

Evaluation of electron or charge transfer processes between chromenylium-based fluorophores and protonated-deprotonated aniline

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(0.1 mM), Try (0.1 mM) and His (0.1 mM) were included: (a, c) tested in Britton-Robinson Buffer (pH = 7.0); (b, d) tested in Britton-Robinson Buffer (pH = 2.0).....	S7
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1. Figures

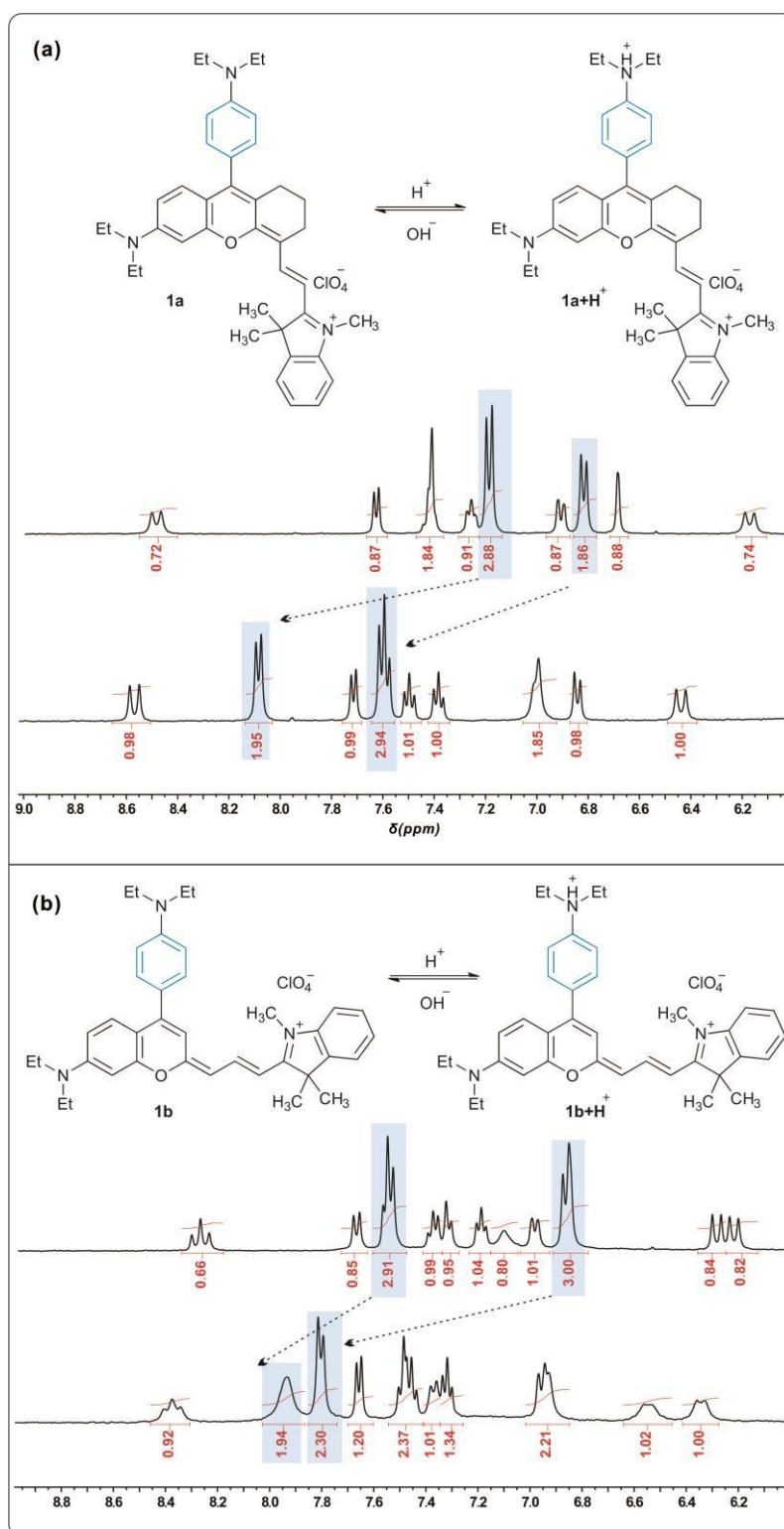


Fig. S1 ^1H NMR of dyes **1a-b** in DMSO- d_6 (top) and the acidic condition (bottom). (a) dye **1a**; (b) dye **1b**.

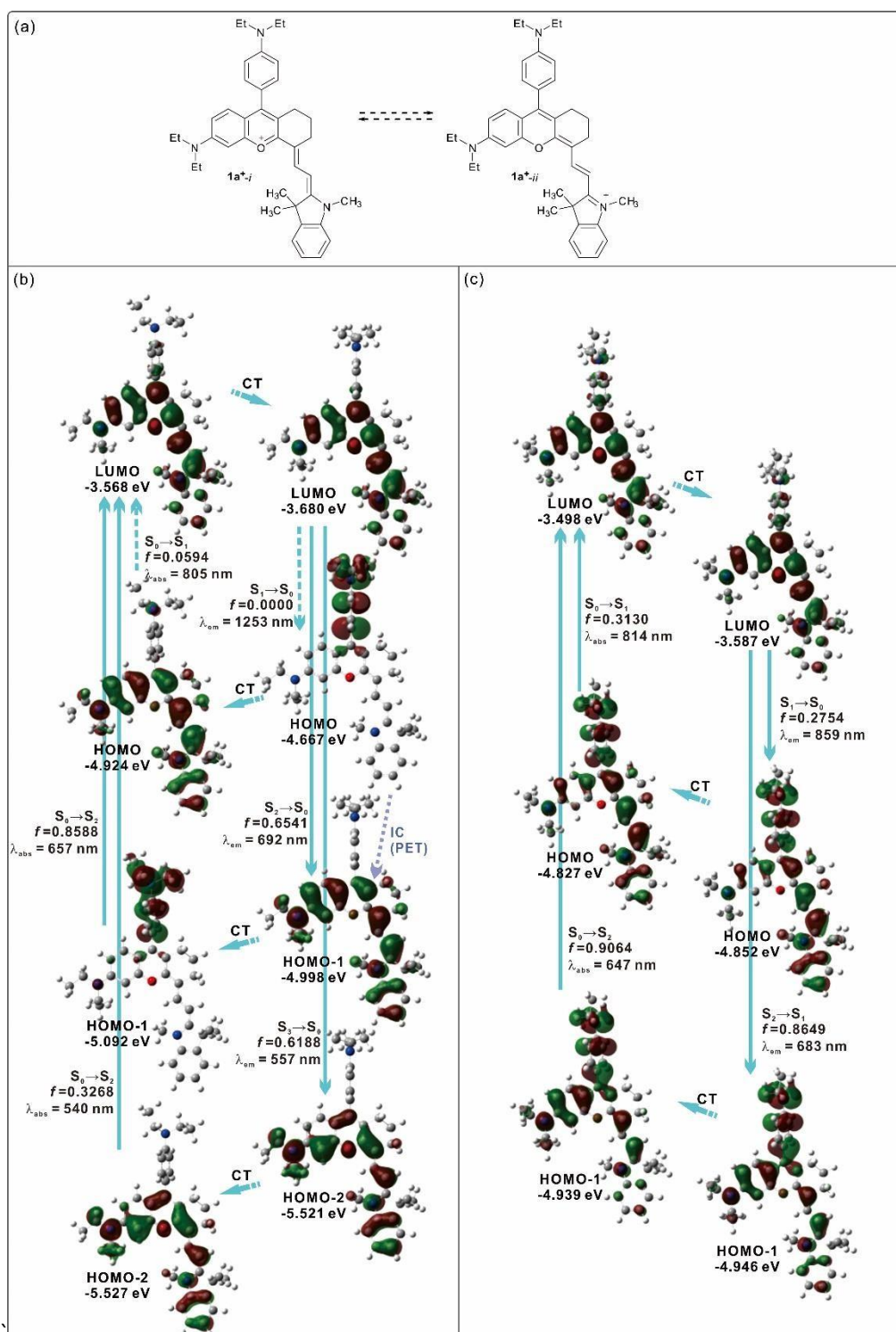


Fig. S2 The resonance equilibrium of $1a^+$ (a) and frontier molecular orbitals (FMOs) involved in the vertical excitation and emission of dyes $1a^{+i}$ (b) and $1a^{+ii}$ (c). CT stands for conformation transformation. Excitation and radiative processes are represented by solid lines and the nonradiative processes by dotted lines. For details please refer to Tables S2 and S3.

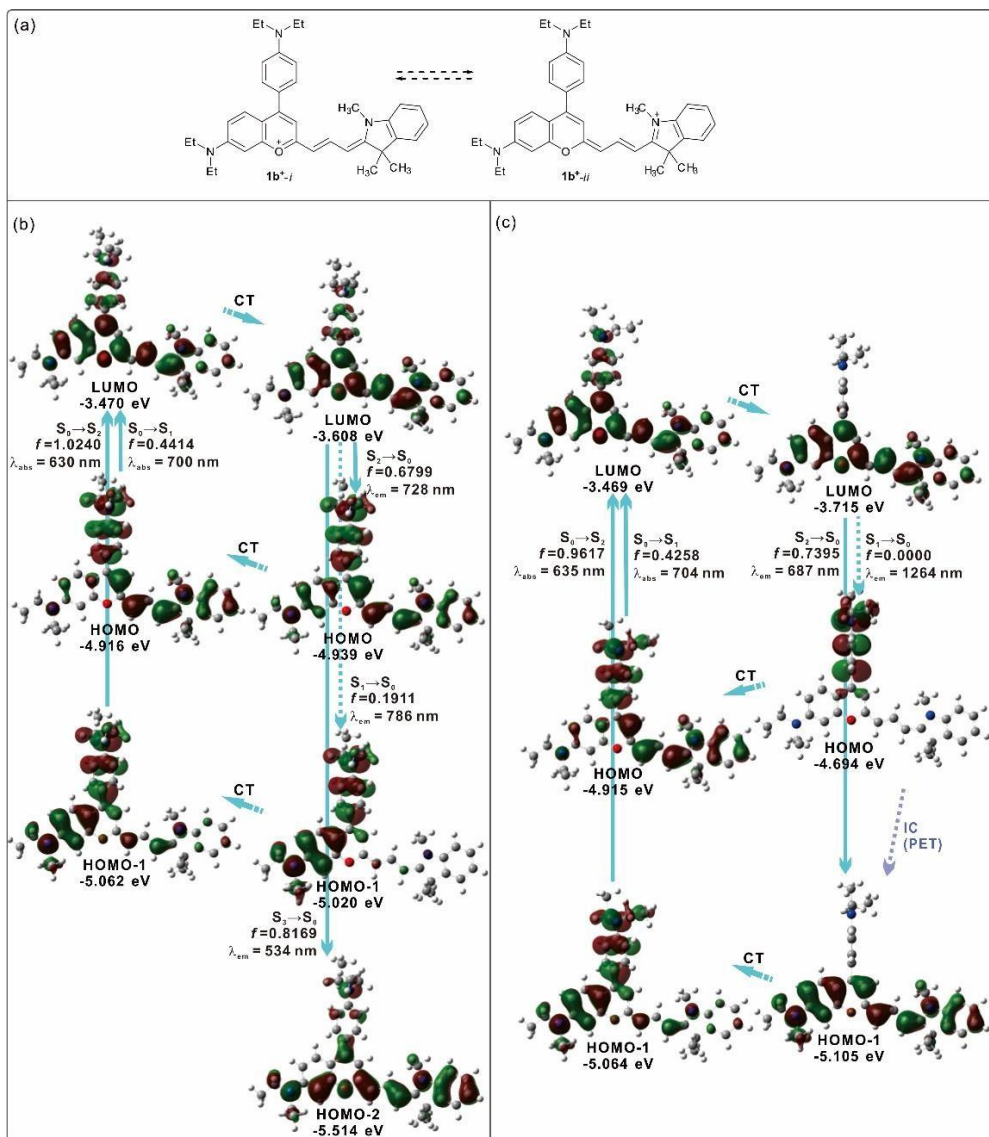


Fig. S3 The resonance equilibrium of $1b^{+}$ (a) and frontier molecular orbitals (FMOs) involved in the vertical excitation and emission of dyes $1b^{+i}$ (b) and $1b^{+ii}$ (c). CT stands for conformation transformation. Excitation and radiative processes are represented by solid lines and the nonradiative processes by dotted lines. For details please refer to Tables S2 and S3.

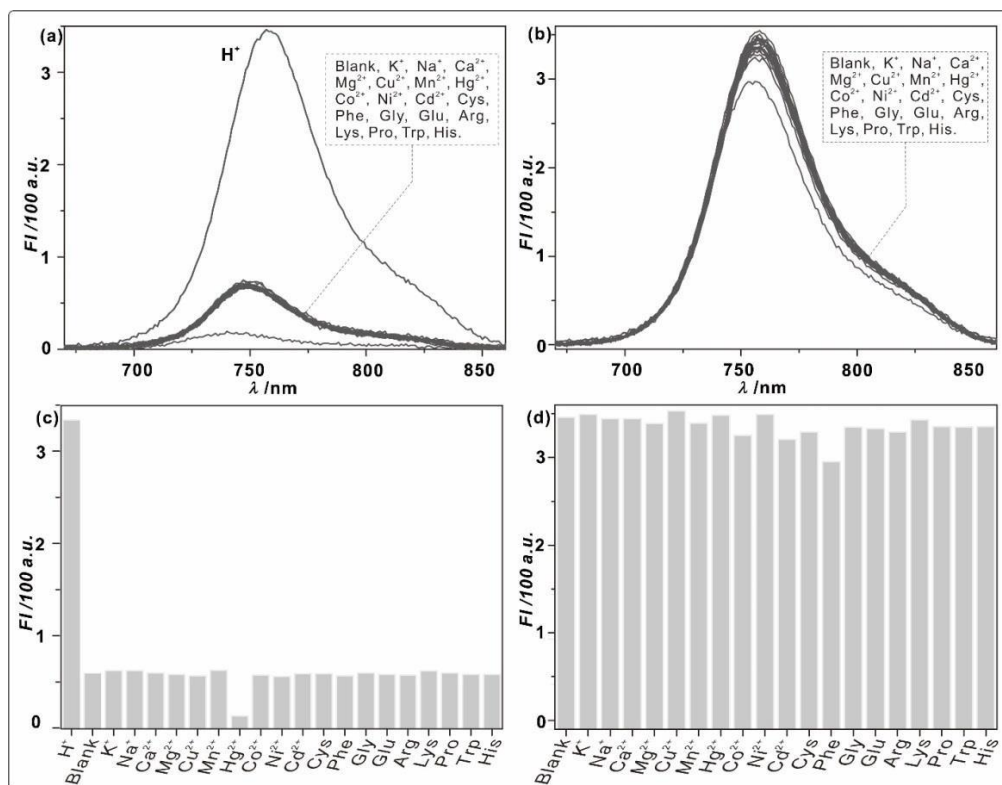


Fig. S4 Fluorescence responses of dye **1a** (10 μM) to different analytes, K^+ (100 mM), Na^+ (100 mM), Ca^{2+} (0.5 mM), Mg^{2+} (0.5 mM), Cd^{2+} (0.3 mM), Cu^{2+} (0.3 mM), Co^{2+} (0.3 mM), Hg^{2+} (0.3 mM), Mn^{2+} (0.3 mM), Ni^{2+} (0.3 mM), Cys (0.1 mM), Phe (0.1 mM), Gly (0.1 mM), Glu (0.1 mM), Arg (0.1 mM), Lys (0.1 mM), Pro (0.1 mM), Try (0.1 mM) and His (0.1 mM) were included: (a, c) tested in Britton-Robinson Buffer (pH = 7.0); (b, d) tested in Britton-Robinson Buffer (pH = 3.0).

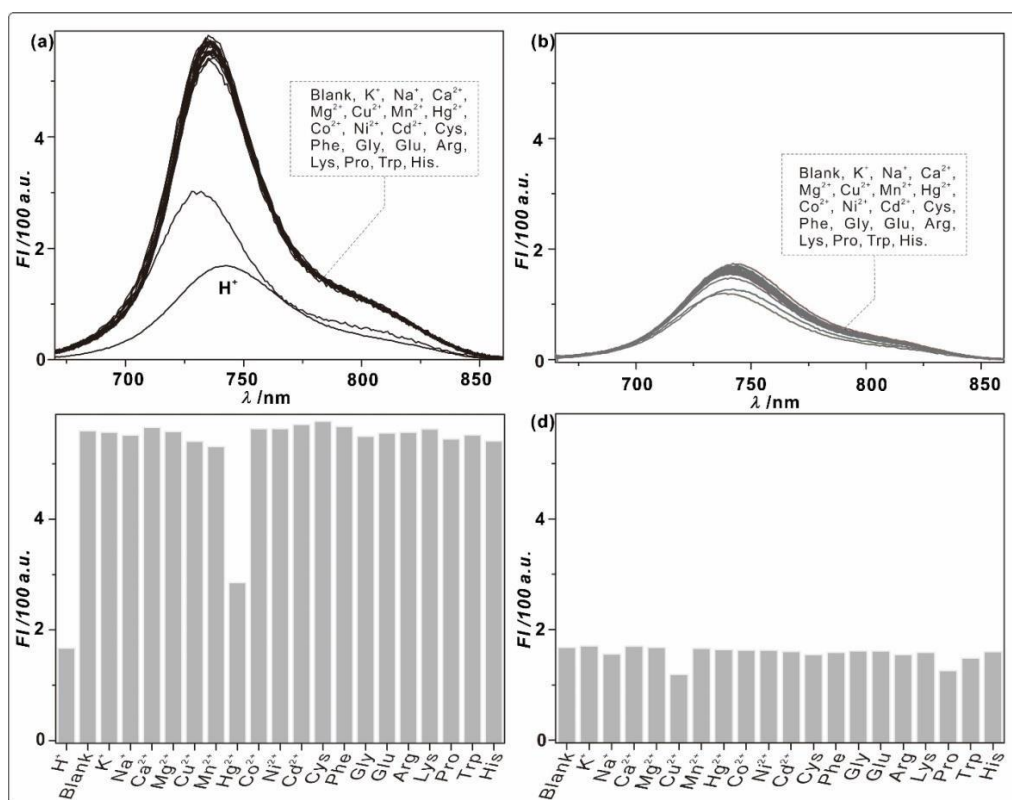


Fig. S5 Fluorescence responses of dye **1b** (10 μ M) to different analytes, K^+ (100 mM), Na^+ (100 mM), Ca^{2+} (0.5 mM), Mg^{2+} (0.5 mM), Cd^{2+} (0.3 mM), Cu^{2+} (0.3 mM), Co^{2+} (0.3 mM), Hg^{2+} (0.3 mM), Mn^{2+} (0.3 mM), Ni^{2+} (0.3 mM), Cys (0.1 mM), Phe (0.1 mM), Gly (0.1 mM), Glu (0.1 mM), Arg (0.1 mM), Lys (0.1 mM), Pro (0.1 mM), Try (0.1 mM) and His (0.1 mM) were included: (a, c) tested in Britton-Robinson Buffer (pH = 7.0); (b, d) tested in Britton-Robinson Buffer (pH = 2.0).

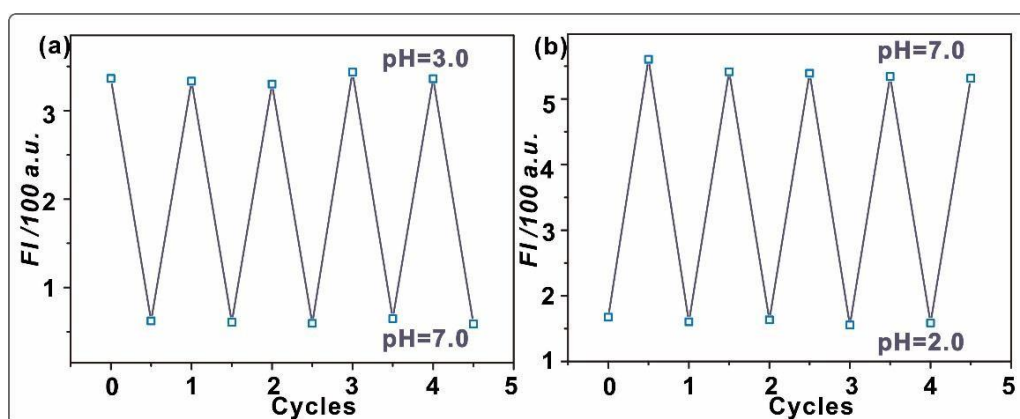


Fig. S6 The reversible optical responses of dyes **1a-b** at different pH conditions: (a) dye **1a**; (b) dye **1b**.

2. Tables

Table S1. Stability of different conjugated structures of dyes **1a⁺-c⁺** and their protonated forms.

Structures				
Dye No.	1a⁺-i	1a⁺-ii	1a⁺-i + H⁺	1a⁺-ii + H⁺
HF(hartree)	-1793.0302226	-1793.0418659 stable	-1793.4811741 stable	-1793.4792696
Structures				
Dye No.	1b⁺-i	1b⁺-ii	1b⁺-i + H⁺	1b⁺-ii + H⁺
HF(hartree)	-1676.268848	-1676.2689758 stable	-1676.7042854 stable	-1676.7042852 stable
Structures				
Dye No.	1c⁺-i	1c⁺-ii	1c⁺-i + H⁺	1c⁺-ii + H⁺
HF(hartree)	-1787.4815541 stable	-1787.4815541 stable	-1787.9135717 stable	-1787.9135717 stable

Table S2 Selected parameters for the vertical excitation (UV-vis absorptions) of dyes **1a⁺-c⁺** and **1c⁺+H⁺** based on the optimized ground state geometries in water.

dyes	Electronic transitions	Excitation energy		$\lambda_{\text{exp.}}/\text{nm}$	f^a	Composition ^b	CI ^c	
		E/eV	λ/nm					
1a⁺-i	S ₀ →S ₁	1.54	805	719	0.0594	H-1→L	0.68998	
						H→L	-0.15369	
						H→L	-0.15369	
	S ₀ →S ₂	1.89	657		0.8588	H-2→L	0.17744	
						H-1→L	0.15168	
						H→L	0.66923	
	S ₀ →S ₃	2.30	540		0.3268	H-2→L	0.64913	
						H→L	-0.17332	
						H→L+1	-0.21105	
1a⁺-ii	S ₀ →S ₁	1.52	814	719	0.3130	H-1→L	0.47843	
						H→L	0.52001	
						H→L	-0.13695	
	S ₀ →S ₂	1.92	647		0.9064	H-2→L	-0.13695	
						H-1→L	0.51057	
						H→L	-0.47092	
	S ₀ →S ₃	2.34	530		0.1881	H-2→L	0.65193	
						H-1→L+1	0.10090	
						H→L+1	-0.21809	
1b⁺-i	S ₀ →S ₁	1.77	700	702	0.4414	H-1→L	-0.44875	
						H→L	0.54037	
						H→L	0.54037	
	S ₀ →S ₂	1.97	630		1.0240	H-2→L	0.15884	
						H-1→L	0.51829	
						H→L	0.44391	
	S ₀ →S ₃	2.35	527		0.1316	H-2→L	0.62009	
						H→L+1	-0.30807	
						H→L+1	-0.30807	
1b⁺-ii	S ₀ →S ₁	1.76	704	702	0.4258	H-1→L	0.44039	
						H→L	0.54760	
						H→L	0.54760	
	S ₀ →S ₂	1.95	635		0.9617	H-2→L	0.16250	
						H-1→L	0.52590	
						H→L	-0.43315	
	S ₀ →S ₃	2.34	529		0.1490	H-2→L	0.62225	
						H→L+1	0.29875	
						H→L+1	0.29875	
1c⁺-i, 1c⁺-ii	S ₀ →S ₁	1.76	703		0.5880	H-1→L	-0.14753	
						H→L	0.67363	
						H→L+1	0.13549	
	S ₀ →S ₂	1.89	656	583	0.9505	H-1→L	0.67754	
						H→L	0.16885	
						H→L	0.16885	
	1c⁺-i + H⁺ 1c⁺-ii + H⁺	S ₀ →S ₁	1.84	674	668	0.9585	H-1→L	-0.10442
							H→L	0.69856
		S ₀ →S ₂	2.11	588		0.1557	H-1→L	0.64355
					H→L	-0.27374		

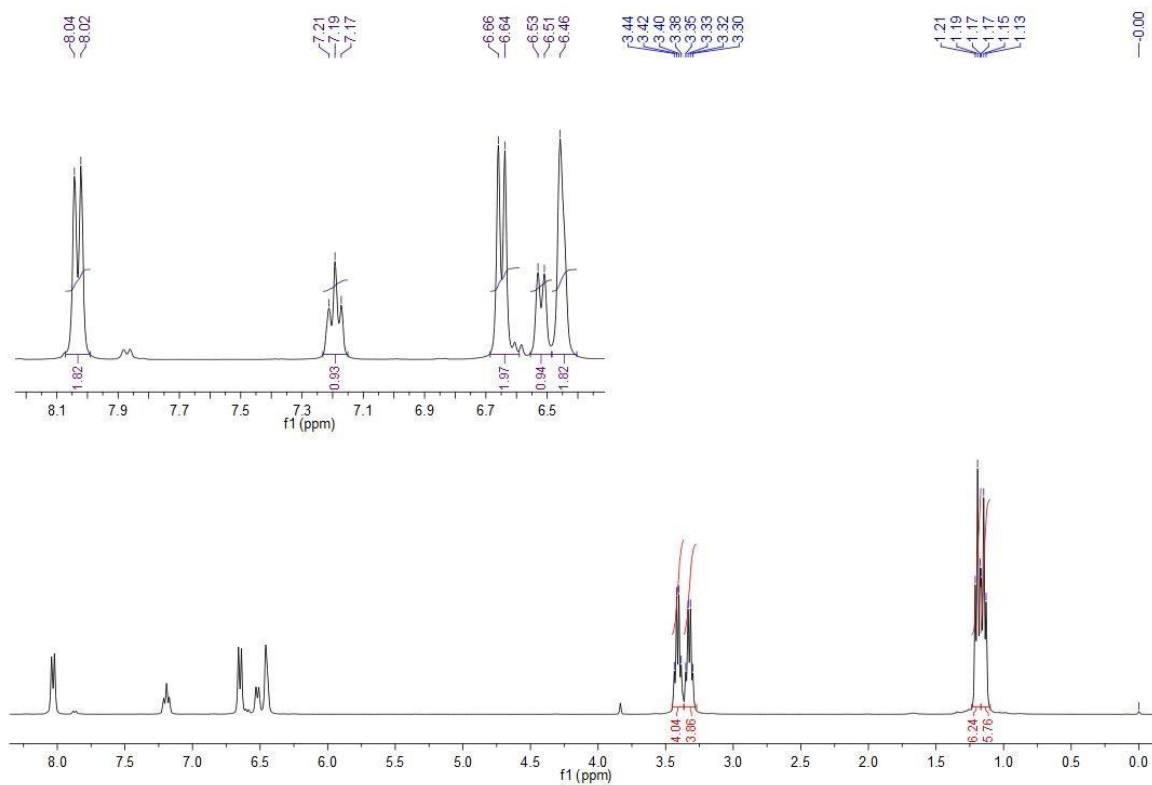
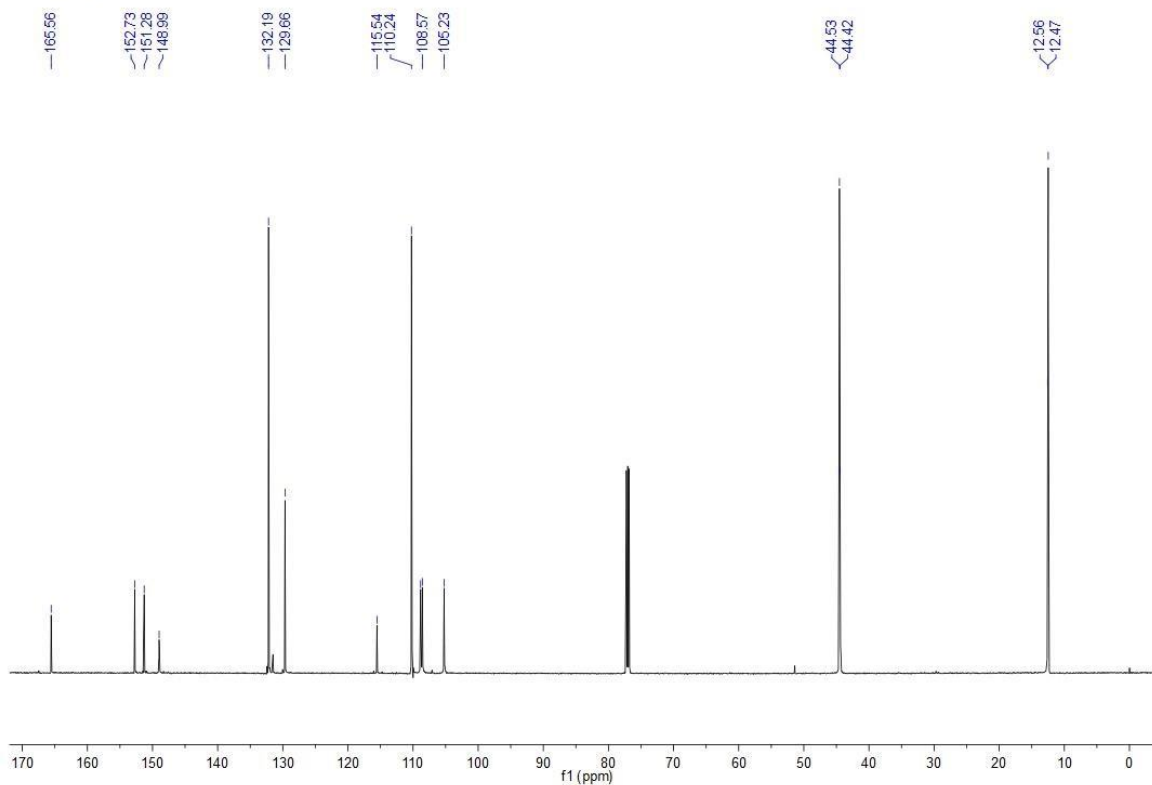
^a Oscillator strength. ^b H stands for HOMO and L stands for LUMO. ^c Coefficient of the wave function for each excitations.

Table S3 Selected parameters for emission related of dyes **1a⁺-c⁺** and **1c⁺+H⁺** based on the optimized lowest singlet excited state geometries in water.

dyes	Electronic transitions	Excitation energy		$\lambda_{\text{exp.}}/\text{nm}$	f^a	Composition ^b	CI ^c	
		E/eV	λ/nm					
1a⁺-i	S ₀ →S ₁	0.99	1253		0.0001	H→L	0.70704	
	S ₀ →S ₂	1.79	692	749	0.6541	H-2→L	0.24650	
						H-1→L	0.66110	
	S ₀ →S ₃	2.22	557			0.6188	H-2→L	0.63765
H-1→L							-0.25265	
1a⁺-ii	S ₀ →S ₁	1.44	859		0.2754	H-1→L	0.48779	
	S ₀ →S ₂	1.82	683	749	0.8649	H→L	0.51099	
						H-1→L	0.50836	
1b⁺-i	S ₀ →S ₁	1.58	786		0.1911	H-1→L	0.64202	
	S ₀ →S ₂	1.70	728	736	0.6799	H→L	-0.28502	
						H-2→L	-0.21337	
						H-1→L	0.26429	
	S ₀ →S ₃	2.32	534		0.8169	H→L	0.61837	
						H-2→L	0.62598	
1b⁺-ii	S ₀ →S ₁	0.98	1264		0.0000	H→L	0.70710	
	S ₀ →S ₂	1.80	687	736	0.7395	H-2→L	0.27270	
						H-1→L	0.64718	
1c⁺-i, 1c⁺-ii	S ₀ →S ₁	0.69	1804		0.0000	H→L	0.70710	
	S ₀ →S ₂	1.80	689	691	0.7900	H-2→L	0.19666	
1c⁺-j + H⁺ 1c⁺-ii + H⁺	S ₀ →S ₁	0.76	1641		0.0000	H→L	0.67687	
	S ₀ →S ₂	1.96	631	719	0.0078	H-2→L	0.69752	
						H-1→L	0.11469	
	S ₀ →S ₃	2.02	615			0.3000	H-2→L	-0.11572
							H-1→L	0.68645
	S ₀ →S ₈	2.85	435			0.4055	H→L+1	0.57753
							H→L+2	0.24345
							H→L+3	0.13786
H→L+4							0.25217	

^a Oscillator strength. ^b H stands for HOMO and L stands for LUMO. ^c Coefficient of the wave function for each excitations.

4. Appendix

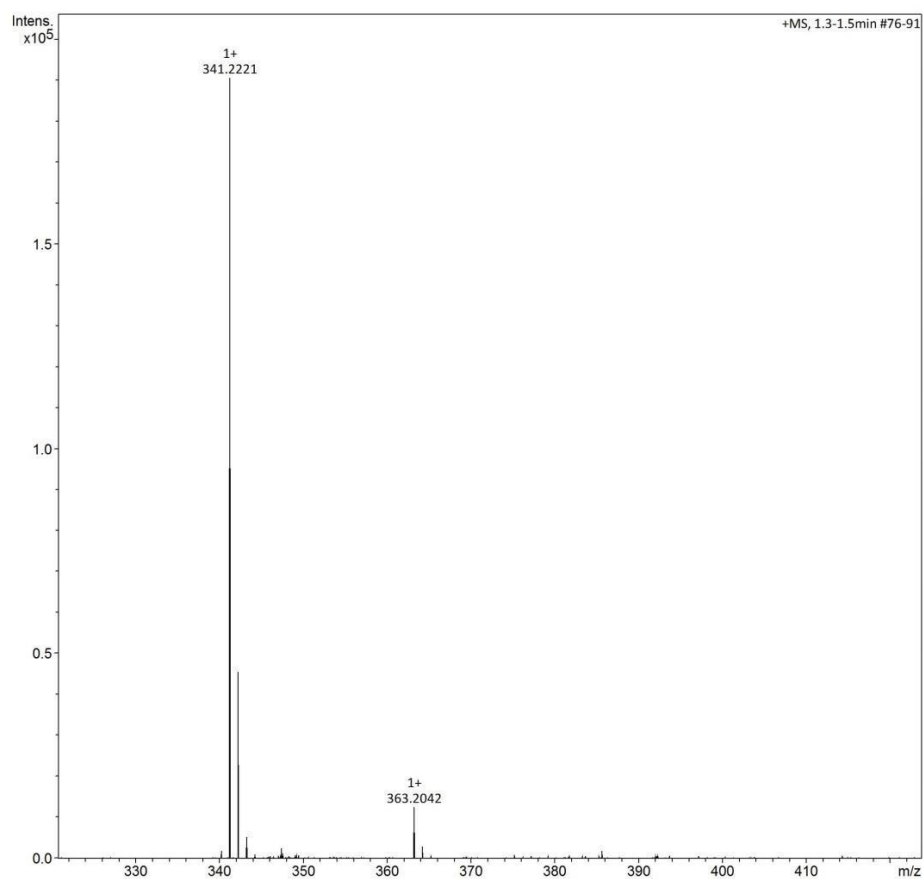
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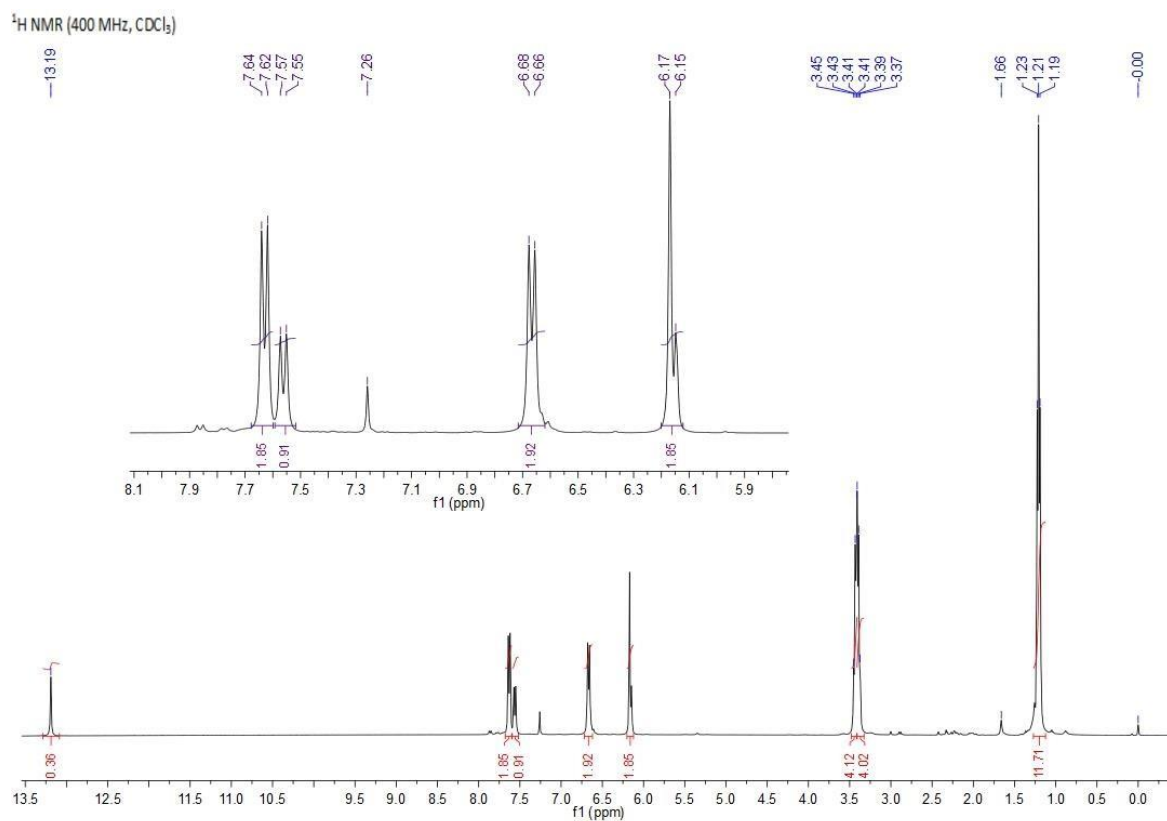
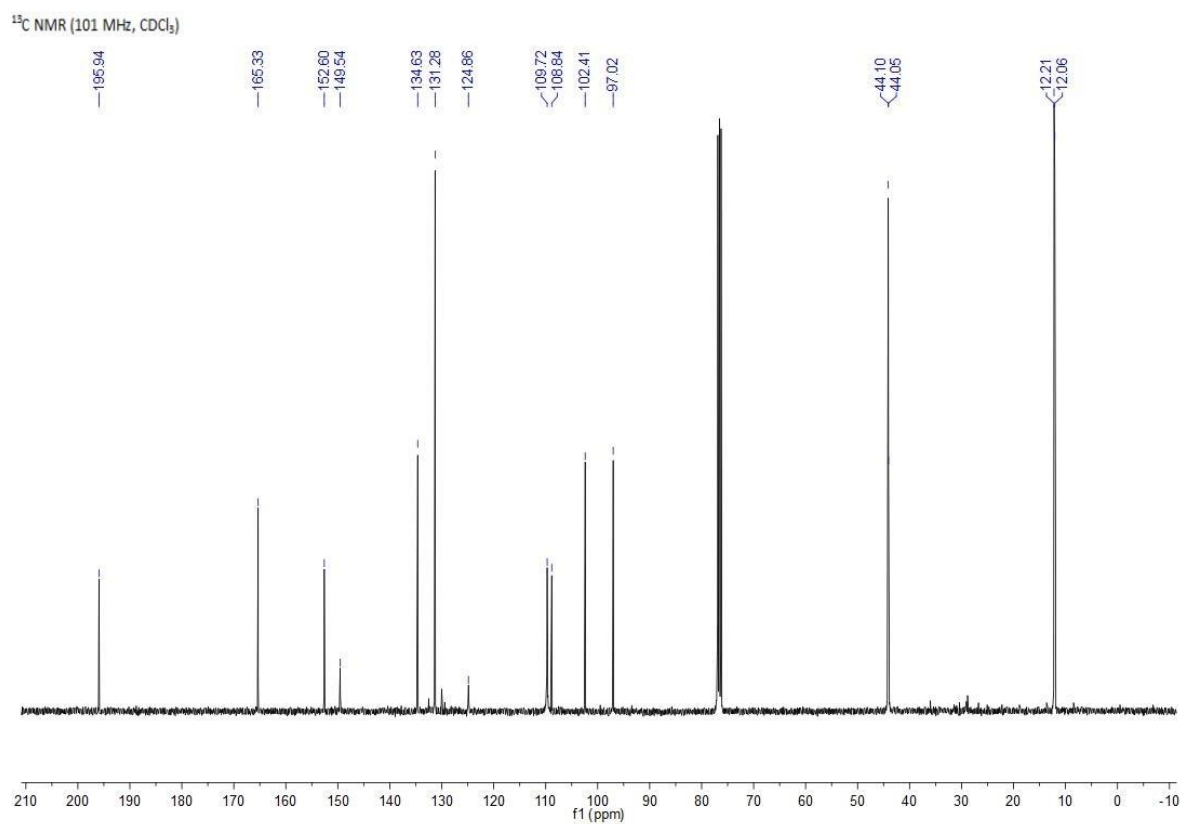
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Fig. S9 HRMS(ESI⁺) of **3**.

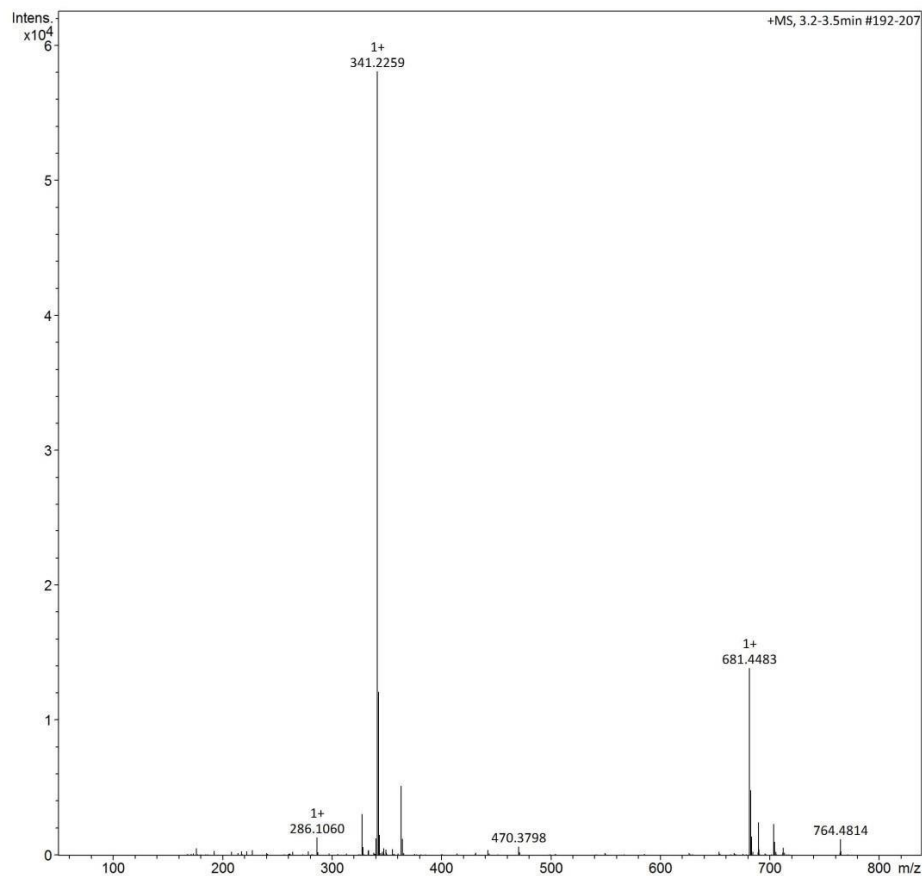
Fig. S10 ^1H NMR of **4**.Fig. S11 ^{13}C NMR of **4**.

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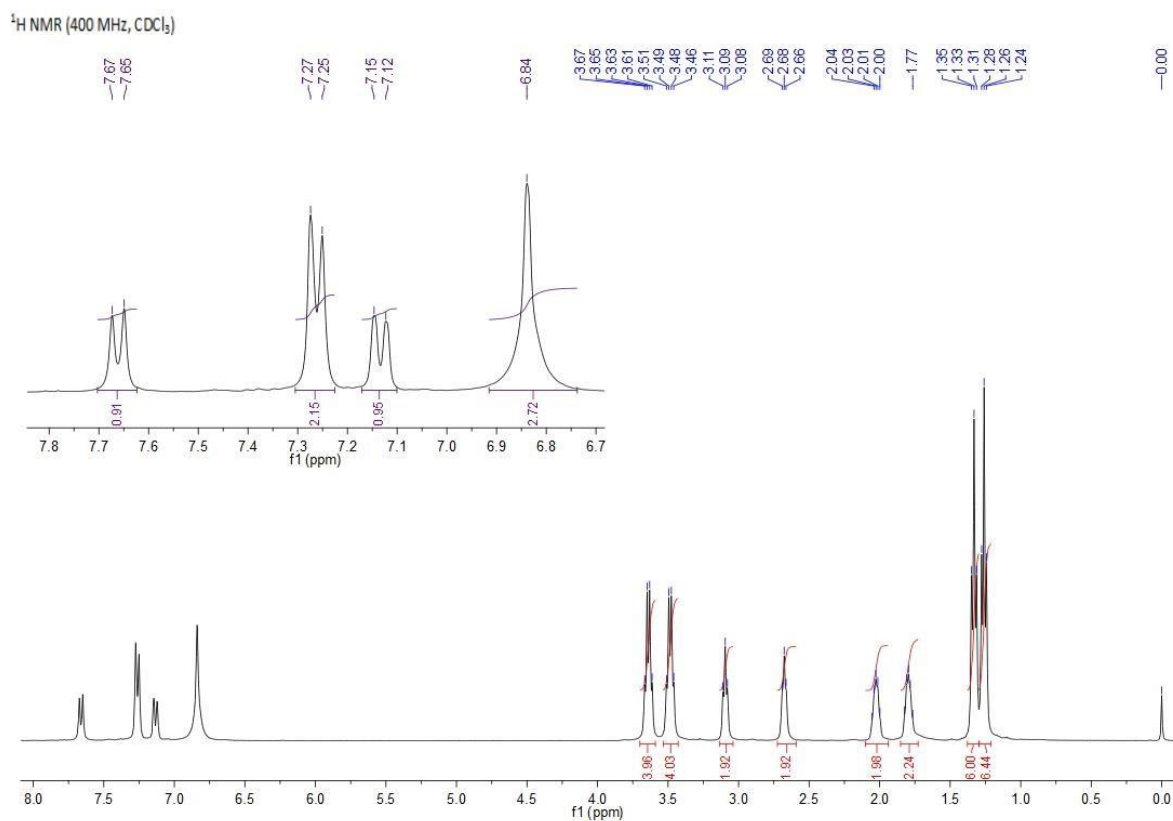
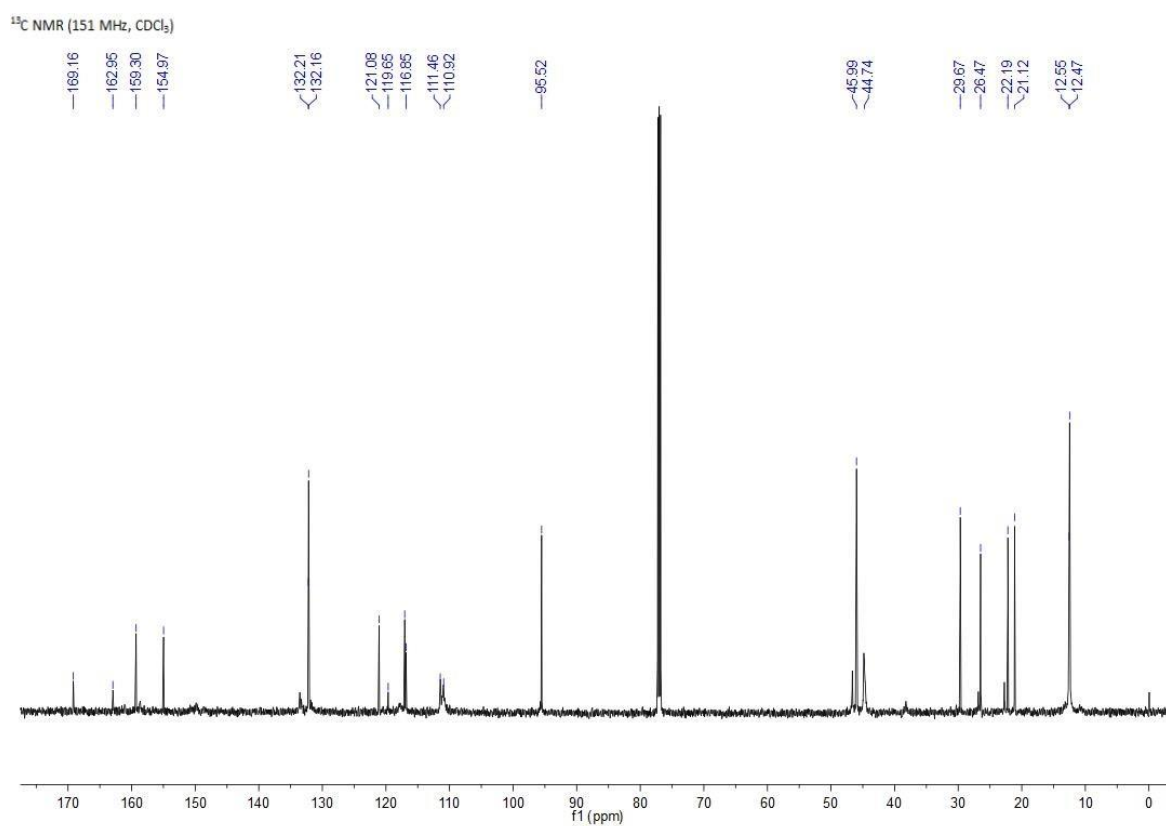
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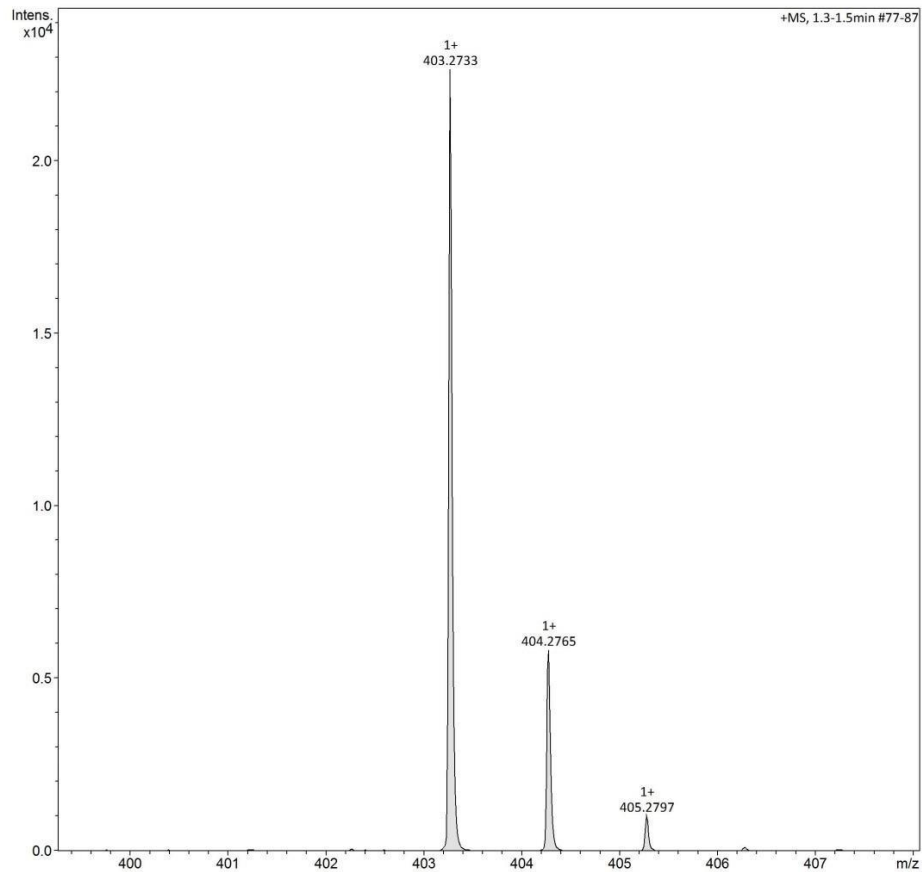
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Fig. S12 HRMS(ESI⁺) of **4**.

Fig. S13 ^1H NMR of 5.Fig. S14 ^{13}C NMR of 5.

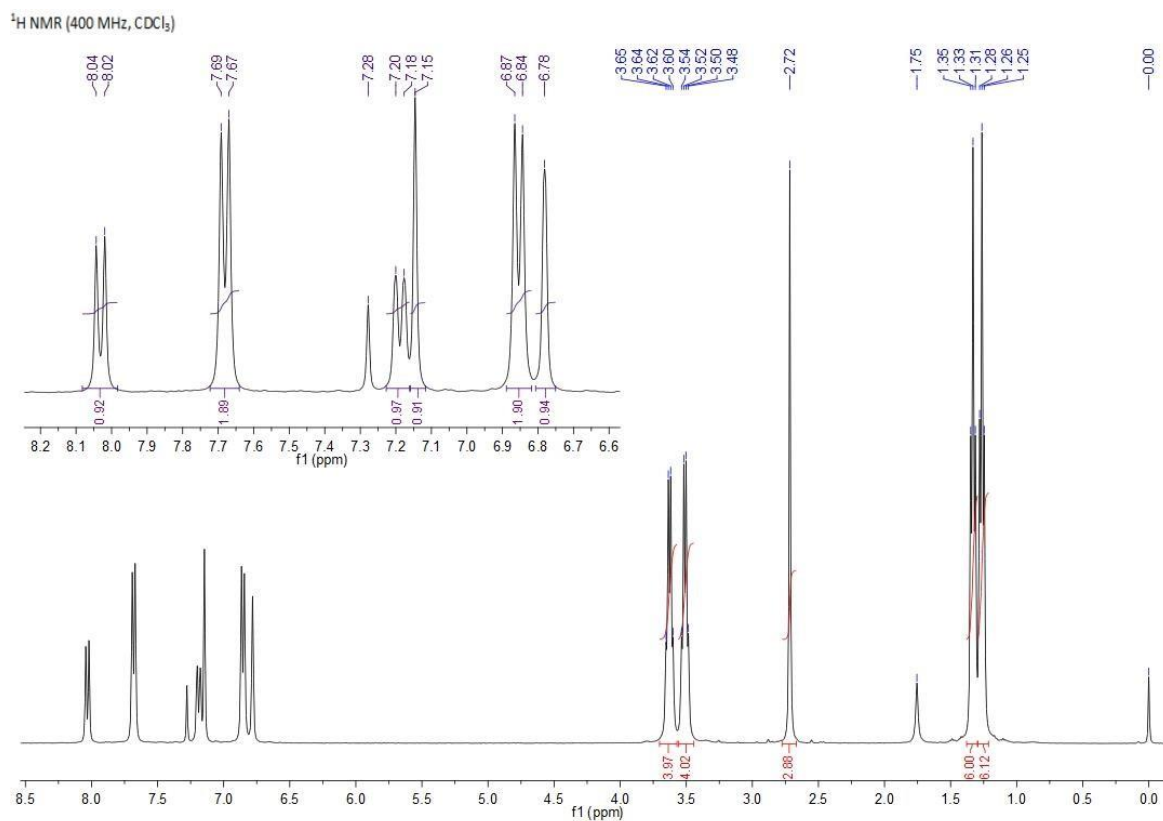
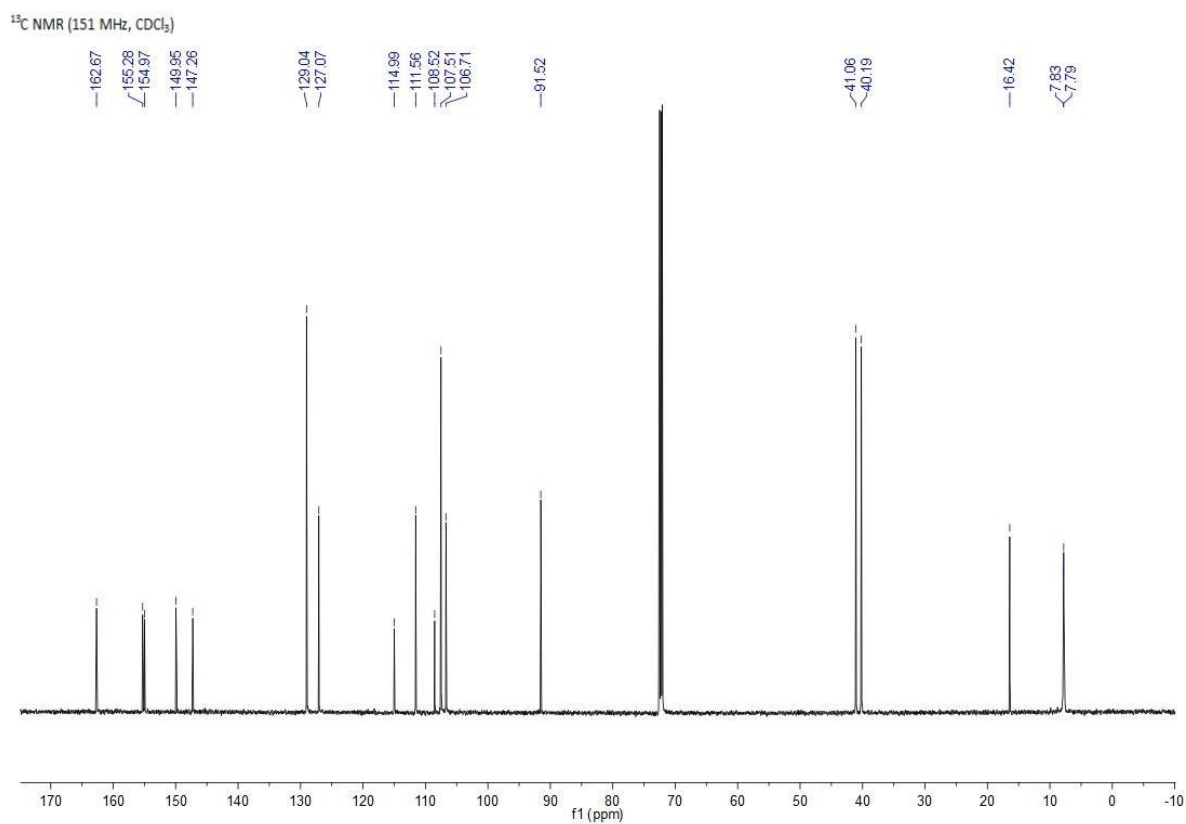
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Fig. S15 HRMS(ESI+) of 5.

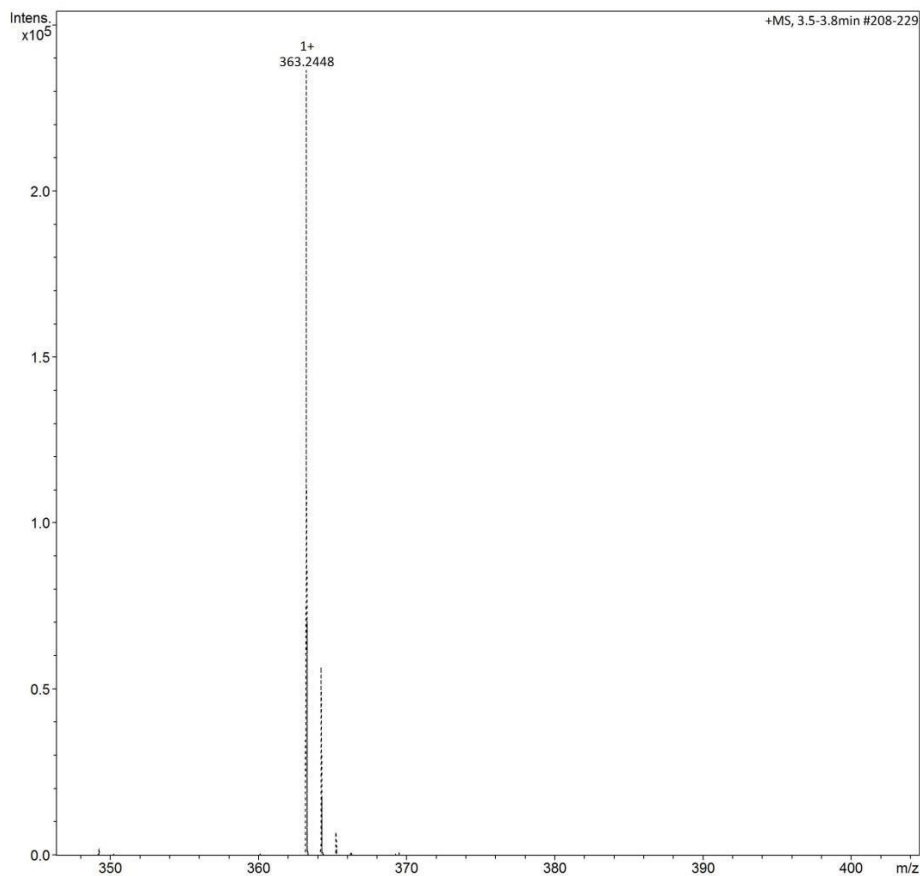
Fig. S16 ^1H NMR of **6**.Fig. S17 ^{13}C NMR of **6**.

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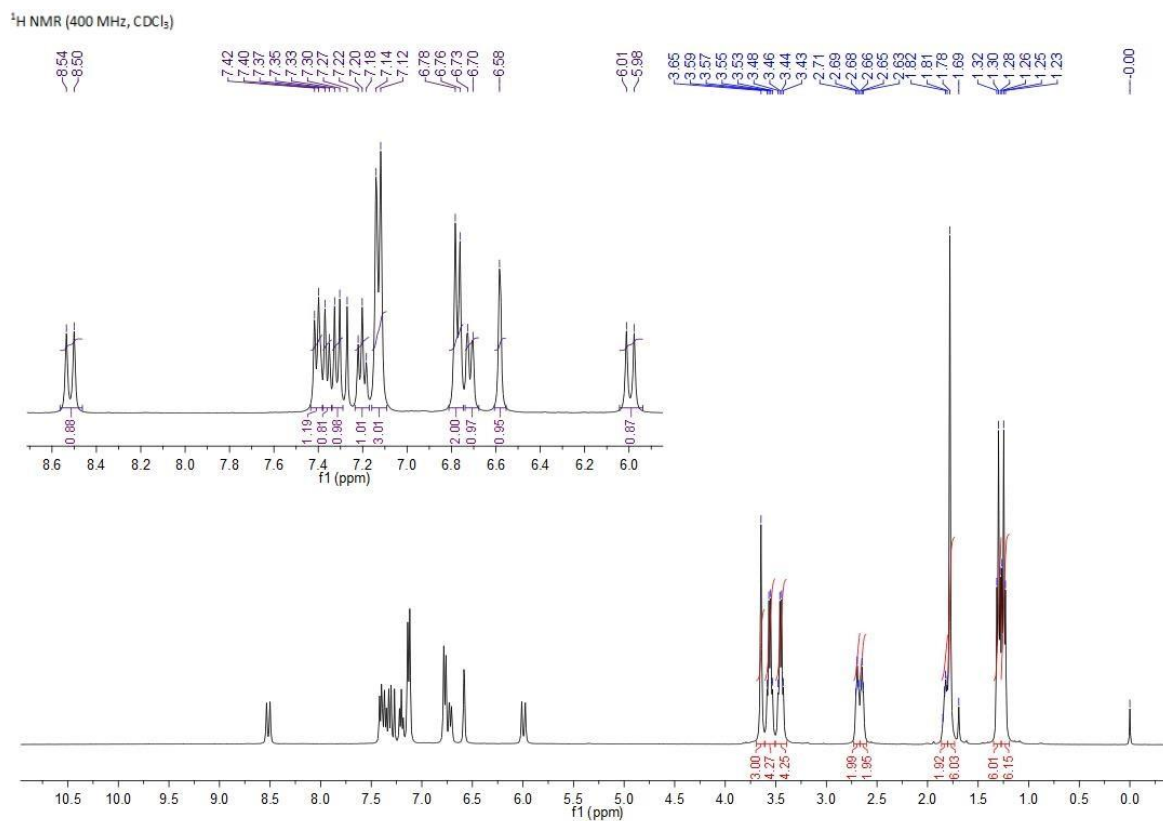
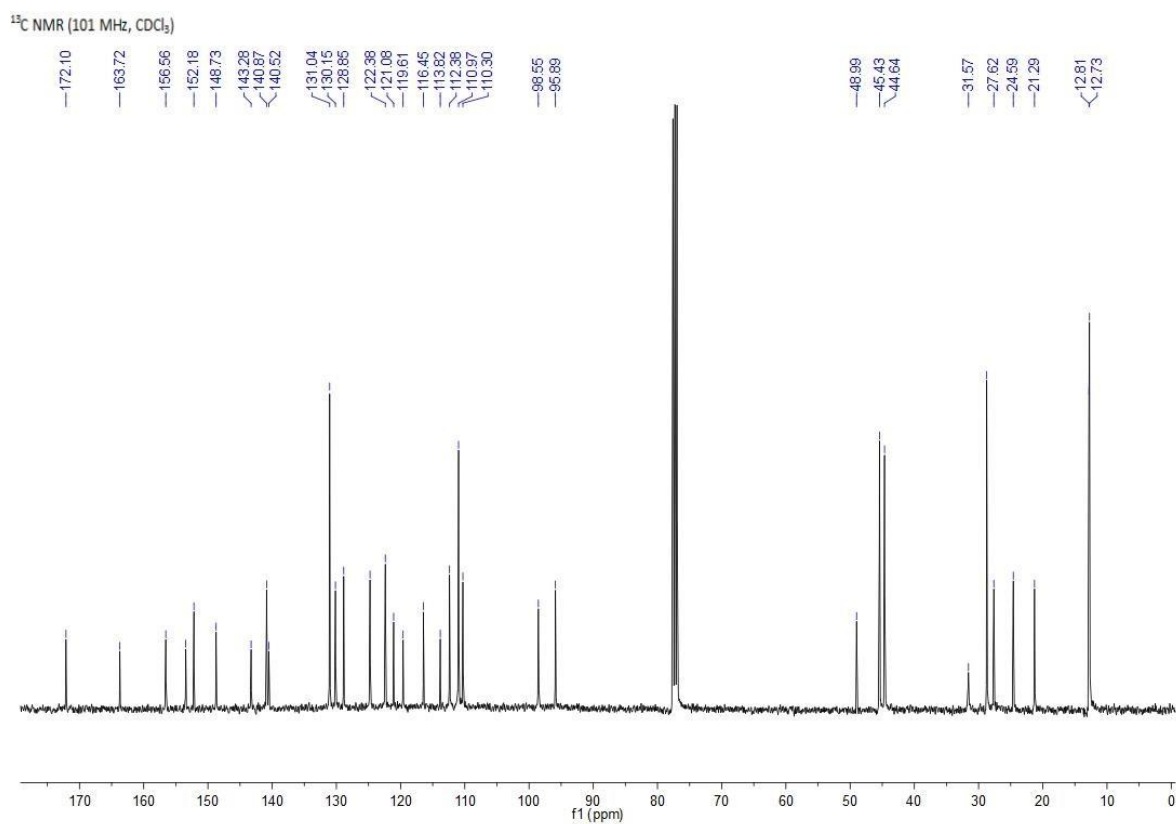
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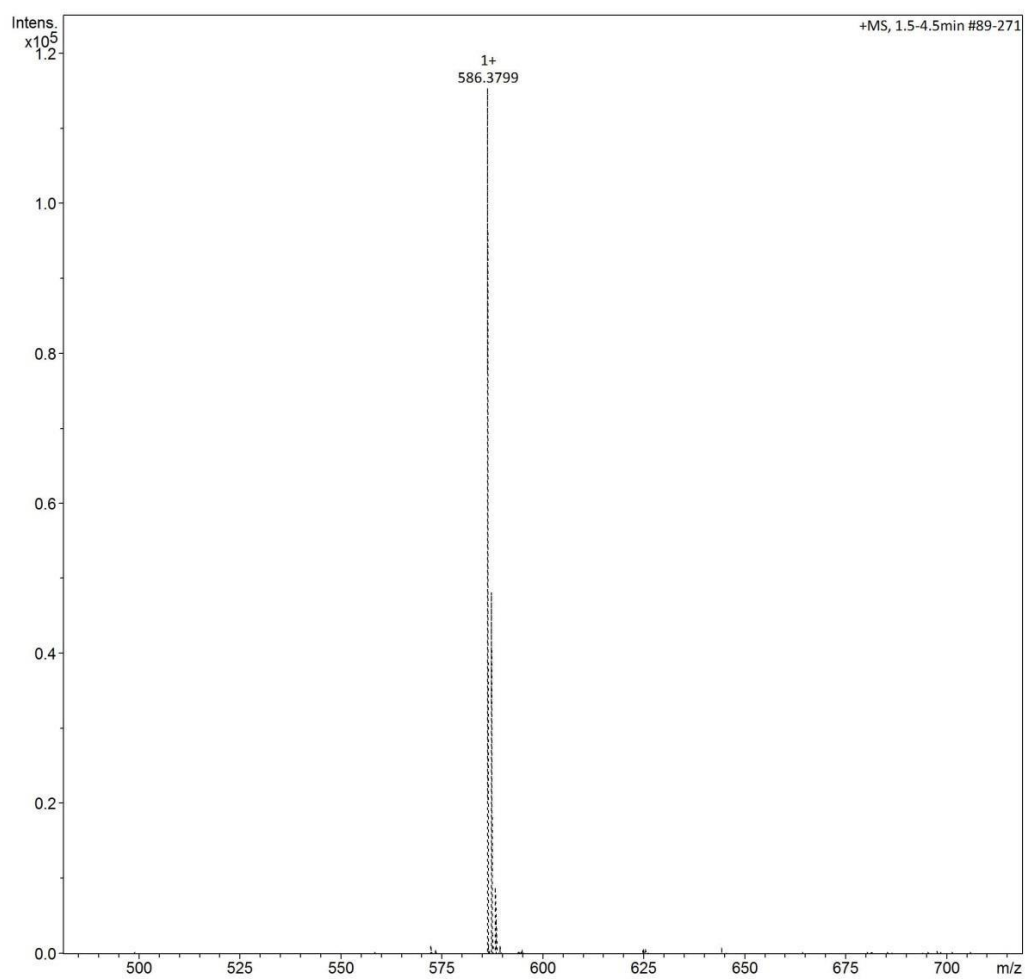
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Fig. S19 ^1H NMR of dye **1a**.Fig. S20 ^{13}C NMR of dye **1a**.

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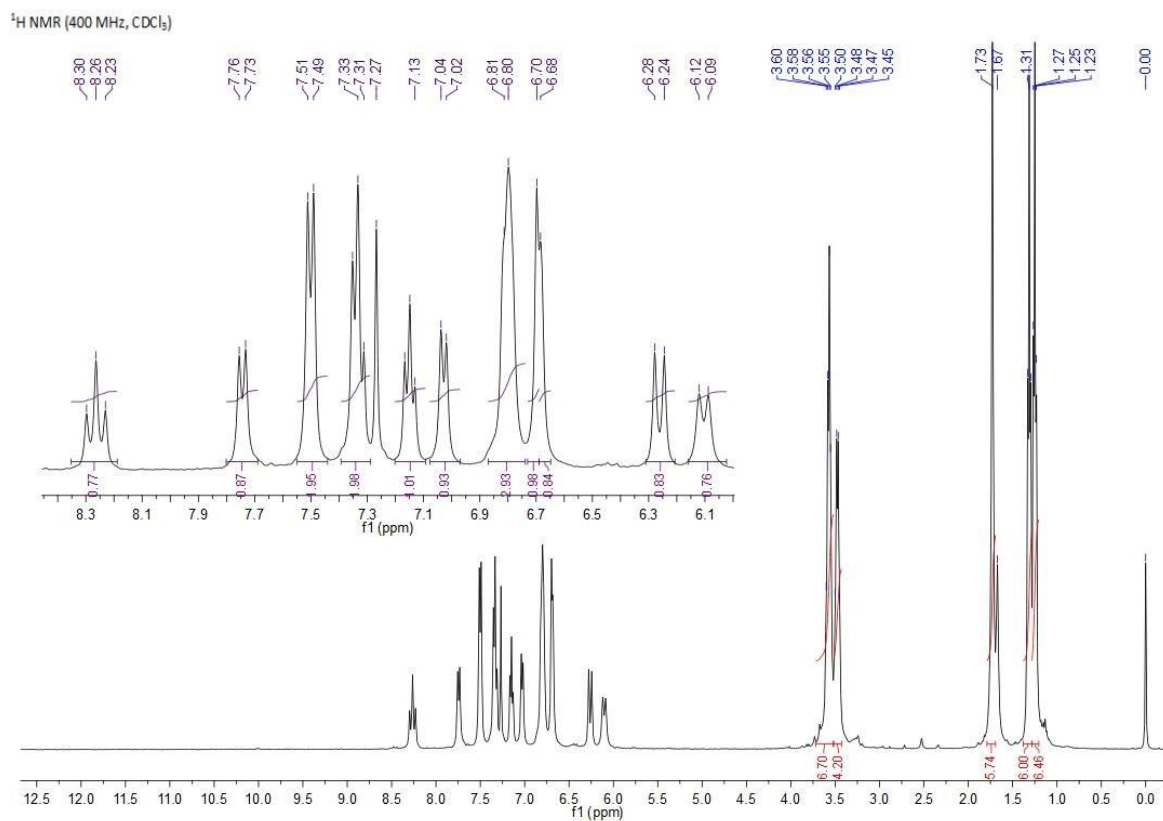
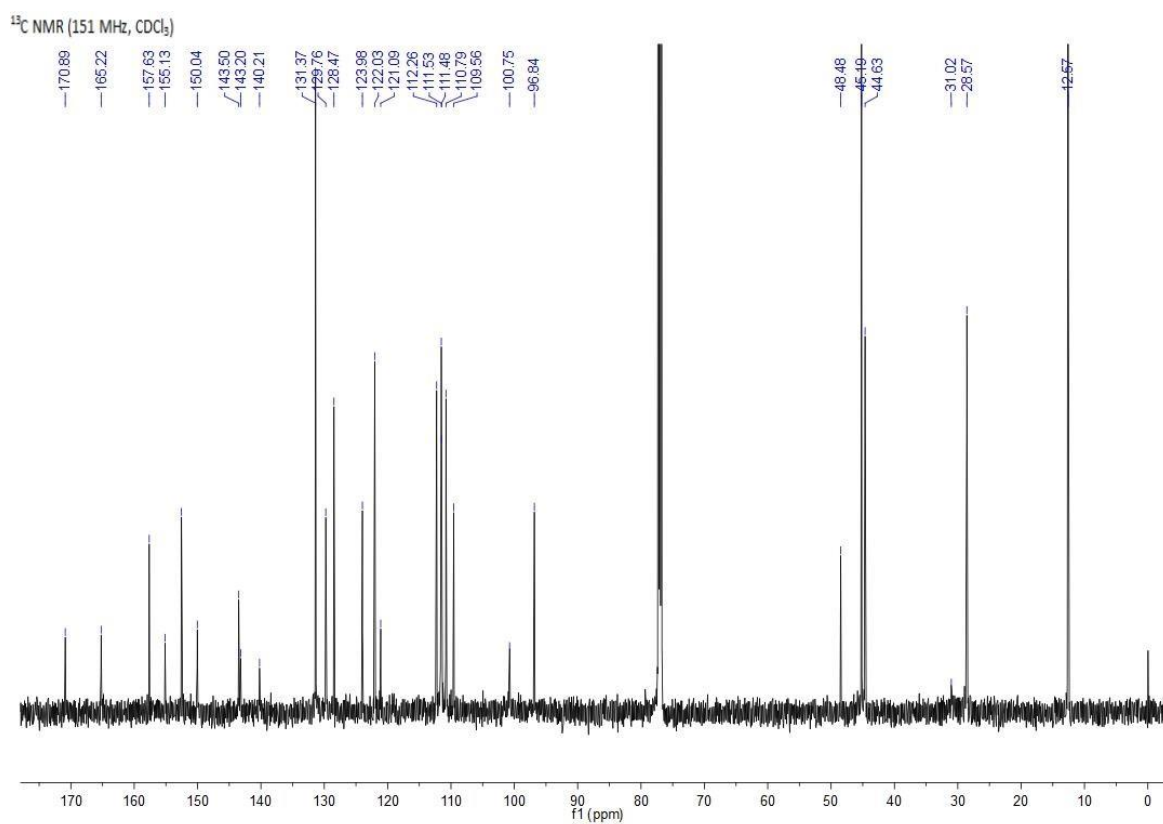
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Fig. S21 HRMS(ESI⁺) of dye **1a**.

Fig. S22 ^1H NMR of dye **1b**.Fig. S23 ^{13}C NMR of dye **1b**.

Display Report

Analysis Info

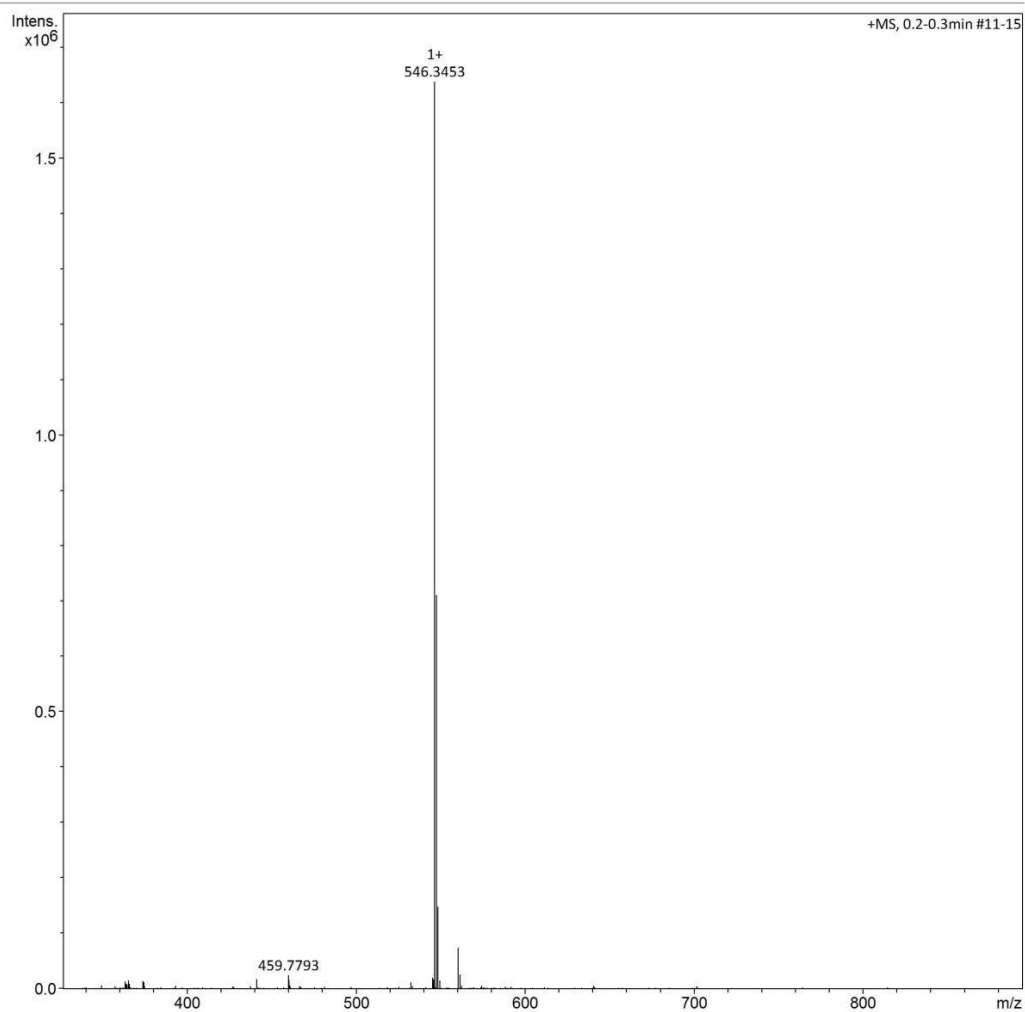
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Sample Name SAM
Comment

Acquisition Date 4/14/2016 3:38:58 PM

Operator bruker
Instrument micrOTOF-Q III 8228888.20487

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	2500 V	Set Dry Heater	180 °C
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Scan End	3000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste



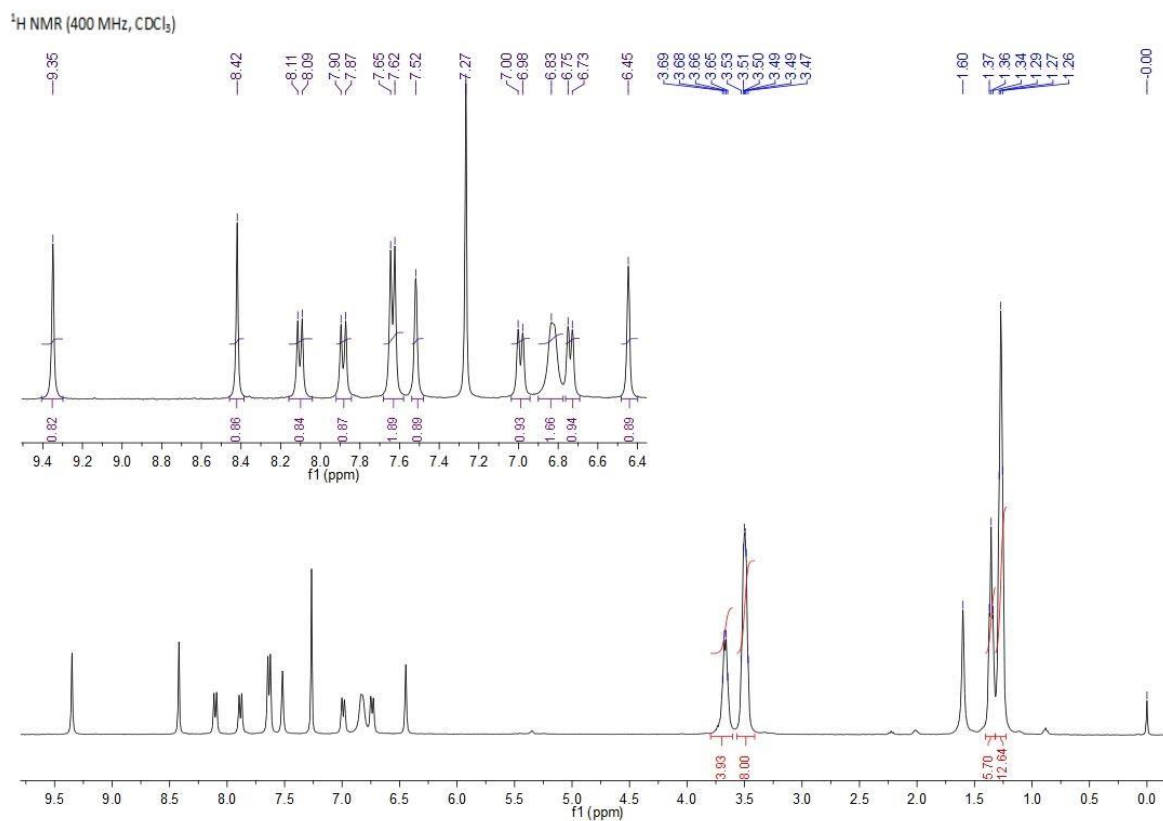
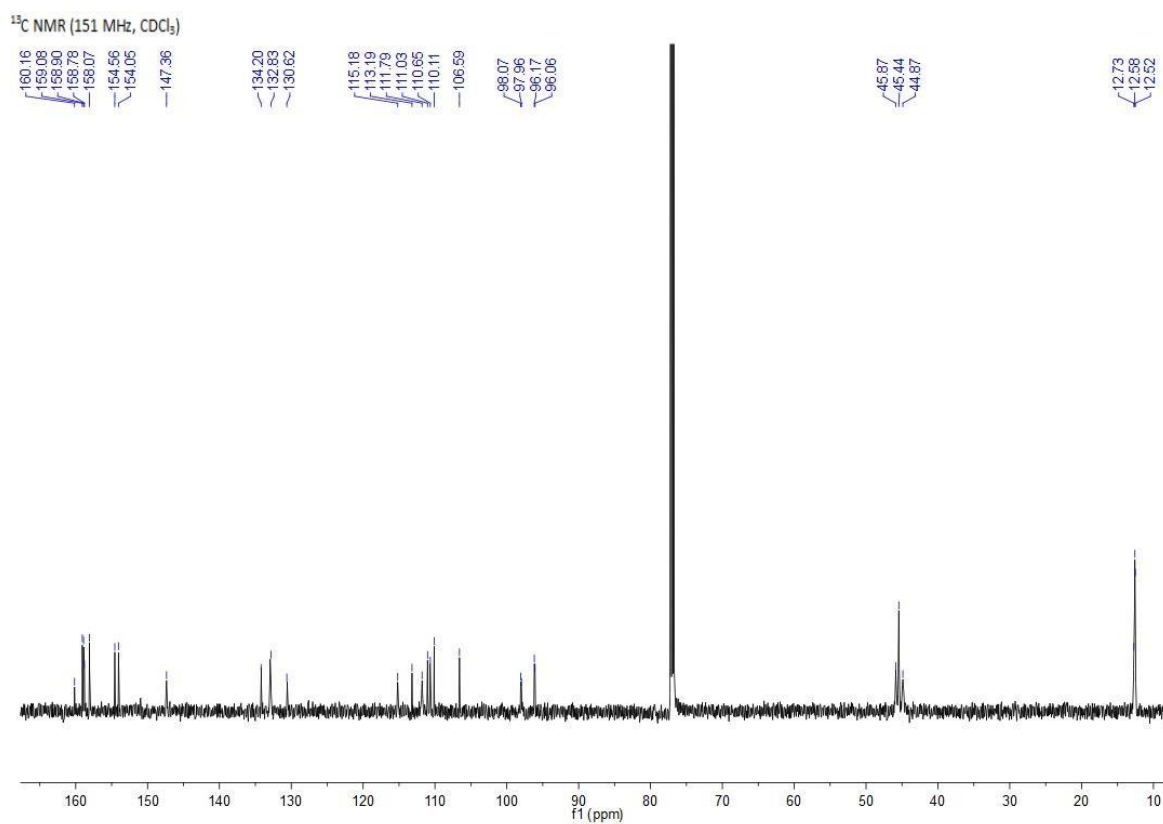
Bruker Compass DataAnalysis 4.2

printed: 4/15/2016 4:07:19 PM

by: bruker

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Fig. S24 HRMS(ESI⁺) of dye 1b.

Fig. S25 ^1H NMR of dye **1c**.Fig. S26 ^{13}C NMR of dye **1c**.

Display Report

Analysis Info

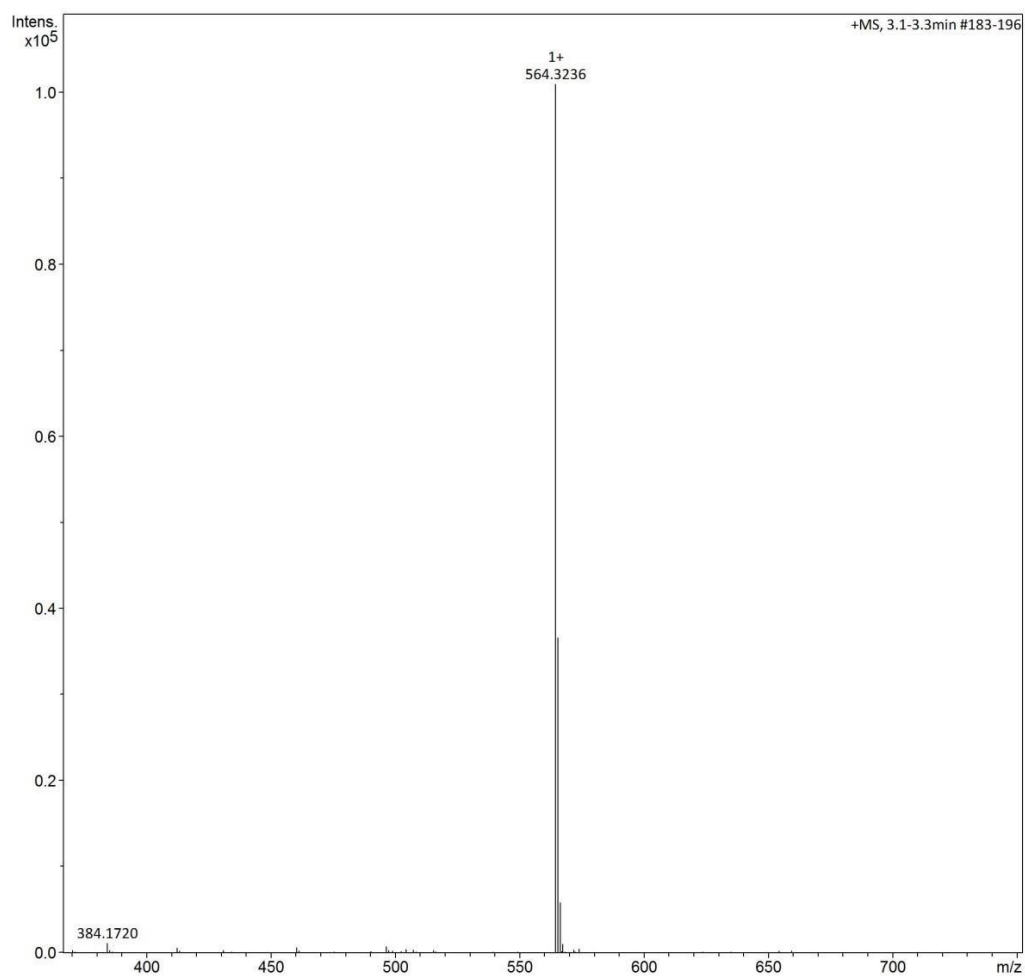
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Sample Name 13
Comment

Acquisition Date 4/1/2016 10:35:02 AM

Operator bruker
Instrument micrOTOF-Q III 8228888.20487

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	120 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Fig. S27 HRMS(ESI⁺) of dye 1c.