The pH influenced PET processes between pyronine and different heterocycles

Ling Yang,[a] Jin-Yun Niu,[b] Yu-Jie Xu,[b] Ru Sun,[*a] Jian-Feng Ge[*a,c]

[a] College of Chemistry, Chemical Engineering and Material Science, Soochow University, 199 Ren'Ai Road, Suzhou 215123, China

[b] Technology School of Radiation Medicine and Protection, Medical College of Soochow University, School for Radiological and Interdisciplinary Sciences (RAD-X), Soochow University, 199 Ren'Ai Road, Suzhou 215123, China

[c] Jiangsu Key Laboratory of Medical Optics, Suzhou Institute of Biomedical Engineering and Technology, Chinese Academy of Sciences, Suzhou 215163, China

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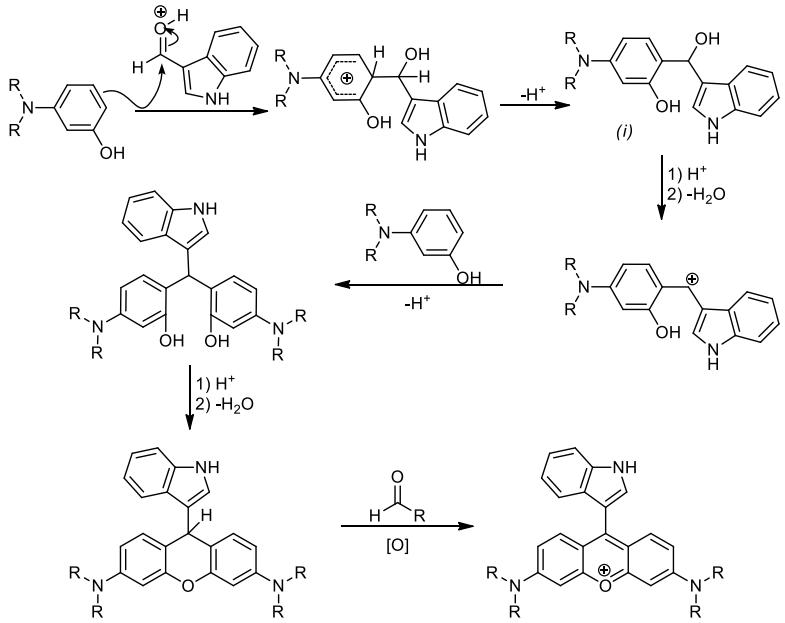
1. Scheme and figures.



Scheme S1 The reaction mechanism illustrated with pyronine-indole skeleton.

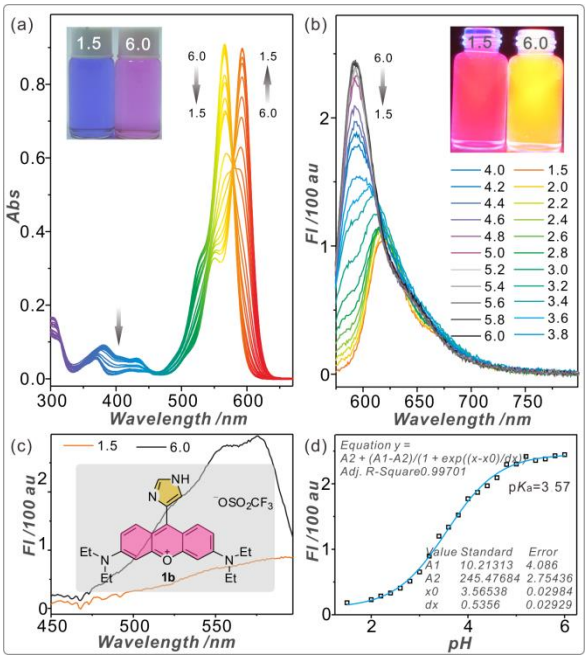


Fig. S1 Optical responses of probe **1b** (10 μM) towards different pH values in B-R buffer-DMSO (9/1, v/v) solutions. (a) Absorption spectra (inset shows photograph of the samples in different pH conditions); (b) emission spectra (λ_{ex} = 568 nm, inset shows photograph of the samples under a lamp at 365 nm); (c) excitation spectra (λ_{em} = 592 nm); (d) fluorescence intensities towards different pH at 592 nm.

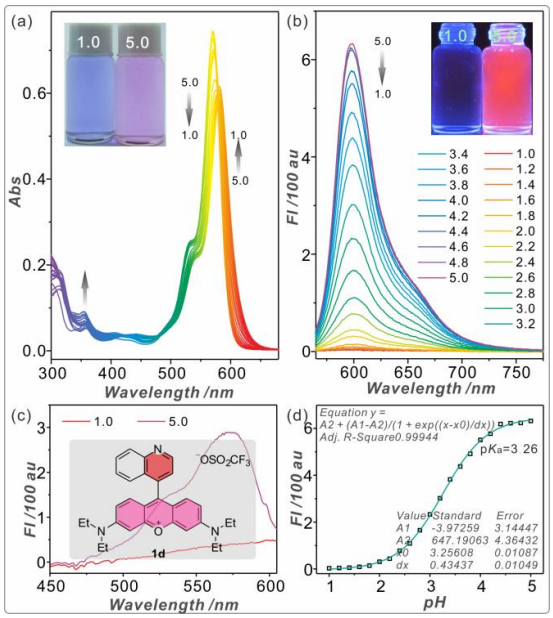


Fig. S2 Optical responses of probe **1c** (10 μM) towards different pH values in B-R buffer-DMSO (9/1, v/v) solutions. (a) Absorption spectra (inset shows photograph of the samples in different pH conditions); (b) emission spectra (λ_{ex} = 548 nm, inset shows photograph of the samples under a lamp at 365 nm); (c) excitation spectra (λ_{em} = 595 nm); (d) fluorescence intensities towards different pH at 595 nm.

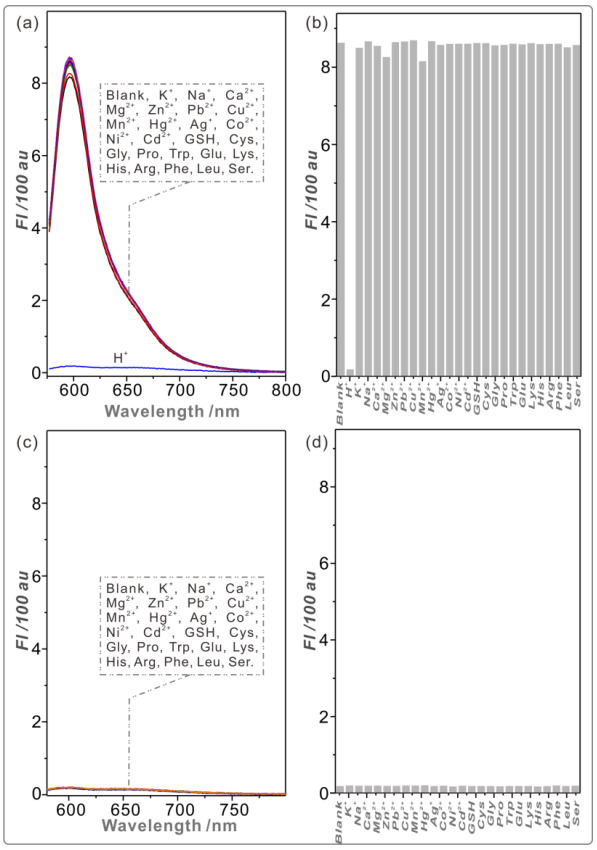


Fig. S3 Selective and competition experiments of probe **1d**. Conditions: 120 mM for K^+ and Na^+; 5.0 mM for Ca^{2+} and Mg^{2+}; 3.0 mM for the other cations and 100 μM for all biomolecules. (a, b) Tested under near neutral conditions (pH = 5.0); (c, d) tested under acidic conditions (pH = 1.0).

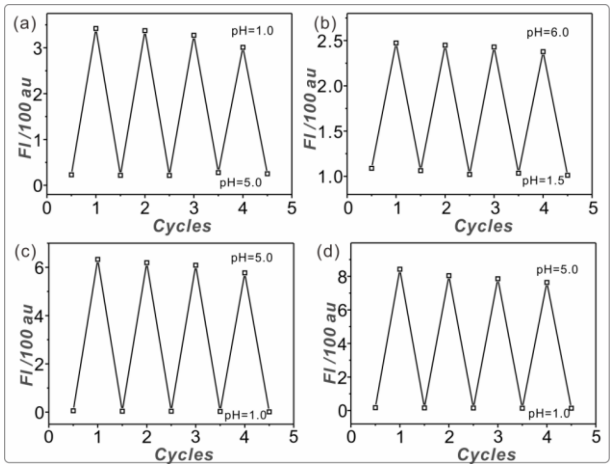


Fig. S4 The reversible emission responses of probes **1a**–**d** with changes between acidic and near neutral conditions. (a) Probe **1a**; (b) probe **1b**; (c) probe **1c**; (d) probe **1d**.

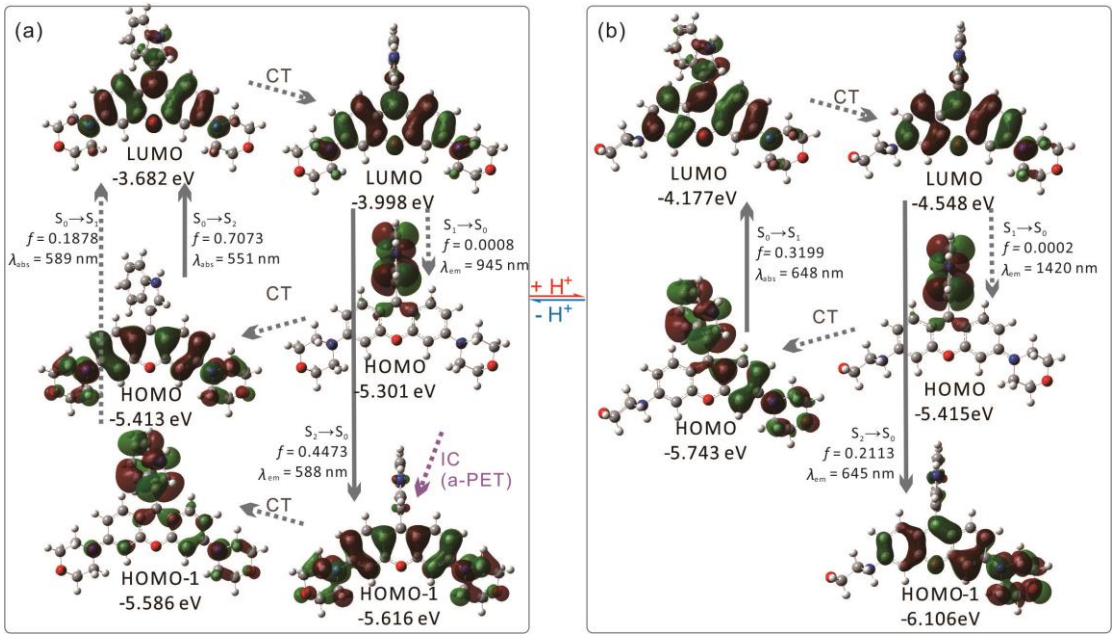


Fig. S5 The frontier molecular orbitals (FMOs) involved in the vertical excitation and emission of probe **1a**$^{+}$ (a) and its protonated form (b). CT stands for conformation transformation. Excitation and radiative processes are marked as solid lines and the non-radiative processes are marked by dotted lines.

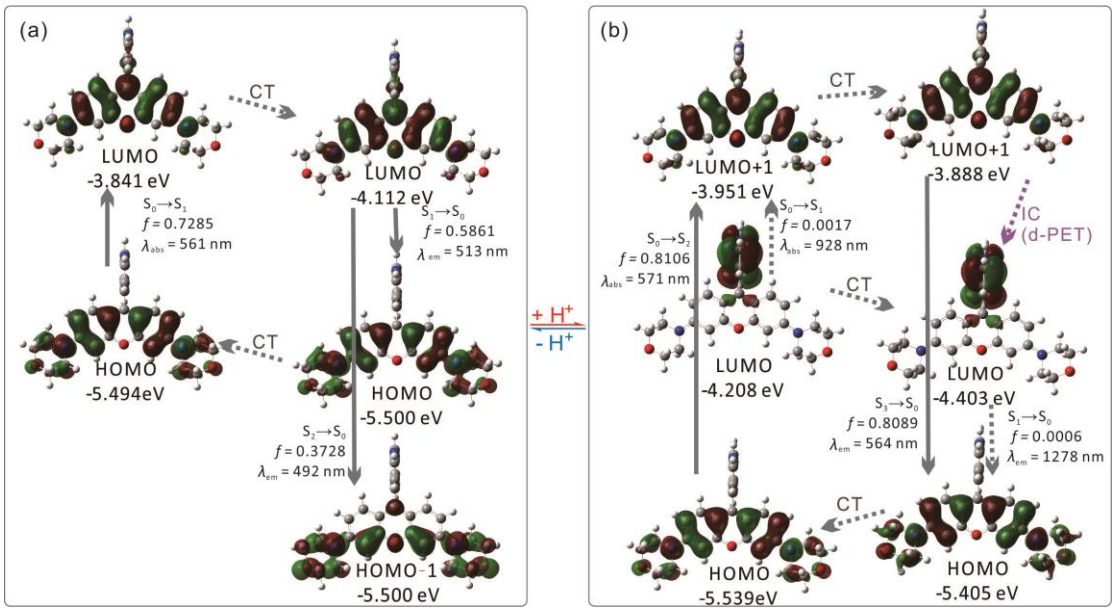


Fig. S6 FMOs involved in the vertical excitation and emission of probe **1d**$^+$ (a) and its protonated form (b). CT stands for conformation transformation. Excitation and radiative processes are marked as solid lines and the non-radiative processes are marked by dotted lines.

2. Tables

Table S1. Selected parameters for the vertical excitation (UV-vis absorptions) of probes **1a**$^+$, **1d**$^+$ and their protonated forms based on the optimized ground state geometries in water.

probe	Electronic transitions	Excitation energy		$\lambda_{exp.}$/nm	f [a]	Composition[b]	CI[c]
		E/eV	λ/nm				
1a$^+$	$S_0 \rightarrow S_1$	2.10	589		0.1878	H-1 → L	0.67323
						H → L	0.18812
	$S_0 \rightarrow S_2$	2.25	551	546	0.7073	H-5 → L	-0.16339
						H-1 → L	-0.18626
						H → L	0.66030
1a$^+$+H$^+$	$S_0 \rightarrow S_1$	1.91	648	546	0.3199	H-4 → L	-0.10386
						H-1 → L	-0.18417
						H → L	0.67021
1d$^+$	$S_0 \rightarrow S_1$	2.21	561	563	0.7285	H-4 → L	0.21148
						H → L	0.67215
1d$^+$+H$^+$	$S_0 \rightarrow S_1$	1.34	928		0.0017	H → L	0.70705
	$S_0 \rightarrow S_3$	2.17	571	575	0.8106	H-2 → L+1	0.22710
						H → L+1	0.67312

[a] Oscillator strength. [b] H stands for HOMO and L stands for LUMO. [c] Coefficient of the wavefunction for each excitations.

Table S2. Selected parameters for emission related of probes **1a**$^+$, **1d**$^+$ and their protonated forms based on the optimized lowest singlet excited state geometries in water.

probe	Electronic transitions	Excitation energy		$\lambda_{exp.}$/nm	f^a	Composition^b	CI^c
		E/eV	λ/nm				
1a$^+$	$S_0 \rightarrow S_1$	1.31	945		0.0008	H → L	0.70383
	$S_0 \rightarrow S_2$	2.11	588	577	0.4473	H-5 → L	0.24400
						H-3 → L	0.29320
						H-1→ L	0.59353
1a$^+$+H$^+$	$S_0 \rightarrow S_1$	0.87	1420		0.0002	H → L	0.70688
	$S_0 \rightarrow S_3$	1.92	645	586	0.2113	H-5 → L	0.10441
						H-3 → L	-0.34419
						H-2 → L	0.12552
						H-1 → L	0.59496
1d$^+$	$S_0 \rightarrow S_1$	2.42	513	593	0.5861	H-1 → L	-0.36727
						H → L	0.60202
	$S_0 \rightarrow S_2$	2.52	492		0.3728	H-1 → L	0.60238
						H → L	0.36689
1d$^+$+H$^+$	$S_0 \rightarrow S_1$	0.97	1278		0.0006	H → L	0.70505
	$S_0 \rightarrow S_3$	2.34	531	615	0.8434	H-2 → L+1	-0.10032
						H → L+1	0.70135

[a] Oscillator strength. [b] H stands for HOMO and L stands for LUMO. [c] Coefficient of the wavefunction for each excitations.

3. Appendix

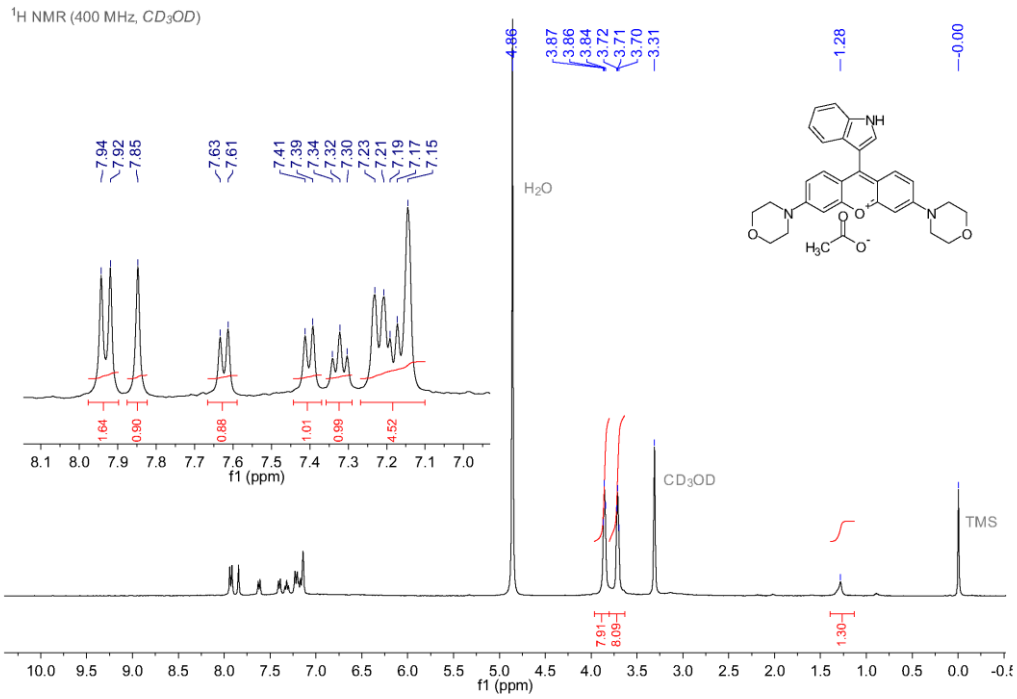


Fig. S7 ^{1}H NMR of probe **1a**.

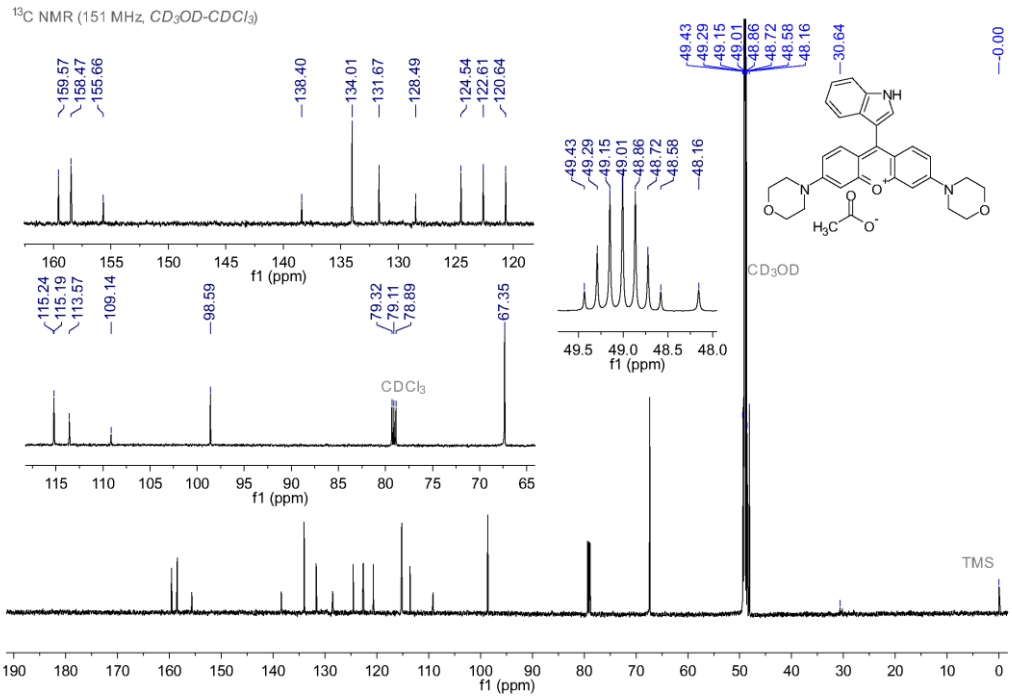


Fig. S8 ^{13}C NMR of probe **1a**.

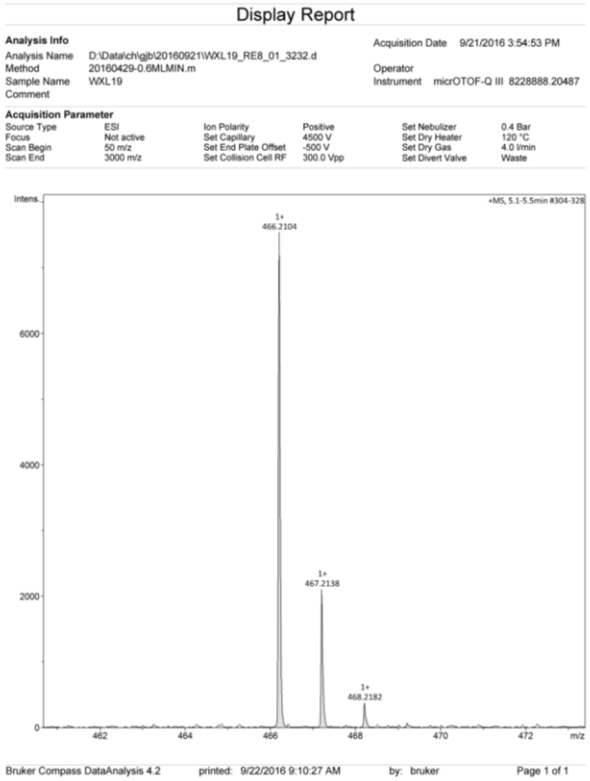


Fig. S9 HRMS of probe **1a**.

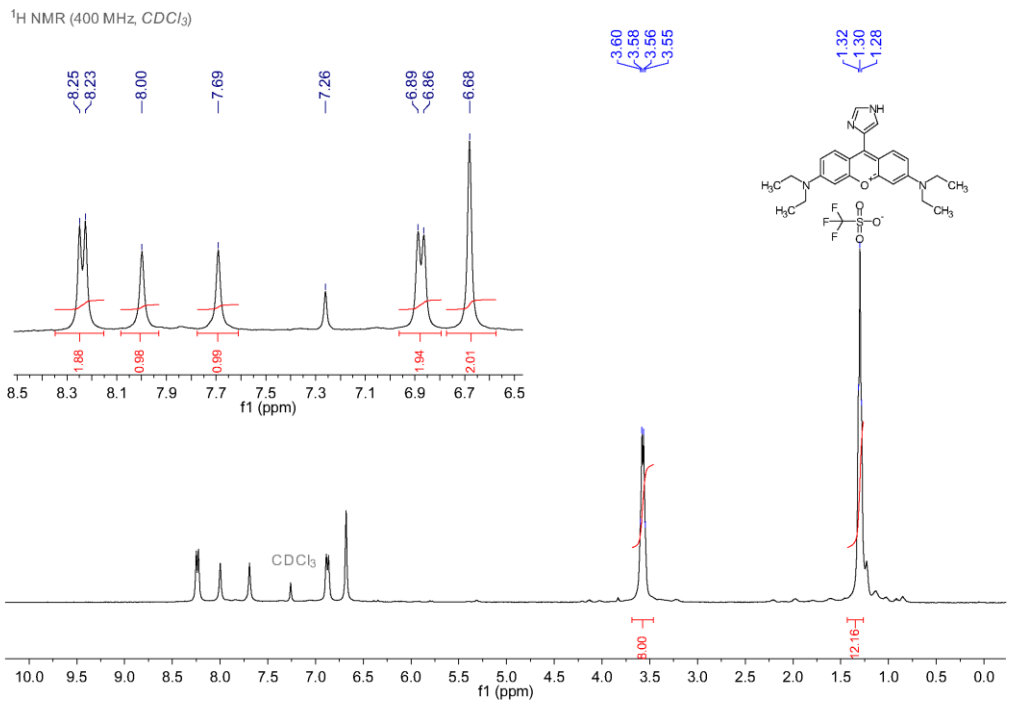


Fig. S10 ^{1}H NMR of probe **1b**.

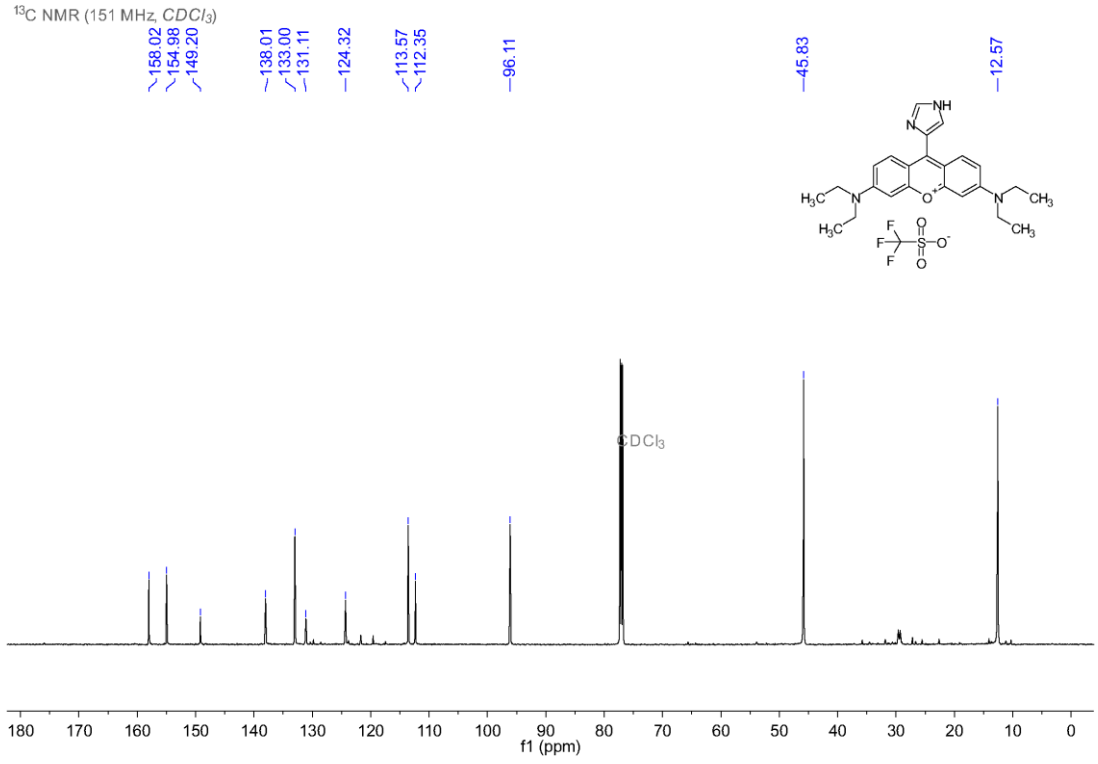


Fig. S11 ^{13}C NMR of probe **1b**.

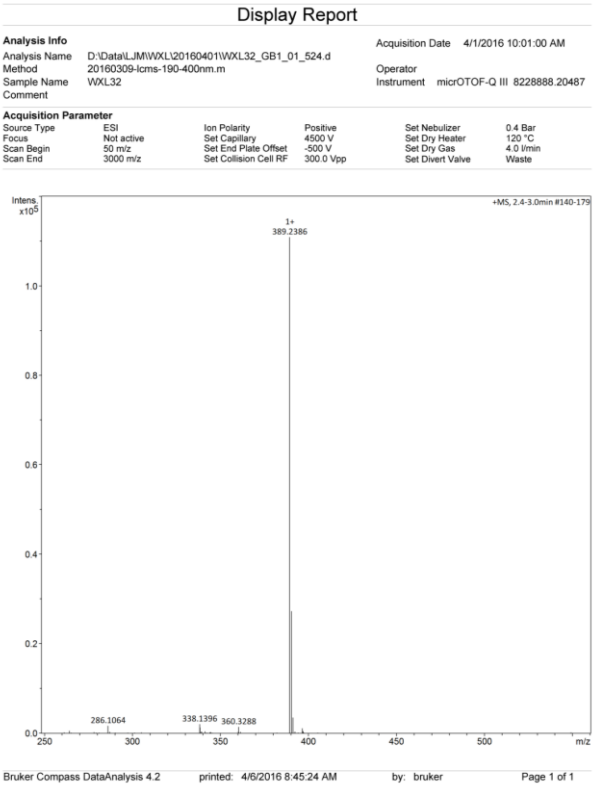


Fig. S12 HRMS of probe **1b**.

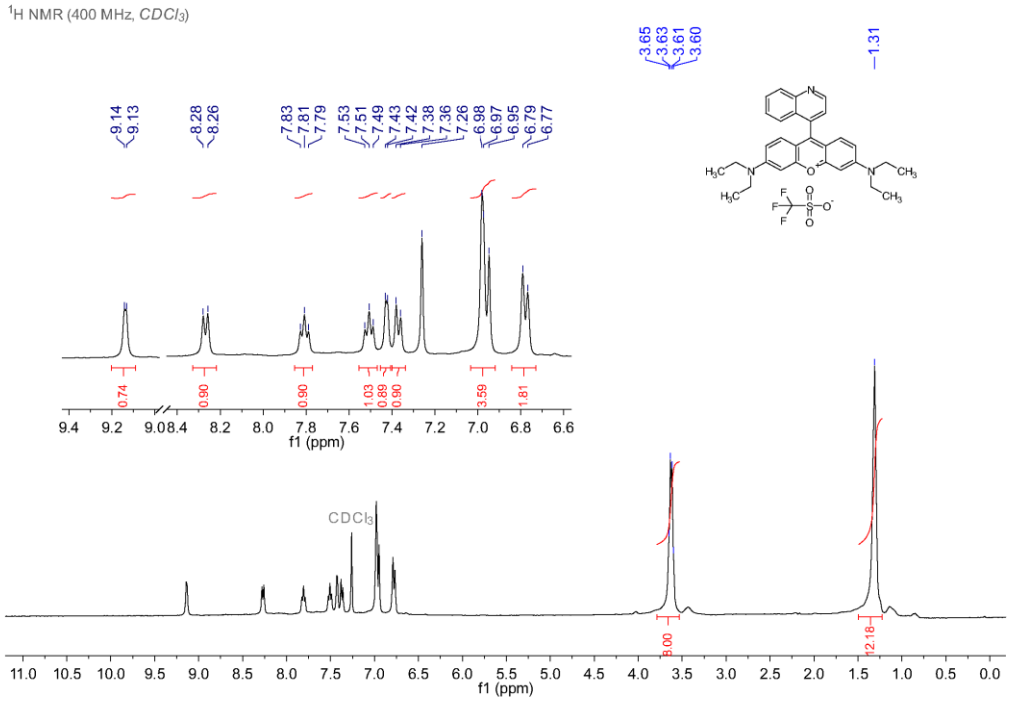


Fig. S13 ^{1}H NMR of probe **1c**.

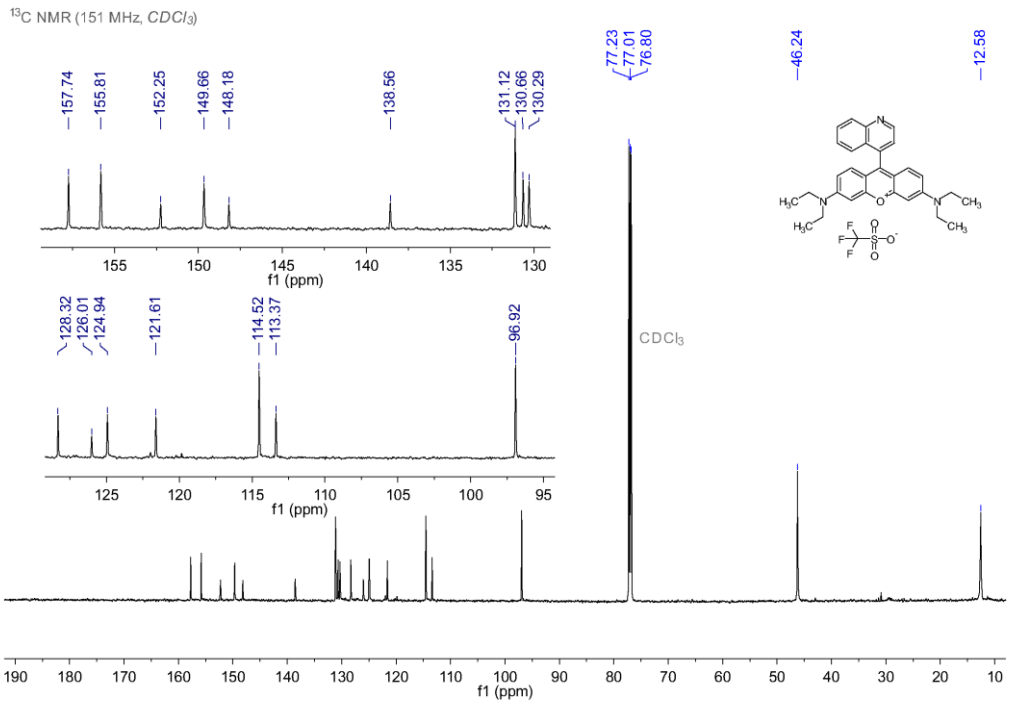


Fig. S14 ^{13}C NMR of probe **1c**.

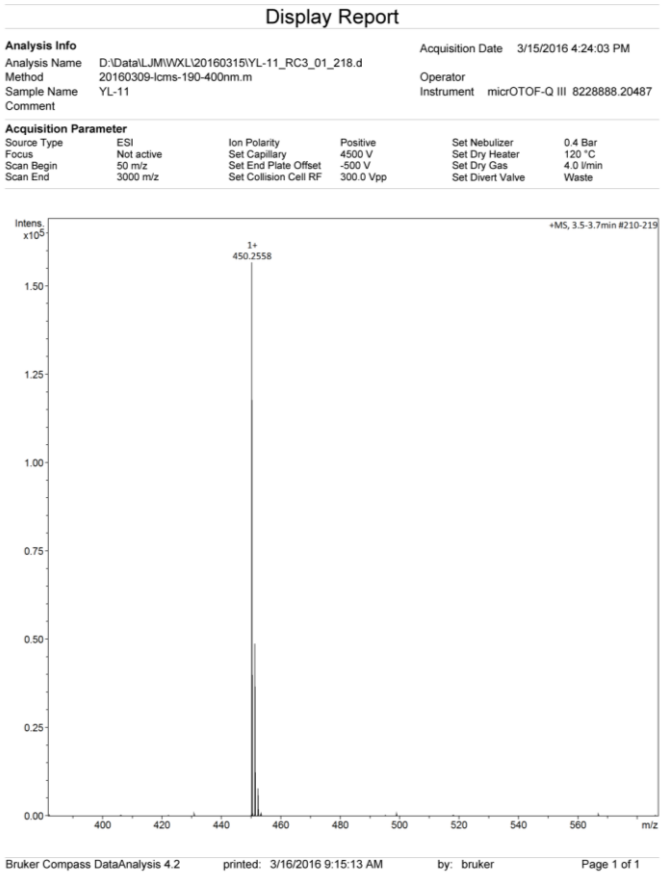


Fig. S15 HRMS of probe **1c**.

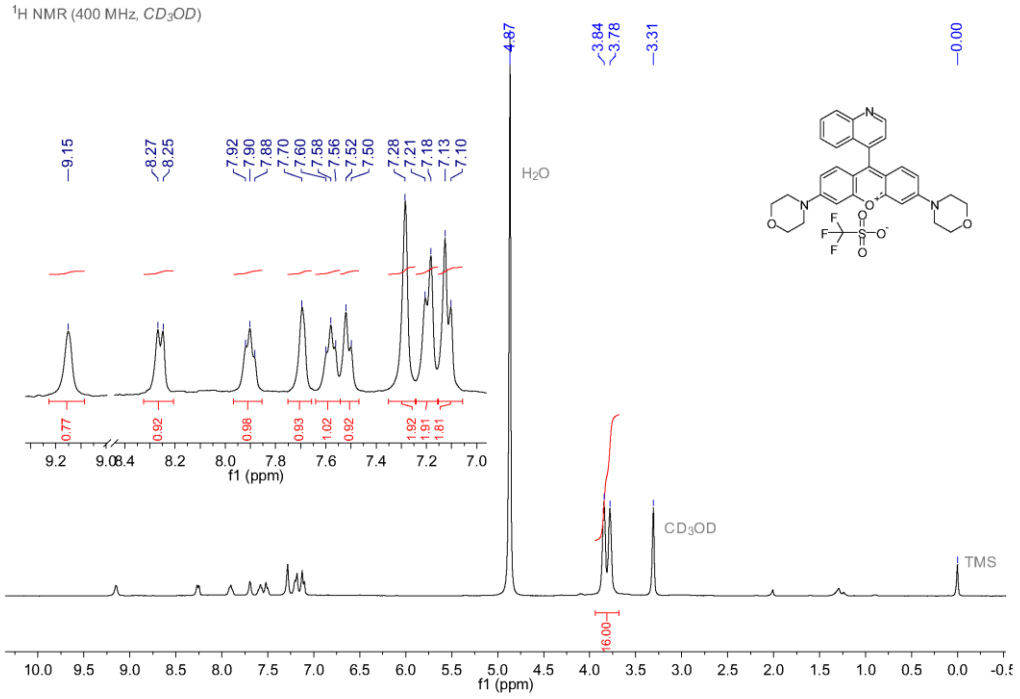


Fig. S16 ^{1}H NMR of probe **1d**.

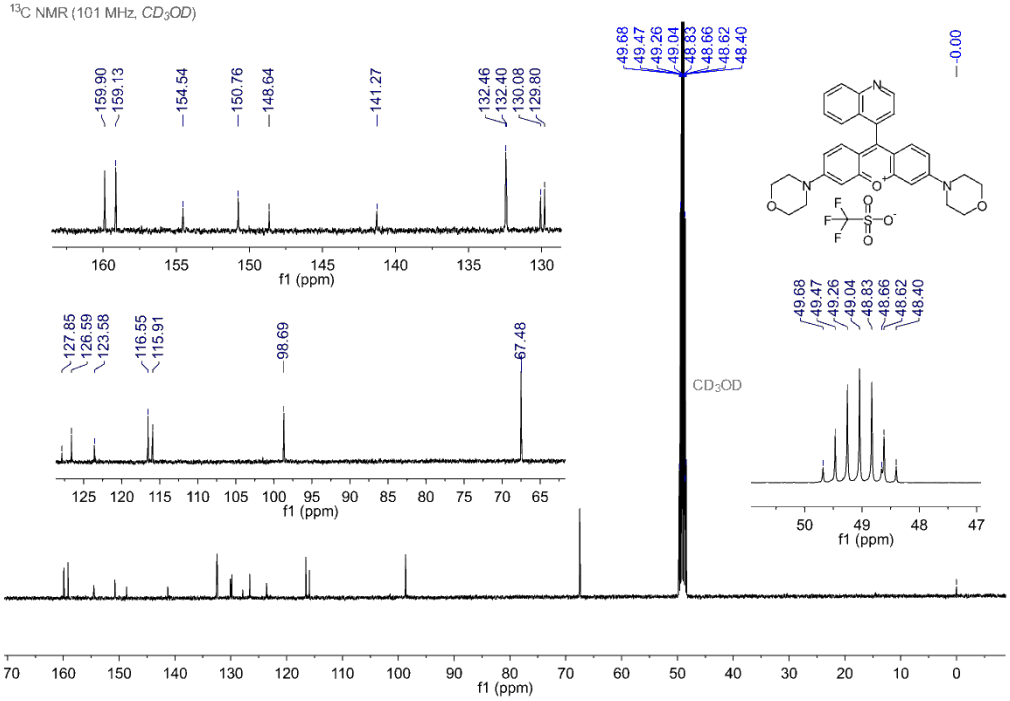


Fig. S17 ^{13}C NMR of probe **1d**.

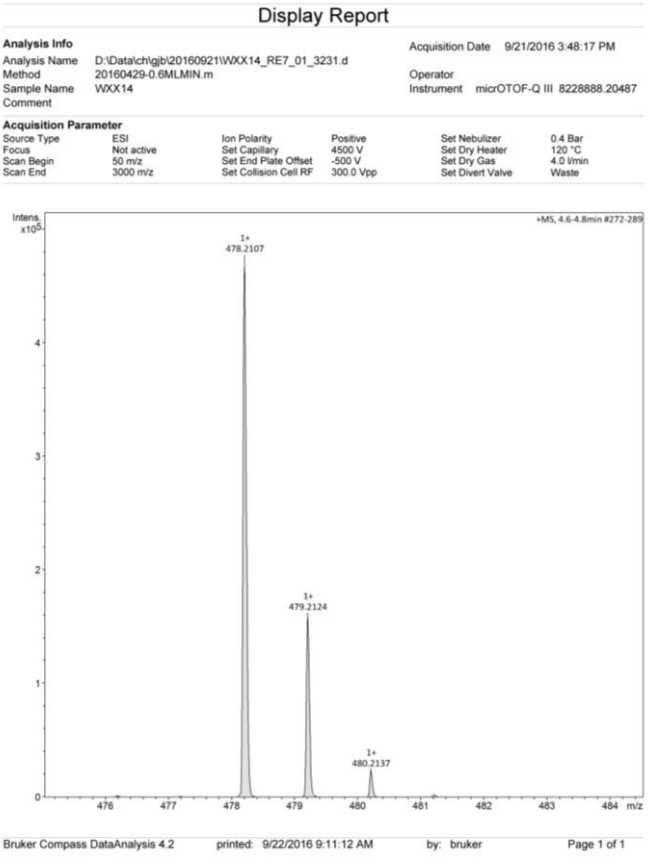


Fig. S18 HRMS of probe **1d**.