 -> 243        -0.43324
    238 -> 243         0.50562
    242 -> 244        -0.19134

 Excited State   6:      Singlet-A      2.9307 eV  423.05 nm  f=0.3465  <S**2>=0.000
    237 -> 243        -0.40762
    238 -> 243        -0.12997
    242 -> 244         0.55416

 Excited State   7:      Singlet-A      2.9582 eV  419.13 nm  f=0.1376  <S**2>=0.000
    237 -> 243         0.36859
    238 -> 243         0.42430
    241 -> 245         0.10876
    242 -> 244         0.38404
```

 AH^{+}-242 HOMO	 AH^{+}-243 LUMO
 AH^{+}-241 HOMO-1	 AH^{+}-244 LUMO+1
 AH^{+}-240 HOMO-2	 AH^{+}-239 HOMO-3

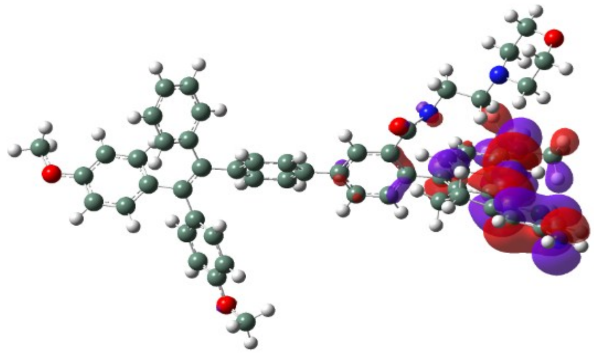
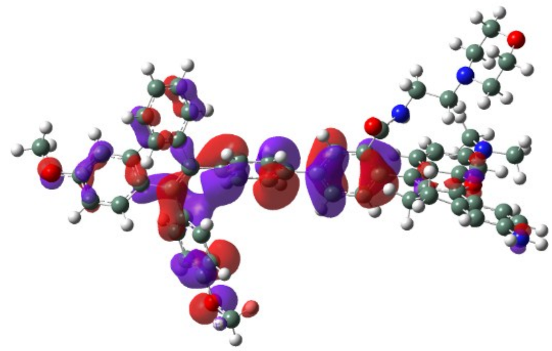
 AH⁺-238 HOMO-4	 AH⁺-237 HOMO-4

Figure S59. Drawings of the highest occupied and lowest unoccupied orbitals for probe AH^+.

Probe B

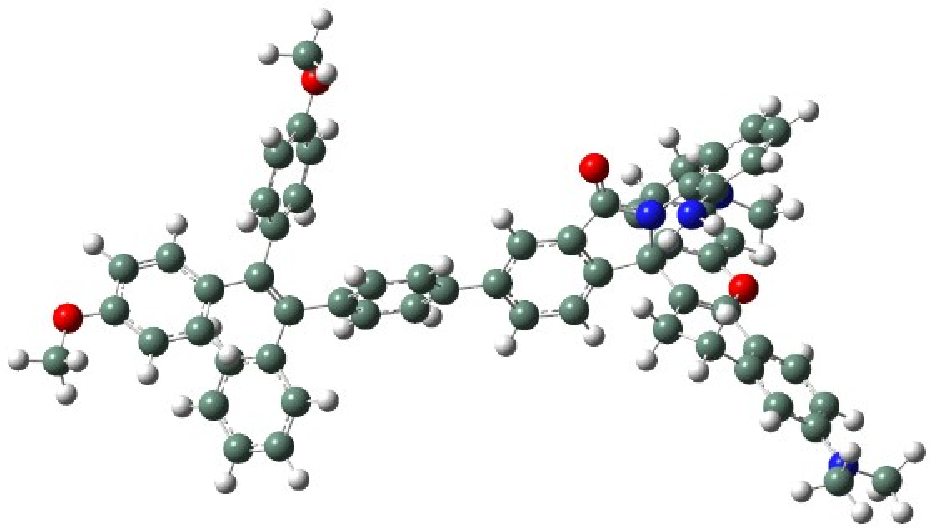


Figure S60. GaussView representation of probe B.

Table S7. Computational results for Probe B.

b (Optimization completed)		
/home/rluck/calculation/liu/tbt/superior/b.log		
File Type	.log	
Calculation Type	SP	
Calculation Method	RTPSSh	
Basis Set	TZVP	
Charge	0	
Spin	Singlet	
Solvation	scrf=solvent=water	
E(RTPSSh)	-2916.154120	Hartree
RMS Gradient Norm	0.000002	Hartree/Bohr
Imaginary Freq		
Dipole Moment	9.592948	Debye
Point Group	C1	
Job cpu time:	11 days 22 hours 13 minutes 5...	

Table S8. Calculated atomic coordinates for probe B.

Row	Symbol	X	Y	Z
1	C	4.388261	-2.92305	3.055563
2	C	5.730366	-2.64137	3.422316
3	C	6.396993	-1.63034	2.707441
4	C	5.762037	-0.97562	1.65598
5	C	4.45759	-1.26726	1.264322
6	C	3.789959	-2.25025	2.007815
7	N	6.355888	-3.33335	4.435153
8	C	5.569889	-4.19046	5.31463
9	C	7.652204	-2.87552	4.916949
10	C	3.826282	-0.59487	0.066447
11	C	2.367387	-0.24356	0.312077
12	C	1.527755	-0.94929	-0.53932
13	C	0.147066	-0.80797	-0.49747
14	C	-0.41422	0.082067	0.428442
15	C	0.448971	0.794229	1.286127
16	C	1.831689	0.639172	1.240706
17	C	2.34127	-1.82837	-1.41283
18	O	6.51238	-0.00338	1.036158
19	C	5.887511	0.81483	0.122075
20	C	4.642469	0.599562	-0.35053
21	C	6.694436	1.97585	-0.24646
22	C	6.294084	2.756282	-1.34894
23	C	5.106859	2.291366	-2.15773
24	C	4.043226	1.638024	-1.27238
25	O	1.940839	-2.62772	-2.25691
26	N	3.656901	-1.57773	-1.09627
27	C	4.748394	-2.26798	-1.70735
28	C	-1.88053	0.27325	0.504173
29	C	7.845837	2.355731	0.454542
30	C	8.577584	3.475741	0.09212
31	C	8.173239	4.283367	-0.99584
32	C	7.020313	3.879774	-1.71158
33	N	8.863321	5.424736	-1.33859
34	C	8.552116	6.108518	-2.58732
35	C	10.15481	5.696289	-0.72052
36	C	5.126131	-1.95021	-3.03069
37	C	5.435248	-3.26116	-1.00585
38	C	6.518709	-3.92421	-1.57306
39	C	6.909436	-3.59624	-2.87175
40	C	6.221156	-2.63019	-3.59127
41	N	4.402075	-1.04945	-3.79486
42	C	-2.67935	0.202857	-0.64771
43	C	-4.0543	0.379525	-0.58013
44	C	-4.69551	0.636327	0.641252
45	C	-3.89322	0.728122	1.788845
46	C	-2.51884	0.540123	1.724617
47	C	-6.16191	0.870986	0.713853
48	C	-6.56951	2.044661	1.536379
49	C	-7.0684	0.071582	0.076458
50	C	-8.48946	0.46743	-0.1034
51	C	-6.70523	-1.2566	-0.48269
52	C	-7.56601	1.930132	2.517044
53	C	-7.91805	3.018784	3.309227
54	C	-7.28209	4.24809	3.137295
55	C	-6.28209	4.374072	2.173735
56	C	-5.92247	3.281062	1.390378
57	C	-9.531	-0.4452	0.1398
58	C	-10.8582	-0.09116	-0.038
59	C	-11.1881	1.19181	-0.49384
60	C	-10.1691	2.108127	-0.76883
61	C	-8.84086	1.738921	-0.56941
62	C	-5.95234	-2.1836	0.258795
63	C	-5.64006	-3.43269	-0.25063
64	C	-6.0699	-3.79687	-1.53348
65	C	-6.83044	-2.89748	-2.28599
66	C	-7.14818	-1.6513	-1.7503
67	O	-5.71028	-5.04438	-1.95438
68	O	-12.5197	1.449373	-0.64759
69	C	-12.8968	2.751948	-1.11054
70	C	-6.1372	-5.45602	-3.25887
71	H	3.818013	-3.66805	3.592934
72	H	7.406342	-1.33041	2.952599
73	H	2.766807	-2.49981	1.746013
74	H	5.055087	-4.96547	4.742114
75	H	6.247131	-4.68296	6.009978
76	H	4.823902	-3.62768	5.891171
77	H	7.602147	-1.87316	5.363441
78	H	8.009134	-3.57501	5.670576
79	H	8.380753	-2.85611	4.102559
80	H	-0.47952	-1.39468	-1.15965
81	H	0.024484	1.500546	1.990575

82	H	2.468167	1.203831	1.913078
83	H	5.461214	1.555049	-2.89087
84	H	4.678133	3.123541	-2.7208
85	H	3.535181	2.408315	-0.67631
86	H	3.265417	1.185403	-1.89506
87	H	8.175298	1.763041	1.299556
88	H	9.463062	3.726098	0.66072
89	H	6.68756	4.450117	-2.5698
90	H	8.749493	5.481883	-3.46731
91	H	7.504082	6.417249	-2.60984
92	H	9.16719	7.004014	-2.65357
93	H	10.05906	5.756205	0.366403
94	H	10.90318	4.92978	-0.9622
95	H	10.51448	6.658749	-1.07958
96	H	5.107133	-3.5083	-0.00433
97	H	7.042218	-4.69032	-1.01348
98	H	7.752381	-4.10052	-3.33189
99	H	6.520486	-2.39035	-4.60659
100	H	4.911558	-0.60047	-4.54326
101	H	3.81786	-0.40801	-3.27777
102	H	-2.21543	0.038667	-1.61429
103	H	-4.64278	0.337259	-1.48926
104	H	-4.35689	0.931916	2.74786
105	H	-1.93734	0.581985	2.639156
106	H	-8.05988	0.975743	2.660018
107	H	-8.68583	2.905485	4.067188
108	H	-7.55747	5.096935	3.753447
109	H	-5.77873	5.324762	2.033933
110	H	-5.13855	3.386595	0.648021
111	H	-9.29331	-1.44473	0.487093
112	H	-11.655	-0.79689	0.167849
113	H	-10.3941	3.098717	-1.14227
114	H	-8.05992	2.456701	-0.79247
115	H	-5.61862	-1.92024	1.255819
116	H	-5.06968	-4.14506	0.334642
117	H	-7.18066	-3.15475	-3.27718
118	H	-7.7448	-0.96615	-2.34272
119	H	-13.9836	2.742378	-1.1519
120	H	-12.5602	3.526703	-0.41591
121	H	-12.4913	2.945606	-2.1076
122	H	-5.74594	-6.46253	-3.38844
123	H	-7.22862	-5.47257	-3.32653
124	H	-5.72716	-4.79835	-4.03044

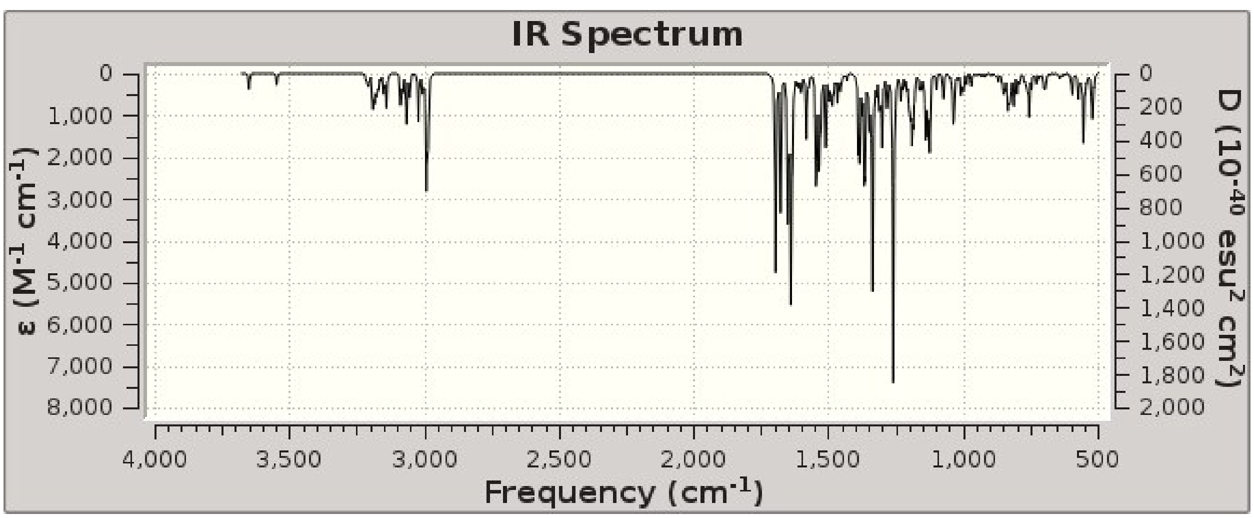


Figure S61. Calculated IR spectrum for probe **B.**

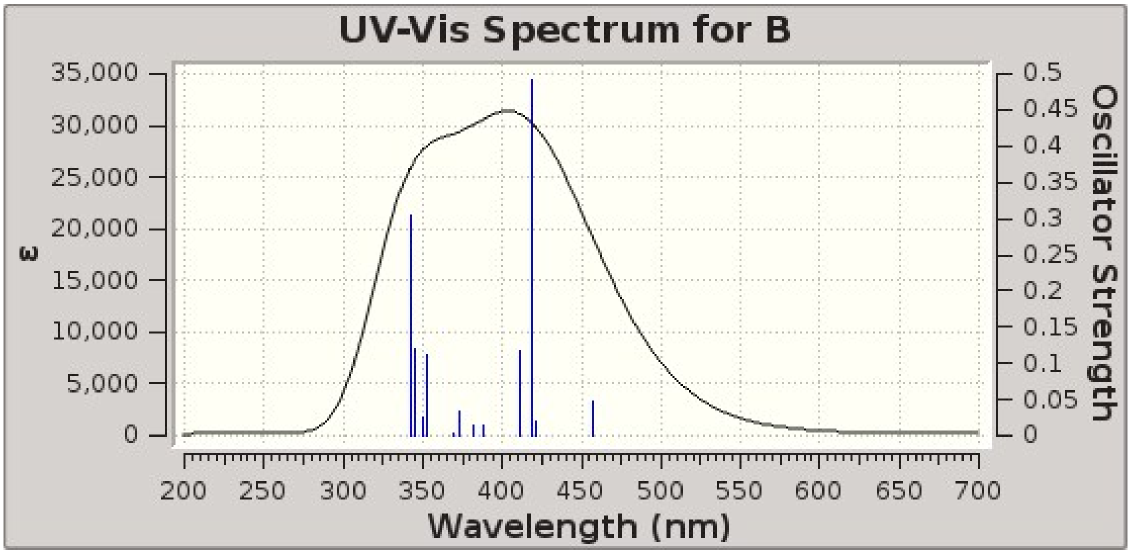


Figure S62. Calculated UV-Vis spectrum for probe **B**.

Table S9. Excitation energies and oscillator strengths listing for probe **B**.

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.7167 eV 456.39 nm f=0.0485 <S**2>=0.000
243 -> 244 0.70097
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -2916.05428490
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.9426 eV 421.35 nm f=0.0192 <S**2>=0.000
243 -> 245 0.69419

Excited State 3: Singlet-A 2.9647 eV 418.21 nm f=0.4925 <S**2>=0.000
241 -> 244 -0.19710
242 -> 244 0.66539

Excited State 4: Singlet-A 3.0196 eV 410.60 nm f=0.1179 <S**2>=0.000
241 -> 244 0.66805
242 -> 244 0.19858

Excited State 5: Singlet-A 3.1965 eV 387.88 nm f=0.0147 <S**2>=0.000
241 -> 245 -0.37463
242 -> 245 0.58870

Excited State 6: Singlet-A 3.2431 eV 382.31 nm f=0.0151 <S**2>=0.000
241 -> 245 0.58607
242 -> 245 0.38032

Excited State 7: Singlet-A 3.3221 eV 373.22 nm f=0.0329 <S**2>=0.000
243 -> 246 0.69120

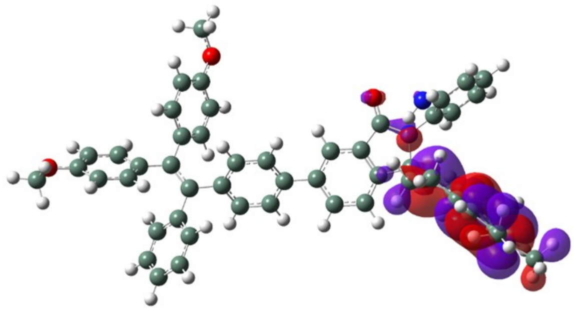
Excited State 8: Singlet-A 3.3548 eV 369.57 nm f=0.0021 <S**2>=0.000
240 -> 244 0.69172
240 -> 245 -0.11560

Excited State 9: Singlet-A 3.5187 eV 352.35 nm f=0.1127 <S**2>=0.000
242 -> 246 0.68334

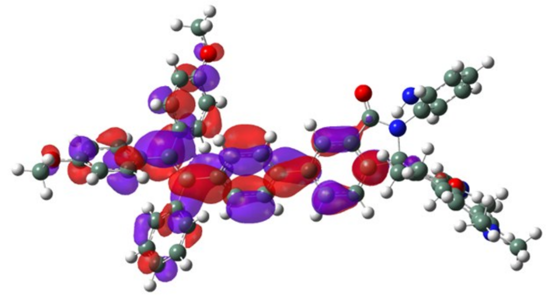
Excited State 10: Singlet-A 3.5446 eV 349.78 nm f=0.0242 <S**2>=0.000
240 -> 244 0.11453
240 -> 245 0.69051

Excited State 11: Singlet-A 3.5934 eV 345.03 nm f=0.1201 <S**2>=0.000
241 -> 246 0.60558
241 -> 247 -0.11616
243 -> 247 0.29956

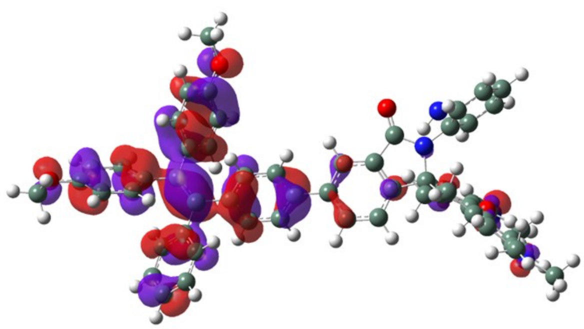
Excited State 12: Singlet-A 3.6197 eV 342.52 nm f=0.3053 <S**2>=0.000
241 -> 246 -0.33094
243 -> 247 0.55596
243 -> 250 0.17836



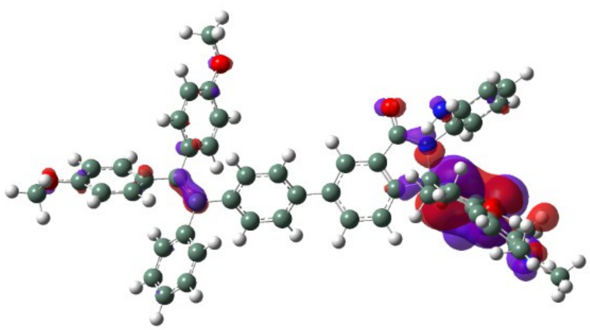
B-243 HOMO



B-244 LUMO



B-242 HOMO-1



B-241 HOMO-2

Figure S63. Drawings of the highest occupied and lowest unoccupied orbitals for probe B.

Probe BH^+

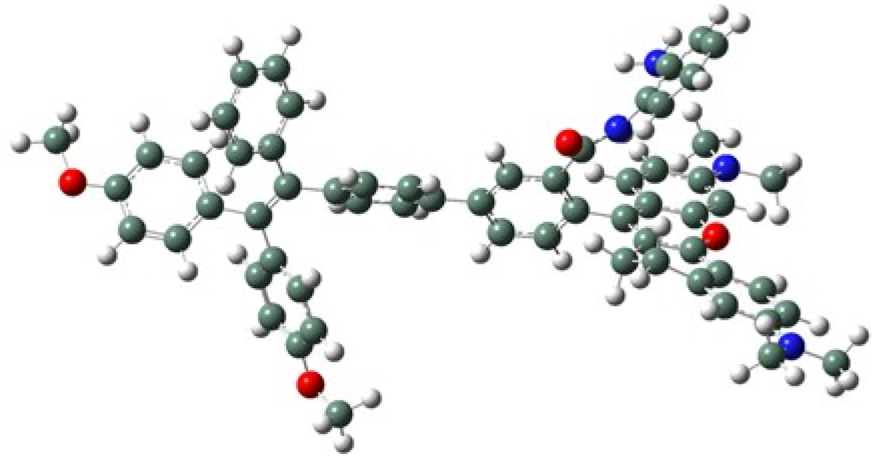


Figure S64. GaussView representation of probe BH^+.

Table S10. Computational results for Probe BH^+.

bh (Optimization completed)		
/home/rluck/calculation/liu/tbt/superior/bh.log		
File Type	.log	
Calculation Type	SP	
Calculation Method	RTPSSh	
Basis Set	TZVP	
Charge	1	
Spin	Singlet	
Solvation	scrf=solvent=water	
E(RTPSSh)	-2916.620324	Hartree
RMS Gradient Norm	0.000002	Hartree/Bohr
Imaginary Freq		
Dipole Moment	32.324085	Debye
Point Group	C1	
Job cpu time:	11 days 11 hours 5 minutes 2...	

Table S11. Calculated atomic coordinates for probe BH^+.

Row	Symbol	X	Y	Z
1	C	4.325151	-1.8404	4.007804
2	C	5.71967	-1.60971	4.230199
3	C	6.416613	-0.81672	3.290569
4	C	5.737988	-0.29665	2.210891
5	C	4.357837	-0.4998	1.976561
6	C	3.679862	-1.30739	2.92398
7	N	6.349194	-2.13786	5.306546
8	C	5.621711	-2.96618	6.26822
9	C	7.775523	-1.897	5.513317
10	C	3.764311	0.079923	0.823308
11	C	2.299381	-0.07352	0.598481
12	C	1.750726	-0.82561	-0.45735
13	C	0.368585	-0.84169	-0.65135
14	C	-0.50634	-0.15174	0.193966
15	C	0.052206	0.579968	1.252449
16	C	1.425096	0.619388	1.445529
17	C	2.566482	-1.62582	-1.43719
18	O	6.473552	0.448005	1.328907
19	C	5.908642	1.018235	0.243936
20	C	4.543461	0.851018	-0.03775
21	C	6.784077	1.813987	-0.54799
22	C	6.348618	2.244365	-1.83058
23	C	5.016417	1.755652	-2.33789
24	C	3.995075	1.6377	-1.20558
25	O	2.319768	-1.59439	-2.64258
26	N	3.545901	-2.39985	-0.88596
27	C	4.490486	-3.20983	-1.55813
28	C	-1.96912	-0.19123	-0.02229
29	C	8.075059	2.187517	-0.10832
30	C	8.892465	2.970546	-0.88279
31	C	8.461067	3.426101	-2.16272
32	C	7.169861	3.029911	-2.60782
33	N	9.255604	4.21139	-2.92818
34	C	8.792638	4.69298	-4.22881
35	C	10.59205	4.589805	-2.46983
36	C	4.960141	-4.34672	-0.86552
37	C	4.993259	-2.89769	-2.82179
38	C	5.985052	-3.68871	-3.39549
39	C	6.481665	-4.79064	-2.70183
40	C	5.973811	-5.11383	-1.44762
41	N	4.464221	-4.62437	0.417723
42	C	-2.86208	-0.14384	1.05944
43	C	-4.23458	-0.17343	0.857326
44	C	-4.77822	-0.24918	-0.43423
45	C	-3.88323	-0.32068	-1.51286
46	C	-2.50983	-0.2829	-1.31332
47	C	-6.24658	-0.31721	-0.65675
48	C	-6.68659	-1.35303	-1.63352
49	C	-7.12748	0.510445	-0.01959
50	C	-8.59183	0.259119	-0.00992
51	C	-6.69128	1.730165	0.708658
52	C	-7.56344	-1.03293	-2.68058
53	C	-7.94496	-1.99341	-3.61246
54	C	-7.45908	-3.29721	-3.51699
55	C	-6.57788	-3.62721	-2.48798
56	C	-6.1875	-2.66241	-1.56359
57	C	-9.50522	1.303396	-0.23809
58	C	-10.8727	1.084277	-0.21872
59	C	-11.3754	-0.19373	0.057748
60	C	-10.4877	-1.24228	0.315799
61	C	-9.11565	-1.00615	0.276851
62	C	-7.20705	2.035422	1.980474
63	C	-6.81658	3.175202	2.6636
64	C	-5.90882	4.068089	2.079199
65	C	-5.40462	3.801329	0.802964
66	C	-5.79714	2.642259	0.137783
67	O	-5.58735	5.167202	2.821544
68	O	-12.7348	-0.31455	0.063534
69	C	-13.2873	-1.60768	0.339122
70	C	-4.65803	6.101893	2.25936
71	H	3.76439	-2.44965	4.702484
72	H	7.472178	-0.60903	3.388846
73	H	2.623507	-1.50212	2.785812
74	H	4.805088	-2.40642	6.732237
75	H	5.214744	-3.8619	5.790704
76	H	6.314367	-3.27432	7.04675
77	H	8.366613	-2.29966	4.685138
78	H	7.981921	-0.8269	5.608582
79	H	8.08138	-2.39209	6.430974
80	H	-0.02228	-1.43564	-1.46885
81	H	-0.58911	1.150754	1.913757

82	H	1.834661	1.221802	2.248455	104	H	-4.89993	-0.15362	1.712471
83	H	5.161881	0.770943	-2.79882	105	H	-4.27132	-0.38766	-2.52324
84	H	4.639951	2.421121	-3.11651	106	H	-1.85057	-0.30207	-2.17427
85	H	3.733644	2.640956	-0.84598	107	H	-7.94028	-0.01988	-2.7638
86	H	3.075656	1.18509	-1.57438	108	H	-8.61792	-1.72196	-4.41883
87	H	3.597503	-2.43266	0.125714	109	H	-7.75775	-4.04629	-4.24202
88	H	8.418918	1.864186	0.866321	110	H	-6.19131	-4.63747	-2.40654
89	H	9.866351	3.249946	-0.50598	111	H	-5.49656	-2.92674	-0.77015
90	H	6.818896	3.33692	-3.58419	112	H	-9.13307	2.300218	-0.44798
91	H	8.618341	3.861884	-4.91865	113	H	-11.5689	1.892422	-0.41212
92	H	7.868409	5.267997	-4.12585	114	H	-10.849	-2.23441	0.553615
93	H	9.557389	5.339823	-4.6503	115	H	-8.43816	-1.82622	0.484894
94	H	10.54083	5.18475	-1.55334	116	H	-7.91517	1.357779	2.444782
95	H	11.20843	3.70581	-2.28549	117	H	-7.20703	3.393756	3.651046
96	H	11.06632	5.186221	-3.24457	118	H	-4.71986	4.485347	0.318592
97	H	4.611268	-2.03149	-3.34313	119	H	-5.4041	2.450051	-0.85401
98	H	6.369662	-3.43756	-4.37701	120	H	-14.3661	-1.48005	0.286399
99	H	7.259035	-5.40751	-3.13844	121	H	-12.9646	-2.33818	-0.40799
100	H	6.344189	-5.9845	-0.91614	122	H	-13.0045	-1.94928	1.338793
101	H	4.815814	-5.49327	0.80045	123	H	-4.54052	6.8813	3.008788
102	H	3.451928	-4.60943	0.483837	124	H	-3.69259	5.625598	2.066812
103	H	-2.47896	-0.11449	2.073668	125	H	-5.04948	6.535082	1.334693

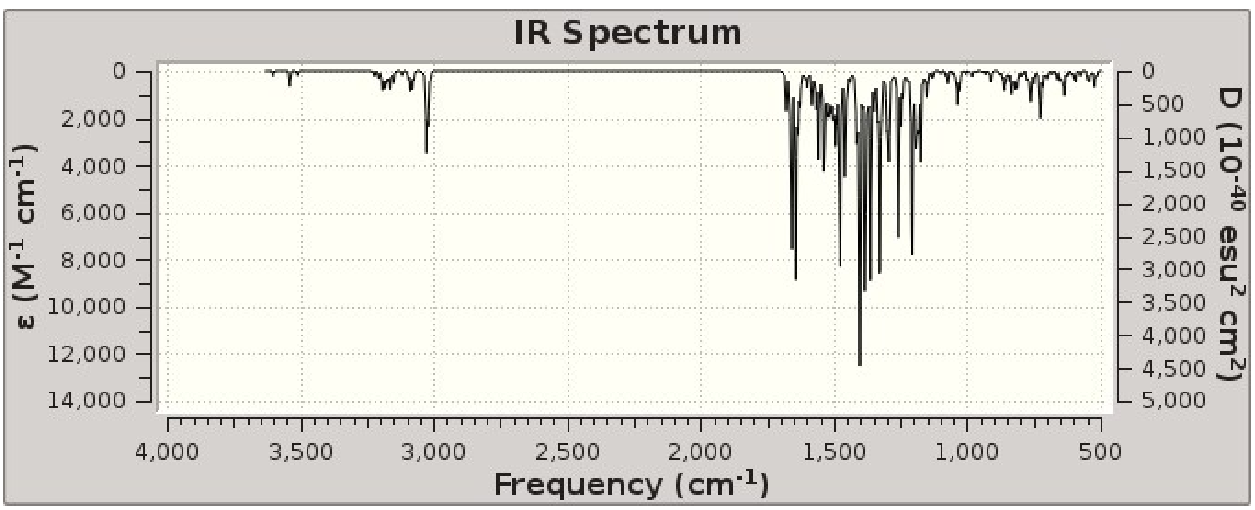


Figure S65. Calculated IR spectrum for probe BH+.

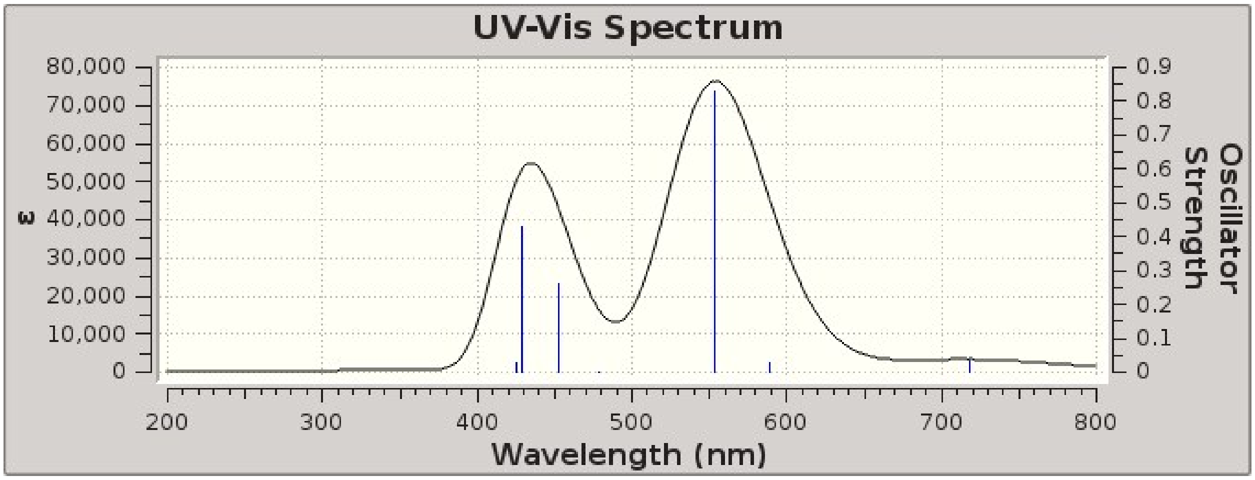
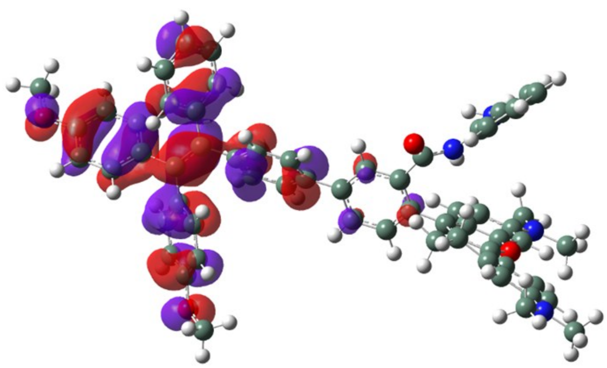


Figure S66. Calculated UV-Vis spectrum for probe **BH⁺**.

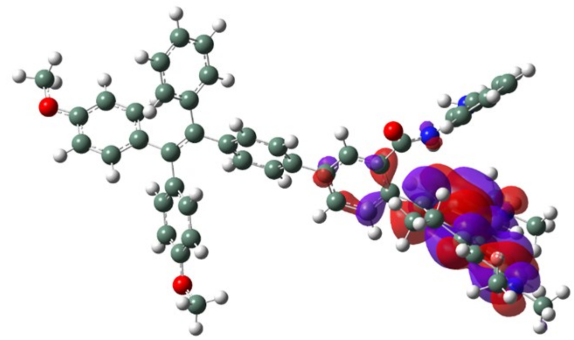
Table S12. Excitation energies and oscillator strengths listing for probe BH⁺.

```
 Excited State   1:      Singlet-A      1.7268 eV  718.00 nm  f=0.0317  <S**2>=0.000
     243 -> 244         0.70674
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -2916.55686528
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      2.1038 eV  589.33 nm  f=0.0278  <S**2>=0.000
     241 -> 244         0.69547
     242 -> 244        -0.12533

 Excited State   3:      Singlet-A      2.2389 eV  553.78 nm  f=0.8284  <S**2>=0.000
     241 -> 244         0.12631
     242 -> 244         0.68934

 Excited State   4:      Singlet-A      2.5909 eV  478.55 nm  f=0.0018  <S**2>=0.000
     240 -> 244         0.70549

 Excited State   5:      Singlet-A      2.7371 eV  452.98 nm  f=0.2589  <S**2>=0.000
     238 -> 244        -0.16803
     239 -> 244         0.64657
     242 -> 247         0.10615
     243 -> 245        -0.11927

 Excited State   6:      Singlet-A      2.8928 eV  428.59 nm  f=0.4283  <S**2>=0.000
     237 -> 244        -0.25626
     243 -> 245         0.64761

 Excited State   7:      Singlet-A      2.9162 eV  425.16 nm  f=0.0292  <S**2>=0.000
     237 -> 244         0.53318
```

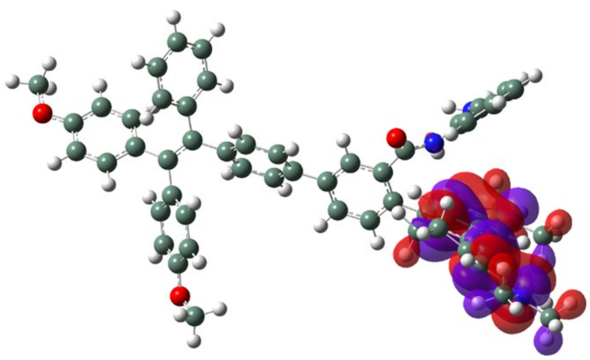
238 -> 244	0.36334
239 -> 244	0.17756
243 -> 245	0.19666



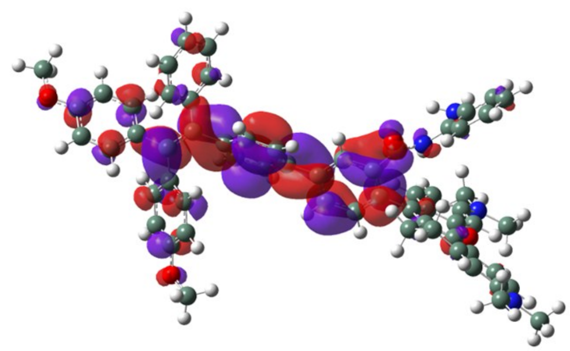
BH^+-243 HOMO



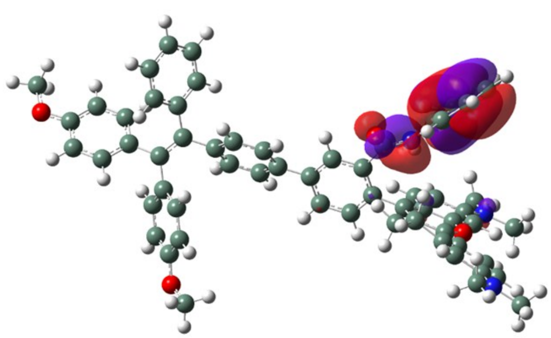
BH^+-244 LUMO



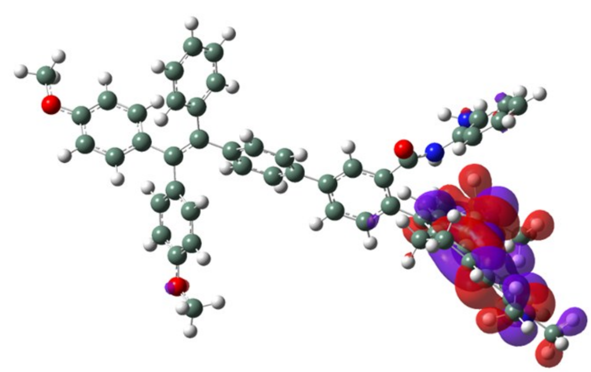
BH^+-242 HOMO-1



BH^+-245 LUMO+1



BH^+-241 HOMO-2



BH^+-239 HOMO-4

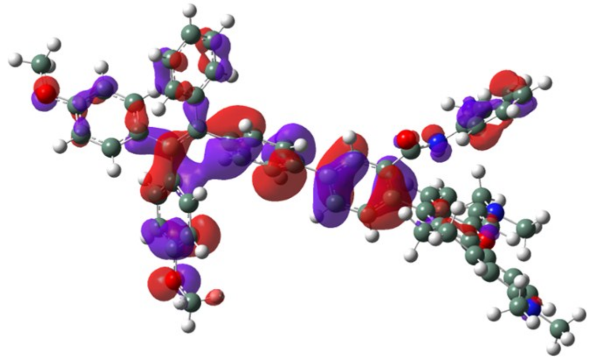
 BH⁺-238 HOMO-5	

Figure S67. Drawings of the highest occupied and lowest unoccupied orbitals for probe BH^+.

Probe C

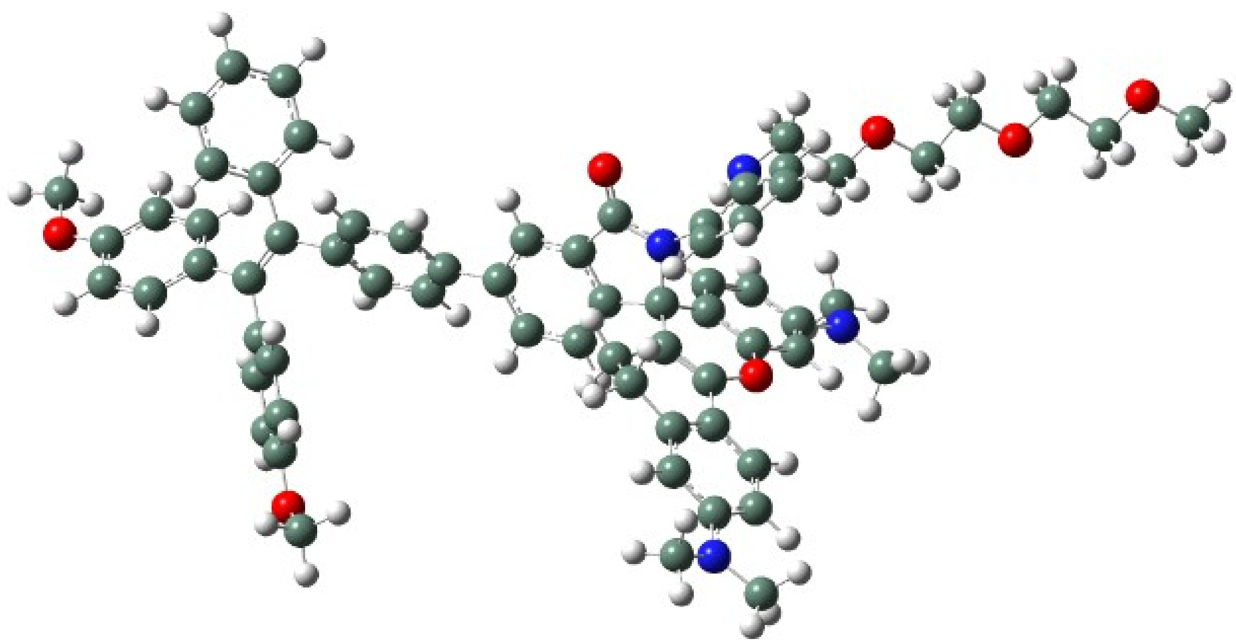


Figure S68. GaussView representation of probe C.

Table S13. Computational results for probe C.

c (Optimization completed)		
/home/rluck/calculation/liu/tbt/superior/c.log		
File Type	.log	
Calculation Type	SP	
Calculation Method	RTPSSh	
Basis Set	TZVP	
Charge	0	
Spin	Singlet	
Solvation	scrf=solvent=water	
E(RTPSSh)	-3417.150421	Hartree
RMS Gradient Norm	0.000001	Hartree/Bohr
Imaginary Freq		
Dipole Moment	11.356903	Debye
Point Group	C1	
Job cpu time: 17 days 16 hours 28 minutes ...		

Table S14. Calculated atomic coordinates for probe C.

Row	Symbol	X	Y	Z
1	C	-3.7022	-1.45431	-1.90355
2	C	-4.85921	-0.81929	-2.42441
3	C	-5.12316	0.494292	-1.99692
4	C	-4.29457	1.111964	-1.06477
5	C	-3.18452	0.481055	-0.50758
6	C	-2.90617	-0.81157	-0.9741
7	N	-5.69284	-1.46492	-3.31118
8	C	-5.25429	-2.70809	-3.93491
9	C	-6.73906	-0.70752	-3.98565
10	C	-2.33933	1.162846	0.544055
11	C	-0.85514	0.887241	0.356813
12	C	-0.31799	0.242035	1.462353
13	C	1.02221	-0.11491	1.529311
14	C	1.858472	0.189992	0.446654
15	C	1.30157	0.847689	-0.66935
16	C	-0.04446	1.19778	-0.72721
17	C	-1.38357	0.028136	2.470319
18	O	-4.62566	2.410992	-0.75641
19	C	-3.71366	3.162053	-0.04726
20	C	-2.63702	2.640405	0.574892
21	C	-4.00376	4.593291	-0.09006
22	C	-3.29161	5.457	0.764436
23	C	-2.35679	4.847119	1.781376
24	C	-1.6704	3.580785	1.259374
25	O	-1.27297	-0.48519	3.581948
26	N	-2.54374	0.524267	1.919638
27	C	-3.76792	0.585025	2.656452
28	C	3.295078	-0.16786	0.470395
29	C	-4.94282	5.150598	-0.96708
30	C	-5.16879	6.517333	-1.01355
31	C	-4.44092	7.399406	-0.18223
32	C	-3.5097	6.825067	0.716345
33	N	-4.61898	8.763313	-0.25122
34	C	-4.01925	9.621268	0.762672
35	C	-5.72617	9.30487	-1.02868
36	C	-4.62228	-0.54611	2.711727
37	C	-4.08101	1.736648	3.372265
38	C	-5.24262	1.826454	4.134895
39	C	-6.09126	0.722847	4.186491

40	C	-5.79071	-0.4425	3.492224	85	H	-6.06527	-3.08578	-4.55496
41	N	-4.26875	-1.71276	2.073388	86	H	-4.36567	-2.57018	-4.56505
42	C	-5.1365	-2.87145	1.956535	87	H	-6.33324	0.077263	-4.63842
43	C	-6.26558	-2.69917	0.939686	88	H	-7.32814	-1.39416	-4.59083
44	O	-7.05408	-3.88718	0.974599	89	H	-7.40697	-0.24205	-3.25698
45	C	-8.12807	-3.8522	0.039526	90	H	1.401661	-0.63971	2.398723
46	C	-8.88173	-5.1637	0.16659	91	H	1.946005	1.10758	-1.50156
47	O	-9.95276	-5.13155	-0.77186	92	H	-0.44033	1.707186	-1.59888
48	C	-10.7296	-6.32562	-0.74309	93	H	-2.94763	4.596262	2.671469
49	C	-11.8318	-6.17569	-1.77568	94	H	-1.60916	5.577673	2.098822
50	O	-12.606	-7.36916	-1.74922	95	H	-0.86996	3.854726	0.559089
51	C	3.97256	-0.53554	-0.70256	96	H	-1.18146	3.065383	2.091743
52	C	5.320056	-0.86748	-0.67922	97	H	-5.50679	4.501667	-1.62625
53	C	6.053083	-0.84962	0.516898	98	H	-5.9089	6.899955	-1.70339
54	C	5.368877	-0.50636	1.692793	99	H	-2.9504	7.457078	1.394876
55	C	4.023873	-0.16183	1.669152	100	H	-4.41005	9.415994	1.768244
56	C	7.486842	-1.24267	0.553591	101	H	-2.93344	9.499321	0.781299
57	C	7.850797	-2.18926	1.645014	102	H	-4.23614	10.65762	0.510657
58	C	8.401482	-0.7701	-0.34445	103	H	-5.65853	8.987068	-2.07202
59	C	9.749471	-1.37501	-0.50304	104	H	-6.70389	8.997666	-0.634
60	C	8.121387	0.38969	-1.23065	105	H	-5.66719	10.39144	-1.00419
61	C	8.95217	-1.94467	2.478791	106	H	-3.38566	2.565097	3.335104
62	C	9.26708	-2.81212	3.520361	107	H	-5.47154	2.733097	4.681949
63	C	8.488029	-3.94577	3.750948	108	H	-7.00214	0.763052	4.774376
64	C	7.383672	-4.19599	2.937296	109	H	-6.46891	-1.28422	3.556161
65	C	7.06259	-3.32096	1.903448	110	H	-3.55885	-1.6145	1.361357
66	C	10.89592	-0.56776	-0.60693	111	H	-4.51588	-3.71941	1.661757
67	C	12.15586	-1.11952	-0.77016	112	H	-5.56063	-3.10841	2.935386
68	C	12.30772	-2.50917	-0.8611	113	H	-6.88452	-1.8276	1.189478
69	C	11.17976	-3.33157	-0.78825	114	H	-5.84912	-2.54833	-0.06383
70	C	9.922643	-2.7593	-0.60885	115	H	-8.79711	-3.00906	0.255861
71	C	8.458583	0.355461	-2.59511	116	H	-7.74292	-3.73585	-0.98195
72	C	8.215444	1.436225	-3.42656	117	H	-8.21095	-6.00617	-0.0468
73	C	7.645638	2.606713	-2.90893	118	H	-9.26999	-5.27928	1.186963
74	C	7.327181	2.675037	-1.54958	119	H	-10.1032	-7.19478	-0.98283
75	C	7.564986	1.572572	-0.73218	120	H	-11.1638	-6.47507	0.254041
76	O	7.450917	3.622791	-3.79929	121	H	-12.4581	-5.30589	-1.53529
77	O	13.58398	-2.96303	-1.02934	122	H	-11.3962	-6.02228	-2.77234
78	C	13.77971	-4.37932	-1.12448	123	H	3.432082	-0.59255	-1.64114
79	C	6.871294	4.837356	-3.30723	124	H	5.812516	-1.16313	-1.59834
80	C	-13.6745	-7.3293	-2.68995	125	H	5.904739	-0.49025	2.635604
81	H	-3.42743	-2.44788	-2.22944	126	H	3.538598	0.135334	2.592486
82	H	-5.95456	1.064029	-2.38808	127	H	9.55845	-1.06221	2.308853
83	H	-2.02649	-1.32642	-0.59946	128	H	10.1186	-2.59906	4.157821
84	H	-5.03118	-3.4632	-3.17799	129	H	8.734373	-4.62269	4.561569

130	H	6.768866	-5.07287	3.110022	140	H	14.8518	-4.51709	-1.24532
131	H	6.197441	-3.5202	1.280108	141	H	13.44269	-4.88283	-0.21402
132	H	10.79571	0.510343	-0.54472	142	H	13.25485	-4.78967	-1.99175
133	H	13.03579	-0.48939	-0.83315	143	H	6.801609	5.496387	-4.16965
134	H	11.26568	-4.40678	-0.87719	144	H	5.873136	4.657006	-2.89837
135	H	9.055398	-3.40768	-0.56062	145	H	7.508123	5.293985	-2.54437
136	H	8.906399	-0.54055	-3.0109	146	H	-14.2111	-8.27355	-2.60271
137	H	8.464179	1.39462	-4.48094	147	H	-14.3596	-6.49995	-2.4736
138	H	6.906305	3.574264	-1.1187	148	H	-13.2947	-7.21969	-3.71354
139	H	7.320047	1.640658	0.321575					

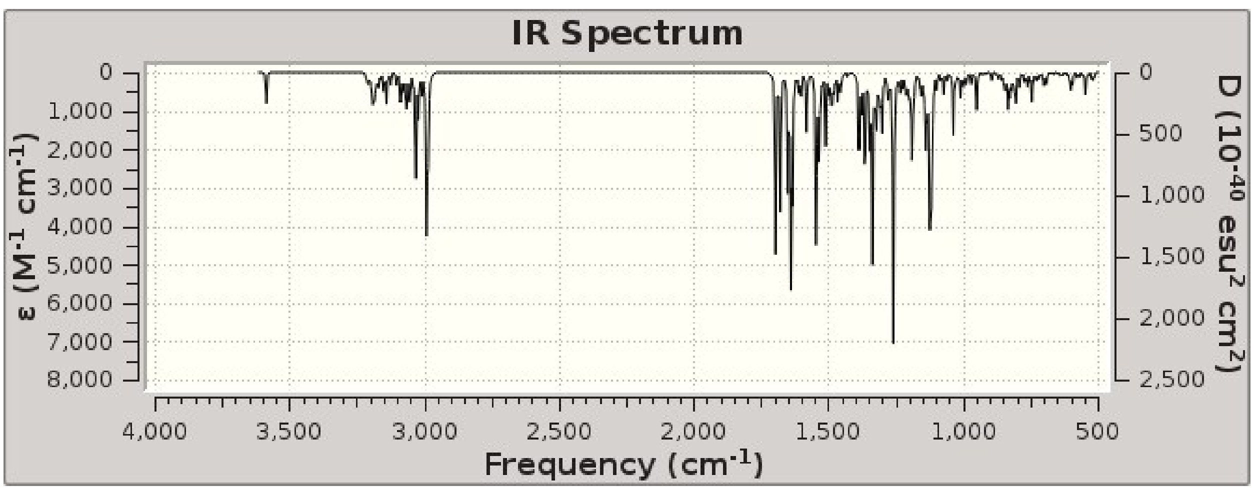


Figure S69. Calculated IR spectrum for probe **C**.

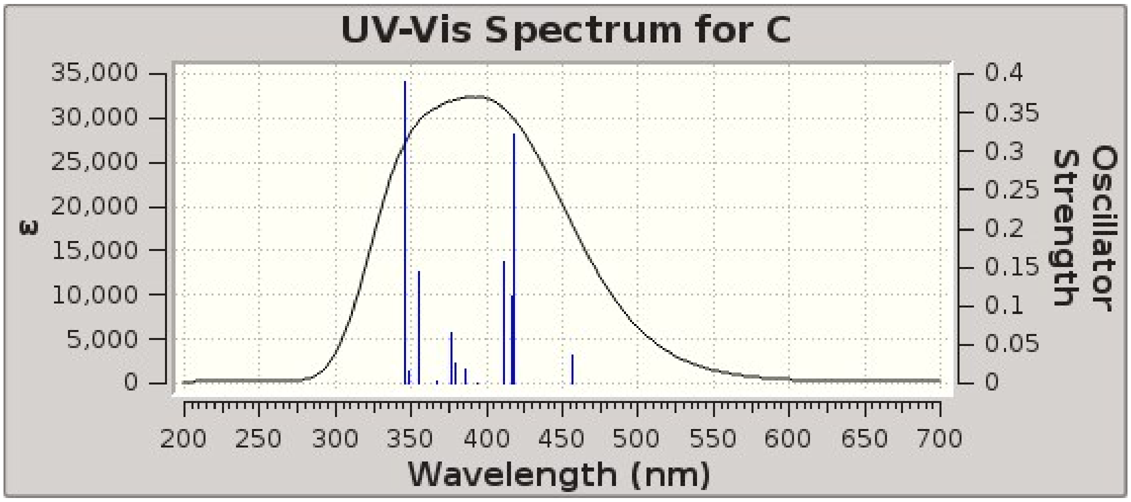


Figure S70. Calculated UV-Vis spectrum for probe **C**.

Table S15. Excitation energies and oscillator strengths listing for Probe C.

Excited State 1: Singlet-A 2.7132 eV 456.97 nm f=0.0379 <S**2>=0.000
283 -> 284 0.70141
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -3417.05071481
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.9645 eV 418.23 nm f=0.3210 <S**2>=0.000
281 -> 284 -0.18114
282 -> 284 0.52811
283 -> 285 -0.42021

Excited State 3: Singlet-A 2.9731 eV 417.01 nm f=0.1115 <S**2>=0.000
281 -> 284 -0.15062
282 -> 284 0.39405
283 -> 285 0.56025

Excited State 4: Singlet-A 3.0166 eV 411.01 nm f=0.1576 <S**2>=0.000
281 -> 284 0.65473
282 -> 284 0.23582

Excited State 5: Singlet-A 3.1504 eV 393.55 nm f=0.0008 <S**2>=0.000
280 -> 284 0.69489
280 -> 285 -0.11045

Excited State 6: Singlet-A 3.2159 eV 385.53 nm f=0.0185 <S**2>=0.000
281 -> 285 -0.48219
282 -> 285 0.49606

```
Excited State   7:      Singlet-A      3.2694 eV  379.23 nm  f=0.0254  <S**2>=0.000
    281 -> 285        0.48286
    282 -> 285        0.48728
    283 -> 286        0.12126

Excited State   8:      Singlet-A      3.2896 eV  376.89 nm  f=0.0650  <S**2>=0.000
    283 -> 286        0.68408

Excited State   9:      Singlet-A      3.3752 eV  367.34 nm  f=0.0017  <S**2>=0.000
    280 -> 284        0.10065
    280 -> 285        0.68817
    281 -> 285       -0.10477

Excited State  10:      Singlet-A      3.4948 eV  354.77 nm  f=0.1443  <S**2>=0.000
    282 -> 286        0.68413

Excited State  11:      Singlet-A      3.5582 eV  348.45 nm  f=0.0147  <S**2>=0.000
    281 -> 286        0.67130
    281 -> 287        0.10409
    283 -> 287        0.12999

Excited State  12:      Singlet-A      3.5884 eV  345.52 nm  f=0.3884  <S**2>=0.000
    281 -> 286       -0.14606
    283 -> 287        0.64387
    283 -> 291        0.15346
```

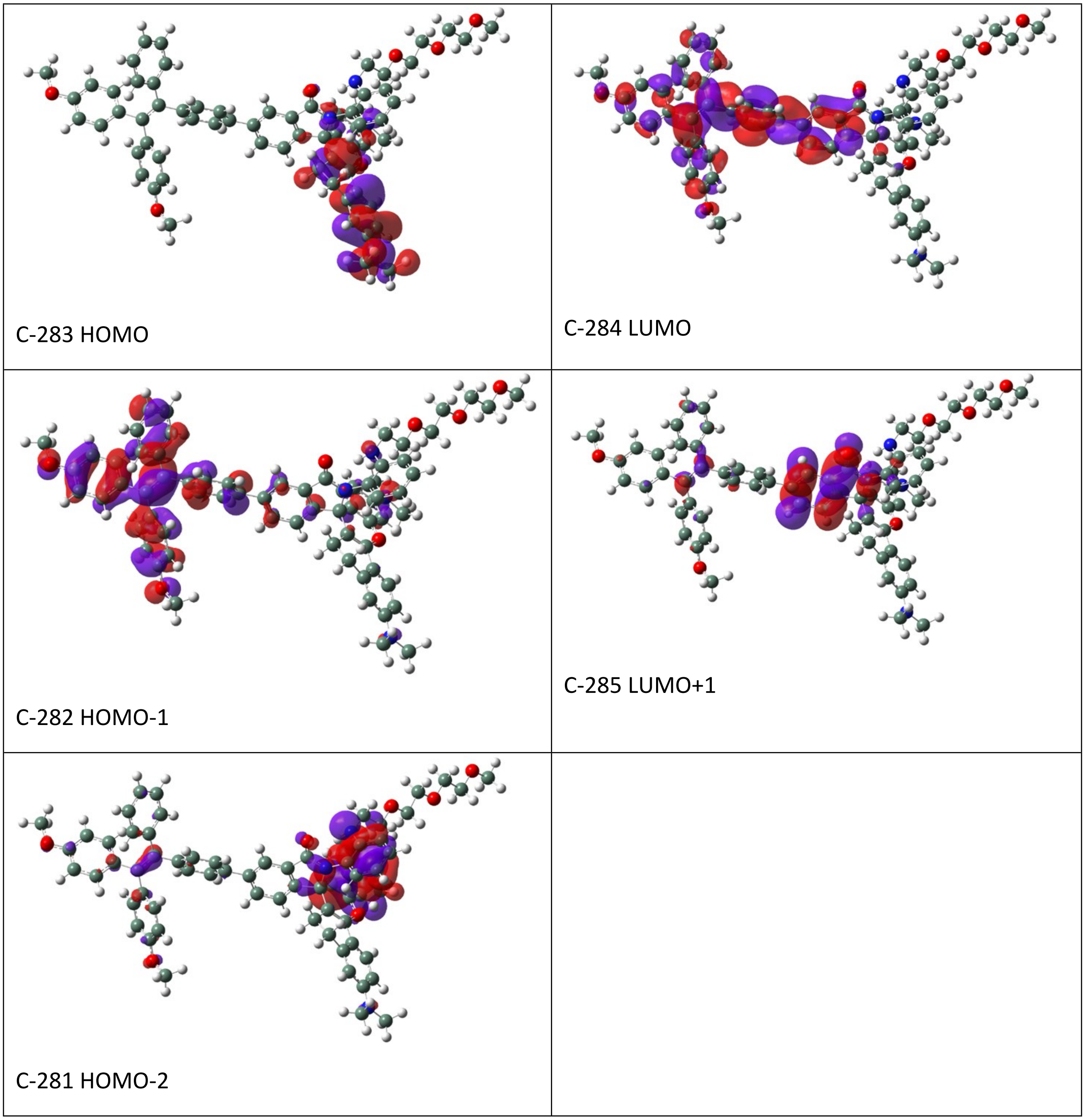


Figure S71. Drawings of the highest occupied and lowest unoccupied orbitals for probe **C**.

Probe CH^+

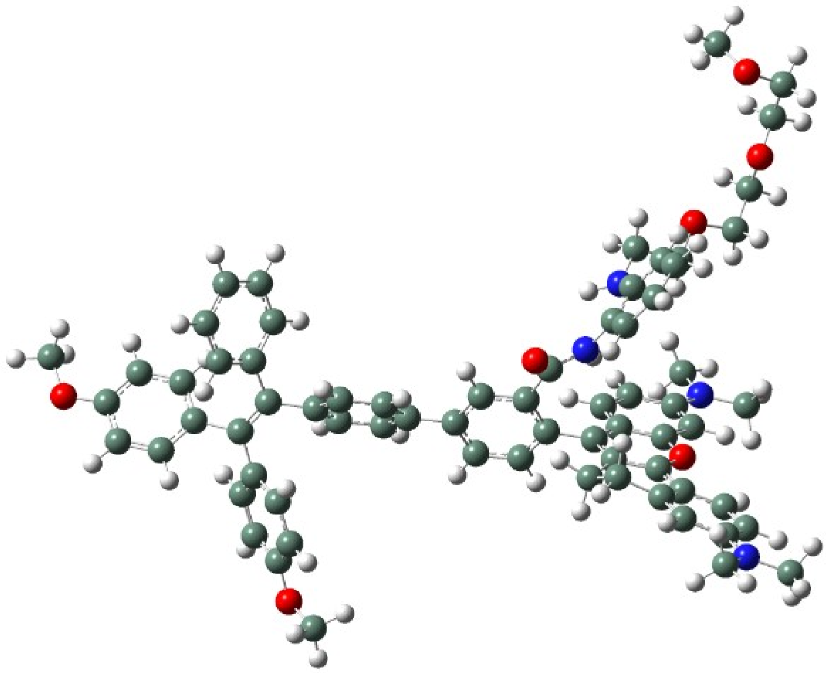


Figure S72. GaussView representation of probe CH^+.

Table S16. Computational results for probe CH^+.

ch (Optimization completed)		
/home/rluck/calculation/liu/tbt/superior/ch.log		
File Type	.log	
Calculation Type	SP	
Calculation Method	RTPSSh	
Basis Set	TZVP	
Charge	1	
Spin	Singlet	
Solvation	scrf=solvent=water	
E(RTPSSh)	-3417.616353	Hartree
RMS Gradient Norm	0.000001	Hartree/Bohr
Imaginary Freq		
Dipole Moment	30.539098	Debye
Point Group	C1	
Job cpu time: 16 days 23 hours 38 minutes ...		

Table S17. Calculated atomic coordinates for probe CH^+.

Row	Symbol	X	Y	Z
1	C	3.551294	-0.32012	3.438335
2	C	4.854269	0.215185	3.689289
3	C	5.265876	1.335808	2.932597
4	C	4.410856	1.865539	1.99185
5	C	3.116182	1.358868	1.731024
6	C	2.72451	0.23189	2.496547
7	N	5.665729	-0.33906	4.62106
8	C	5.234821	-1.50673	5.389892
9	C	6.998534	0.212585	4.854915
10	C	2.325439	1.978295	0.726124
11	C	0.937674	1.489625	0.485518
12	C	0.544387	0.800091	-0.67693
13	C	-0.79531	0.448041	-0.85174
14	C	-1.76994	0.734631	0.109161
15	C	-1.36201	1.412336	1.267609
16	C	-0.03756	1.782957	1.447083
17	C	1.476421	0.406959	-1.79199
18	O	4.874958	2.938238	1.27969
19	C	4.11821	3.542889	0.339936
20	C	2.826928	3.08101	0.037835
21	C	4.711156	4.680806	-0.27556
22	C	4.103667	5.226772	-1.4386
23	C	2.913814	4.514727	-2.02916
24	C	2.026064	3.906208	-0.94222
25	O	1.14225	0.530388	-2.96961
26	N	2.669219	-0.12944	-1.39967
27	C	3.737972	-0.5412	-2.23462
28	C	-3.17982	0.33298	-0.08959
29	C	5.88842	5.284702	0.223626
30	C	6.431923	6.390619	-0.37822
31	C	5.822993	6.96012	-1.53456
32	C	4.649675	6.337104	-2.04235
33	N	6.34546	8.058828	-2.12899
34	C	5.703238	8.642647	-3.30573
35	C	7.570769	8.671617	-1.6164
36	C	4.474849	-1.68051	-1.82829
37	C	4.09114	0.159903	-3.38462
38	C	5.192582	-0.23528	-4.14007
39	C	5.94832	-1.32939	-3.72782
40	C	5.598905	-2.04158	-2.58384
41	N	4.081094	-2.35851	-0.67561
42	C	4.752088	-3.57913	-0.2386
43	C	5.980295	-3.26053	0.608953
44	O	6.626727	-4.49338	0.905682
45	C	7.805953	-4.31079	1.68631
46	C	8.469907	-5.6468	1.916804
47	O	9.027229	-6.12028	0.693773
48	C	9.647302	-7.39349	0.847316
49	C	10.19898	-7.84636	-0.49261
50	O	9.211693	-8.08655	-1.49394
51	C	-3.99017	-0.02608	0.998556
52	C	-5.31231	-0.40513	0.813247
53	C	-5.88543	-0.4427	-0.46688
54	C	-5.06768	-0.10313	-1.55557
55	C	-3.74793	0.286295	-1.37135
56	C	-7.28702	-0.89279	-0.6773
57	C	-7.46855	-1.87802	-1.78032
58	C	-8.32795	-0.43852	0.081659
59	C	-9.66296	-1.09093	0.076758
60	C	-8.20784	0.747151	0.969595
61	C	-8.45418	-1.69531	-2.76155
62	C	-8.5948	-2.59937	-3.81018
63	C	-7.75373	-3.7083	-3.90002
64	C	-6.76274	-3.8973	-2.93746
65	C	-6.61521	-2.98575	-1.89599
66	C	-10.8401	-0.32495	0.010347
67	C	-12.0907	-0.92001	0.020244
68	C	-12.2054	-2.31234	0.124118
69	C	-11.0501	-3.09356	0.218967
70	C	-9.80073	-2.47846	0.191813
71	C	-8.71767	0.722676	2.279644
72	C	-8.62224	1.82518	3.112387
73	C	-8.03166	3.007573	2.647662
74	C	-7.54291	3.065649	1.339332
75	C	-7.63384	1.941696	0.521605
76	O	-7.98914	4.044307	3.534211
77	O	-13.4764	-2.80948	0.135386
78	C	-13.6354	-4.22963	0.241411
79	C	-7.39213	5.271163	3.096412
80	C	8.474763	-9.2885	-1.28613
81	H	3.207597	-1.17952	3.996403

82	H	6.237658	1.789194	3.063958	116	H	8.498034	-3.63131	1.171053
83	H	1.744233	-0.19818	2.331597	117	H	7.549681	-3.86877	2.659195
84	H	4.329164	-1.28904	5.962299	118	H	9.260161	-5.52285	2.670663
85	H	5.047317	-2.36354	4.736389	119	H	7.736784	-6.36744	2.304064
86	H	6.026935	-1.76937	6.085907	120	H	10.48237	-7.32808	1.560345
87	H	7.609971	0.160378	3.948982	121	H	8.925008	-8.11802	1.24715
88	H	6.938977	1.254493	5.183016	122	H	10.8463	-7.06592	-0.89743
89	H	7.483018	-0.36911	5.634404	123	H	10.80128	-8.75158	-0.33206
90	H	-1.06322	-0.09015	-1.75299	124	H	-3.57325	-0.0408	1.999661
91	H	-2.09038	1.679138	2.024369	125	H	-5.90891	-0.69541	1.670147
92	H	0.247286	2.33448	2.335927	126	H	-5.47879	-0.1285	-2.55878
93	H	3.280962	3.716521	-2.68574	127	H	-3.15824	0.576715	-2.23396
94	H	2.333024	5.198264	-2.65064	128	H	-9.10745	-0.83231	-2.70096
95	H	1.53128	4.710955	-0.38393	129	H	-9.35845	-2.43426	-4.56275
96	H	1.238107	3.304121	-1.39327	130	H	-7.86444	-4.41358	-4.71629
97	H	2.813111	-0.26441	-0.40576	131	H	-6.10115	-4.75471	-2.99951
98	H	6.360945	4.876653	1.108416	132	H	-5.8371	-3.13727	-1.15549
99	H	7.324021	6.834301	0.041161	133	H	-10.7696	0.754741	-0.0639
100	H	4.174127	6.728202	-2.93205	134	H	-12.9924	-0.32203	-0.04759
101	H	5.706589	7.942128	-4.14616	135	H	-11.1097	-4.16935	0.321707
102	H	4.670918	8.927717	-3.08587	136	H	-8.91295	-3.09499	0.27279
103	H	6.254345	9.533758	-3.59378	137	H	-9.1836	-0.18269	2.653068
104	H	7.433162	9.029599	-0.59215	138	H	-9.00367	1.791589	4.126606
105	H	8.402655	7.96221	-1.63614	139	H	-7.1019	3.972967	0.947287
106	H	7.823281	9.518628	-2.24862	140	H	-7.2574	2.001631	-0.49317
107	H	3.503539	1.018967	-3.67777	141	H	-14.7088	-4.40386	0.225329
108	H	5.460872	0.317501	-5.03254	142	H	-13.1654	-4.74013	-0.60388
109	H	6.816177	-1.64008	-4.29887	143	H	-13.2152	-4.60158	1.180086
110	H	6.194661	-2.89613	-2.2892	144	H	-7.45585	5.945275	3.947555
111	H	3.078858	-2.38527	-0.54451	145	H	-6.34428	5.120225	2.822147
112	H	4.041286	-4.14735	0.36177	146	H	-7.94065	5.693187	2.249668
113	H	5.04521	-4.21033	-1.08589	147	H	7.841777	-9.23492	-0.39323
114	H	6.664567	-2.5955	0.065188	148	H	7.838902	-9.42044	-2.16129
115	H	5.675528	-2.75171	1.533166	149	H	9.149156	-10.1496	-1.19375

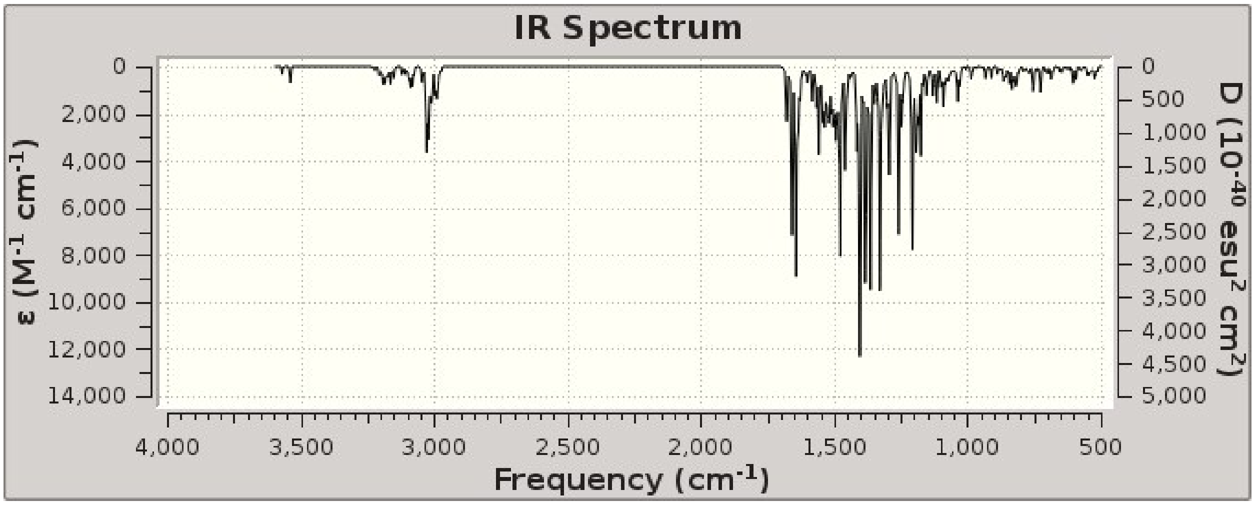


Figure S73. Calculated IR spectrum for probe **CH⁺**.

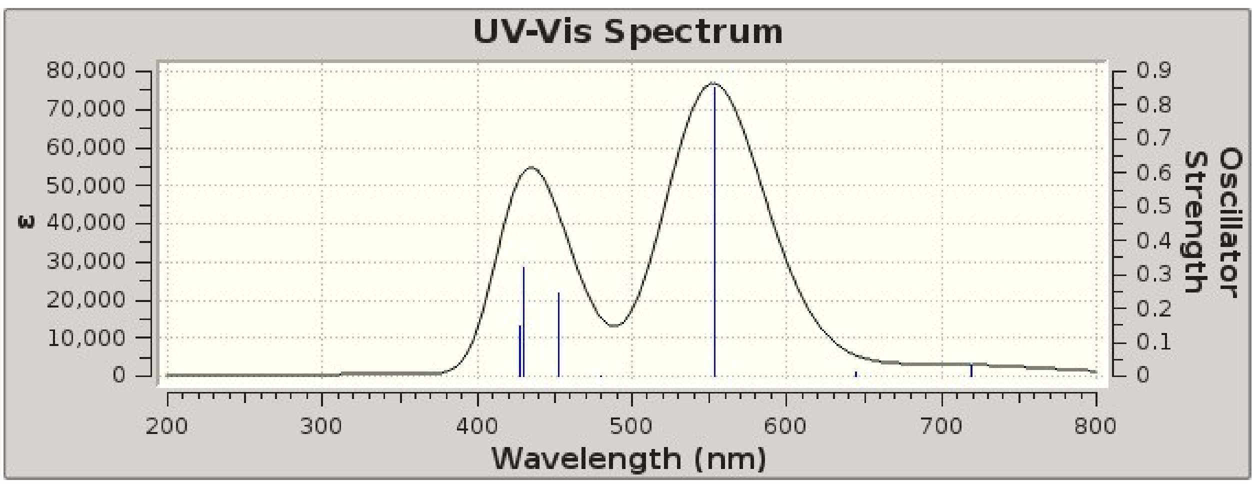


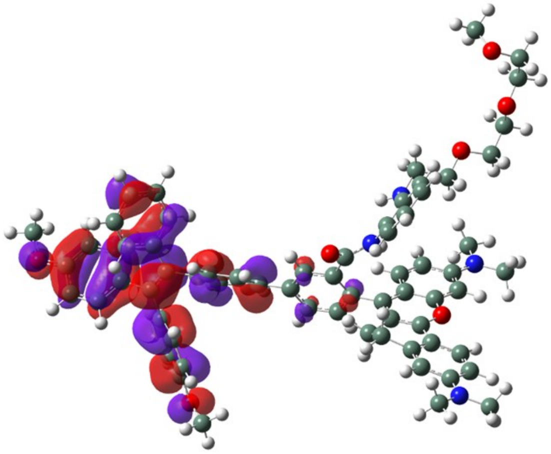
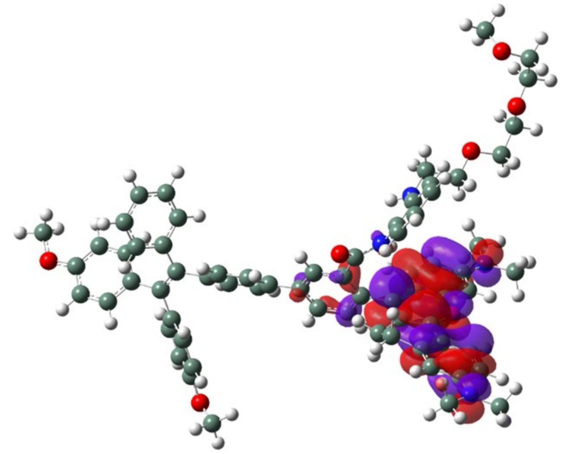
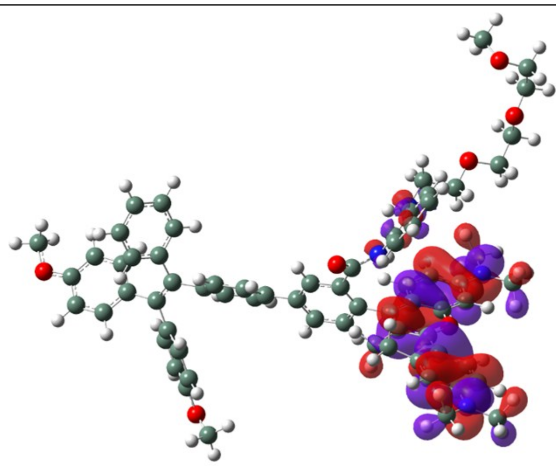
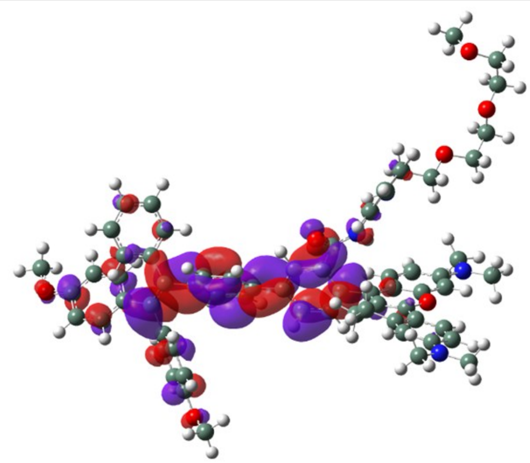
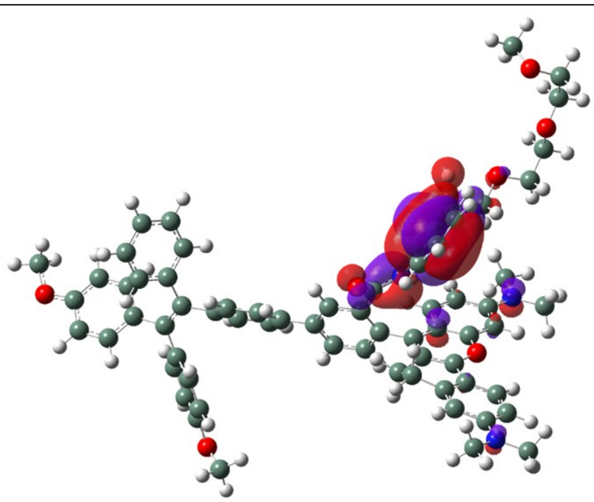
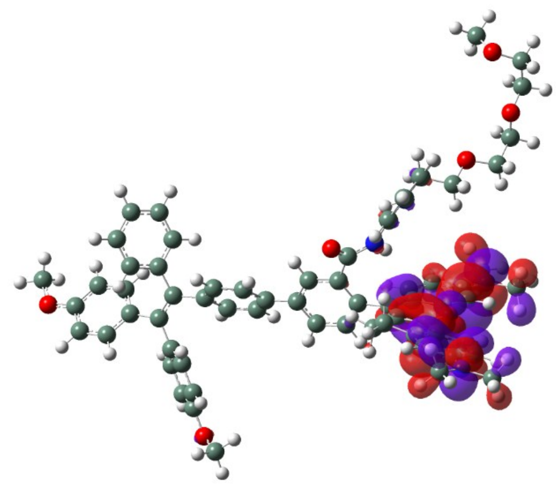
Figure S74. Calculated UV-Vis spectrum for probe **CH⁺**.

Table S18. Excitation energies and oscillator strengths listing for Probe CH⁺.

Excited State 1: Singlet-A 1.7234 eV 719.42 nm f=0.0247 <S**2>=0.000
283 -> 284 0.70674
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -3417.55301986
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.9224 eV 644.96 nm f=0.0124 <S**2>=0.000
281 -> 284 0.68540
282 -> 284 -0.17316

```
Excited State   3:      Singlet-A      2.2419 eV  553.02 nm  f=0.8492  <S**2>=0.000
    281 -> 284        0.17173
    282 -> 284        0.67894

Excited State   4:      Singlet-A      2.5855 eV  479.54 nm  f=0.0015  <S**2>=0.000
    280 -> 284        0.70620

Excited State   5:      Singlet-A      2.7365 eV  453.08 nm  f=0.2433  <S**2>=0.000
    277 -> 284       -0.10817
    278 -> 284       -0.19676
    279 -> 284        0.63831
    282 -> 287        0.10278
    283 -> 285       -0.11238

Excited State   6:      Singlet-A      2.8850 eV  429.75 nm  f=0.3205  <S**2>=0.000
    277 -> 284       -0.45476
    278 -> 284       -0.17219
    283 -> 285        0.50633

Excited State   7:      Singlet-A      2.9028 eV  427.12 nm  f=0.1441  <S**2>=0.000
    277 -> 284        0.33398
    278 -> 284        0.36421
    279 -> 284        0.21488
    283 -> 285        0.43561
```

 CH^{+}-283 HOMO	 CH^{+}-284 LUMO
 CH^{+}-282 HOMO-1	 CH^{+}-285 LUMO+1
 CH^{+}-281 HOMO-2	 CH^{+}-279 HOMO-4

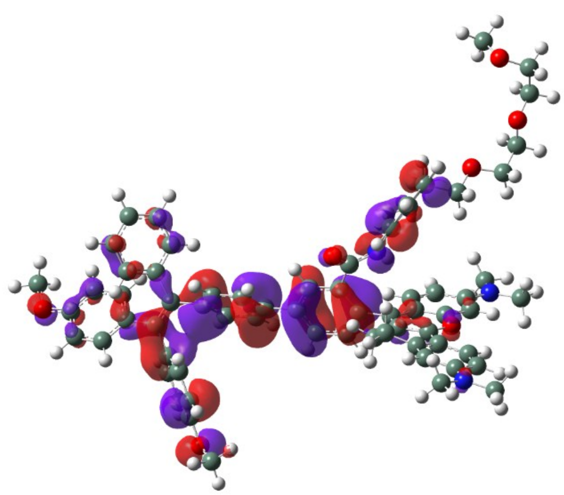
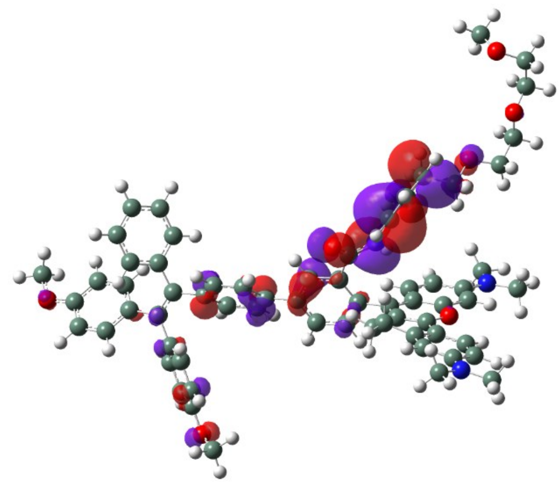
 CH^{+}-278 HOMO-5	 CH^{+}-277 HOMO-6

Figure S75. Drawings of the highest occupied and lowest unoccupied orbitals for probe **CH^{+}**.

17. REFERENCES

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