

## Near-infrared emission of dibenzoxanthonium and its application in the design of nitric oxide probes

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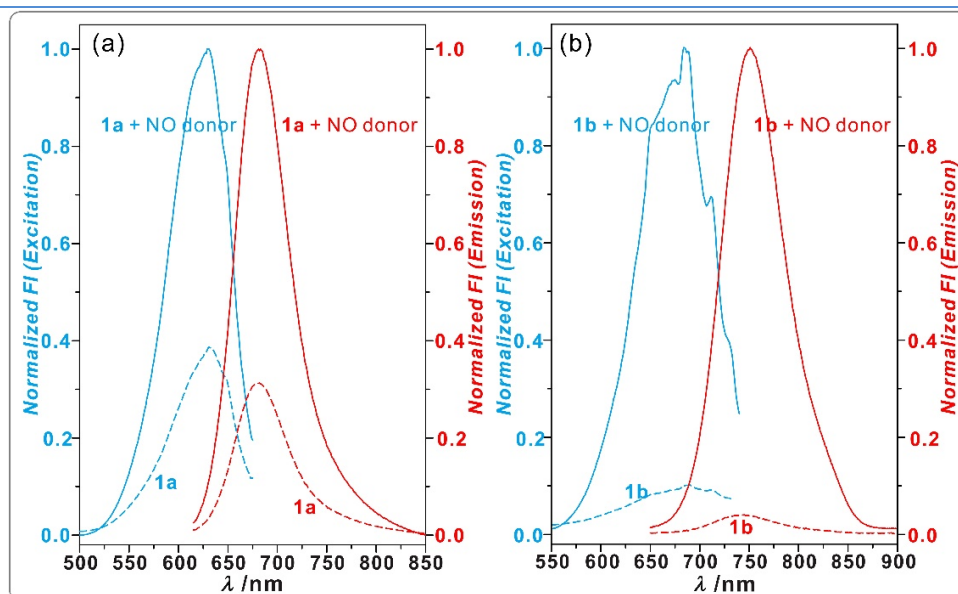
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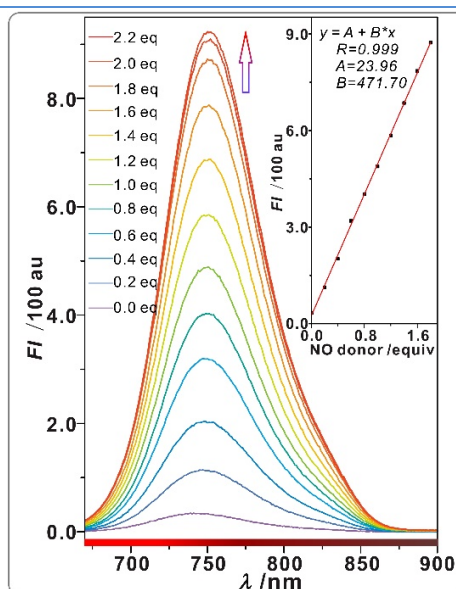
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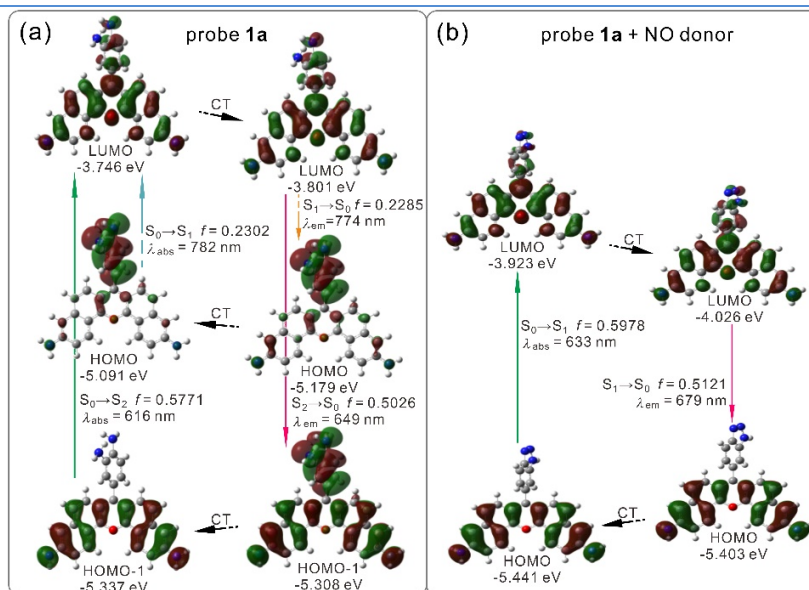
## 1. Figures



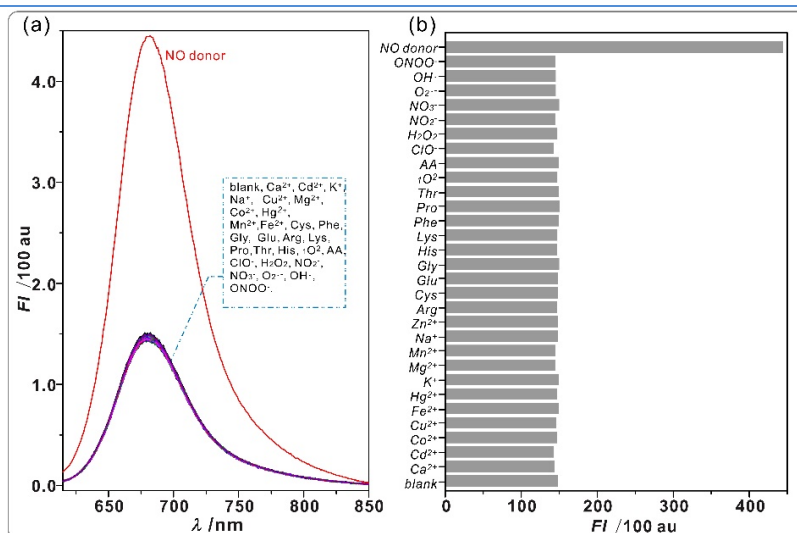
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**Fig. S2** Emission spectra of probe **1b** ( $\lambda_{ex} = 663$  nm) towards different amount of NO donor (0–2.2 equiv.) in HEPES buffer (20 mM, pH = 7.4)–DMSO (1/1, v/v) solutions, inset is the linear response of fluorescence intensities ( $\lambda_{em} = 750$  nm) towards NO donor concentrations (0–1.8 equiv.).



**Fig. S3** The frontier molecular orbitals (FMOs) involved in the vertical excitation and emission of probe **1a** and **1a** + NO. (a) probe **1a**, (b) probe **1a**+NO. CT, IC and PET stand for conformation transformation, internal conversion and photoinduced electron transfer respectively. Excitation and radiative processes are marked as solid lines and the non-radiative processes are marked by dotted lines. For details please refer to Tables S1 and S2.



**Fig. S4** Fluorescent responses of probe **1a** (10  $\mu$ M) to different analytes; (a) emission spectra; (b) fluorescent intensities. NO donor (25  $\mu$ M); common cations:  $K^+$  (100 mM),  $Na^+$  (100 mM),  $Ca^{2+}$  (0.5 mM),  $Cd^{2+}$  (0.3 mM),  $Cu^{2+}$  (0.3 mM),  $Mg^{2+}$  (0.5 mM),  $Co^{2+}$  (0.3 mM),  $Hg^{2+}$  (0.3 mM),  $Mn^{2+}$  (0.3 mM),  $Fe^{2+}$  (0.3 mM); bioactive amino acids (0.1 mM): Cys, Phe, Gly, Glu, Arg, Lys, Pro, Try, His; reactive oxygen and nitrogen species (50  $\mu$ M):  $HO\cdot$ ,  $H_2O_2$ ,  $ClO^-$ ,  $O_2^{\cdot-}$ , and  $ONOO^-$ ; oxidized forms of NO (50  $\mu$ M):  $NO_2^-$  and  $NO_3^-$ ; and ascorbic acid (AA, 50  $\mu$ M).

## 2. Tables

**Table S1** Selected parameters for the vertical excitation (UV-vis absorptions) of probes **1a–1b** and **1a/b** + NO based on the optimized ground state geometries in water.

probe	Electronic transitions	Excitation energy		$\lambda_{\text{exp.}}/\text{nm}$	$f^a$	Composition <sup>b</sup>	CI <sup>c</sup>
		E/eV	$\lambda/\text{nm}$				
<b>1a</b>	$S_0 \rightarrow S_1$	1.58	782		0.2302	H→L	0.70114
	$S_0 \rightarrow S_2$	2.01	<u>616</u>	599	0.5771	H-1→L	0.70137
<b>1a</b> + NO	$S_0 \rightarrow S_1$	1.96	<u>633</u>	608	0.5978	H→L	0.70097
<b>1b</b>	$S_0 \rightarrow S_1$	1.59	780		0.2451	H-1→L	-0.23159
						H→L	0.66245
	$S_0 \rightarrow S_2$	1.80	<u>687</u>	664	0.7188	H-1→L	0.66350
<b>1b</b> + NO						H→L	0.23216
	$S_0 \rightarrow S_1$	1.76	<u>706</u>	679	0.7462	H→L	0.70333

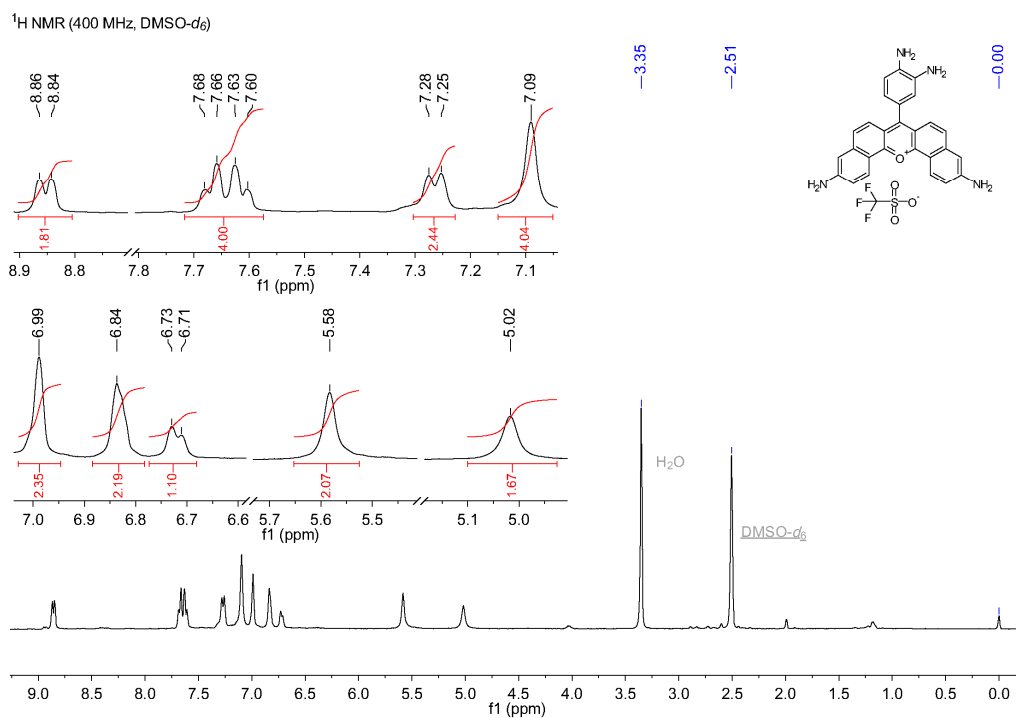
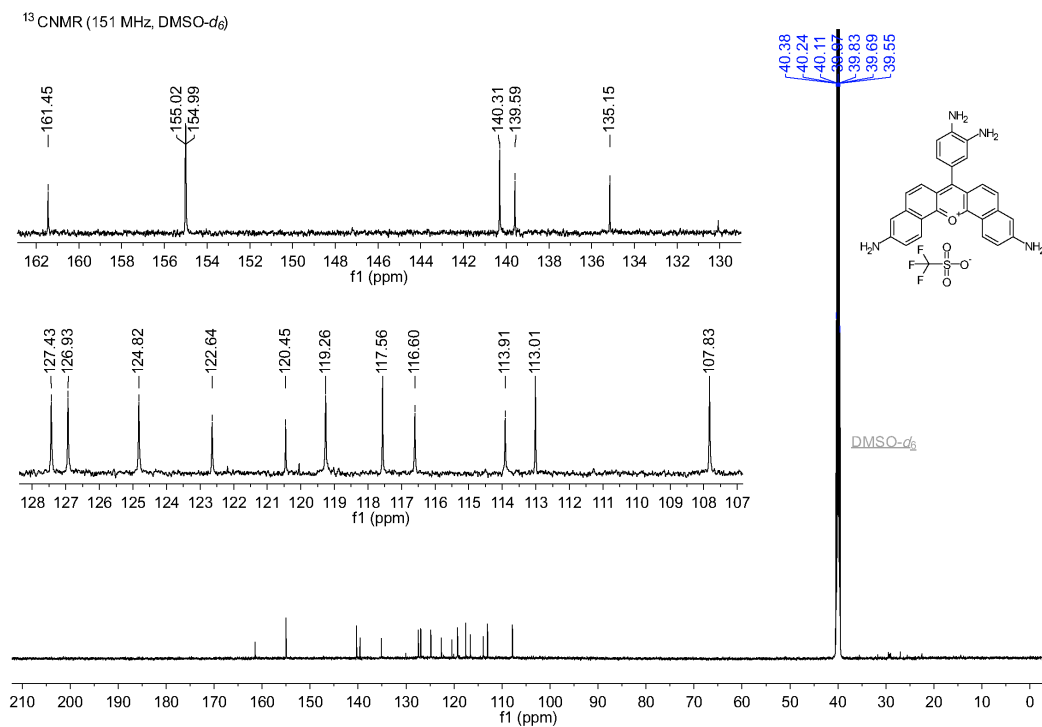
<sup>a</sup> Oscillator strength. <sup>b</sup> H stands for HOMO and L stands for LUMO. <sup>c</sup> Coefficient of the wavefunction for each excitations.

**Table S2** Selected parameters for emission related of probes **1a–1b** and **1a/b** + NO based on the optimized lowest singlet excited state geometries in water.

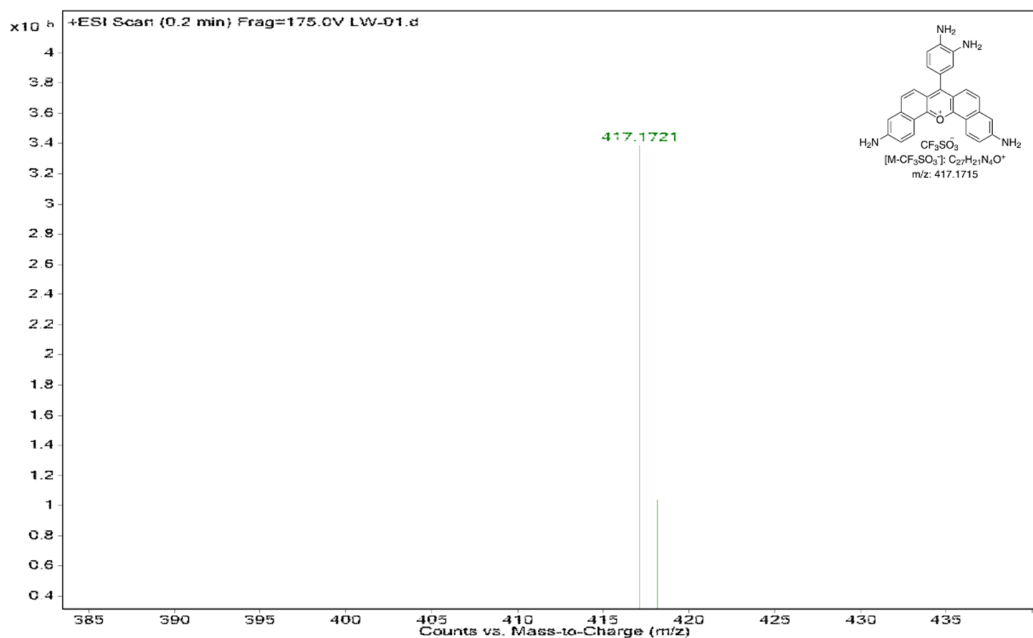
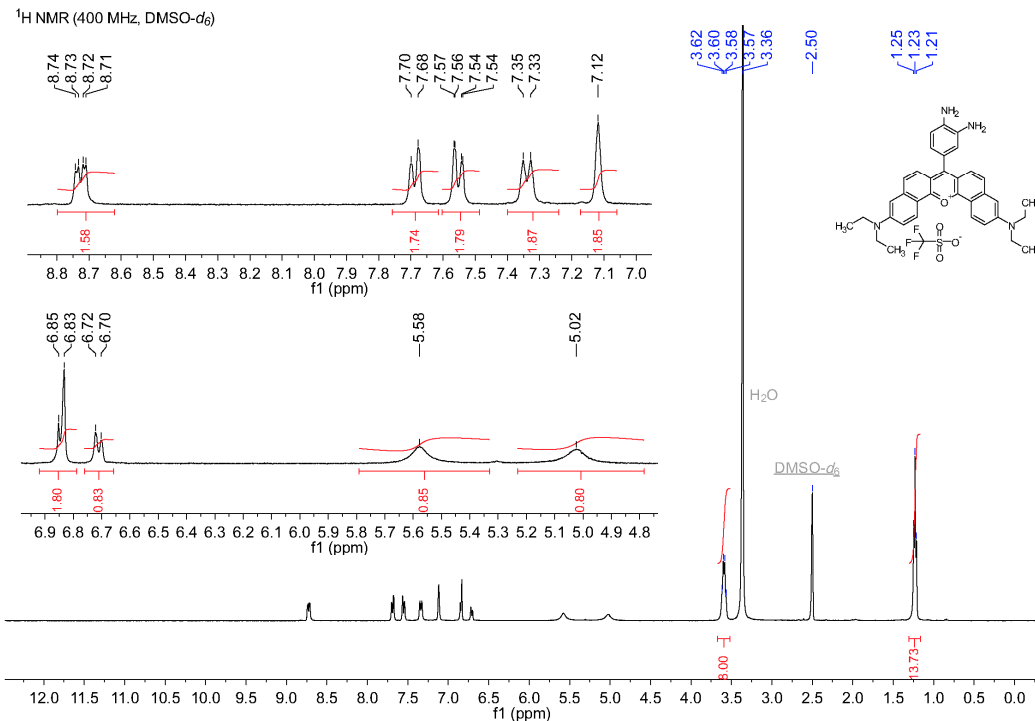
probe	Electronic transitions	Excitation energy		$\lambda_{\text{exp.}}/\text{nm}$	$f^a$	Composition <sup>b</sup>	CI <sup>c</sup>
		E/eV	$\lambda/\text{nm}$				
<b>1a</b>	$S_0 \rightarrow S_1$	1.67	744		0.2885	H-3→L	-0.10252
						H→L	0.69646
<b>1a</b> +NO	$S_0 \rightarrow S_2$	1.91	<u>649</u>	676	0.5026	H-1→L	0.70280
	$S_0 \rightarrow S_1$	1.82	<u>679</u>	678	0.5121	H→L	0.70212
<b>1b</b>	$S_0 \rightarrow S_1$	0.60	2060		0.0001	H→L	0.70704
	$S_0 \rightarrow S_2$	1.75	709		0.0160	H→L+1	0.70584
	$S_0 \rightarrow S_3$	1.76	<u>703</u>	733	0.7657	H-1→L	0.70246
<b>1b</b> +NO	$S_0 \rightarrow S_1$	1.62	<u>765</u>	745	0.6446	H→L	0.70374

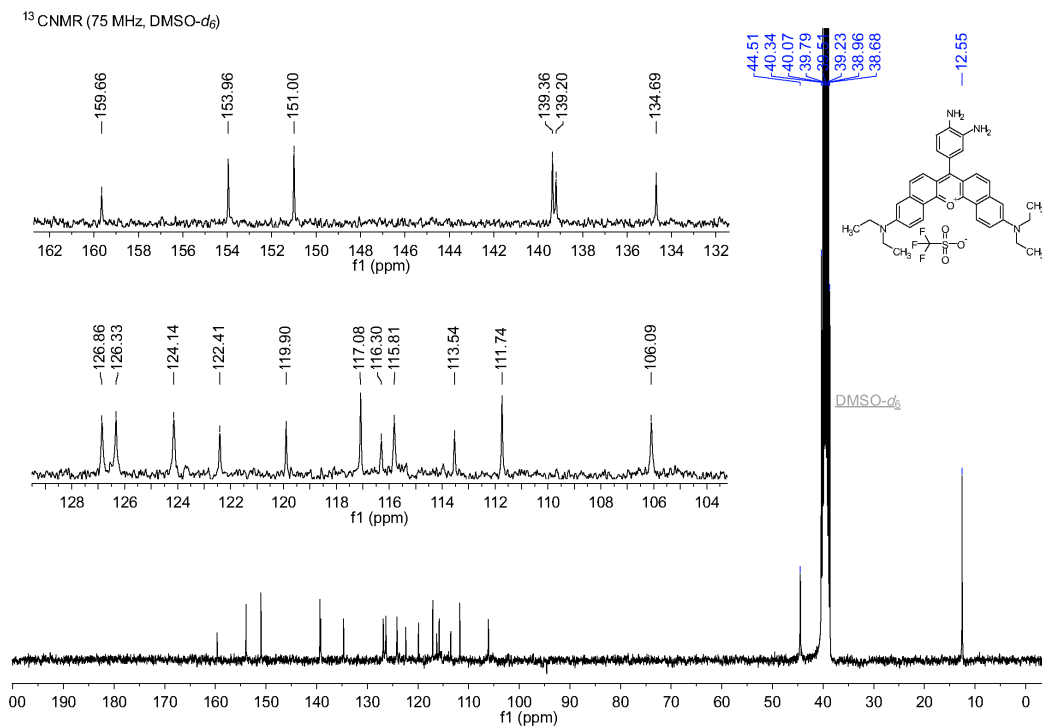
<sup>a</sup> Oscillator strength. <sup>b</sup> H stands for HOMO and L stands for LUMO. <sup>c</sup> Coefficient of the wavefunction for each excitations.

## 3. Appendix

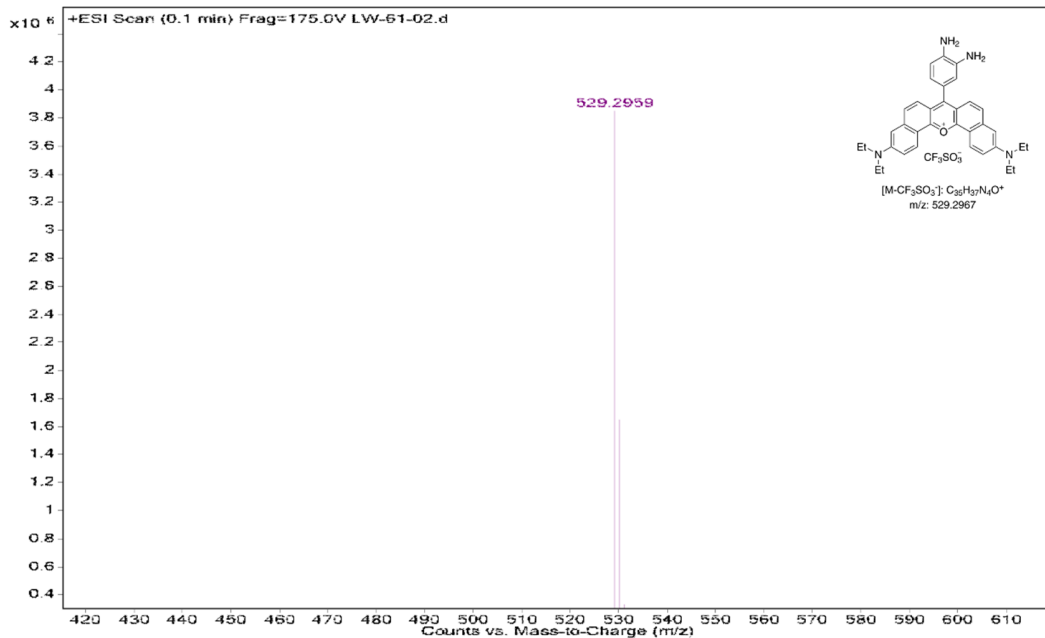
Fig. S5 <sup>1</sup>H-NMR of probe 1a.Fig. S6 <sup>13</sup>C-NMR of probe 1a.

Sample Name	LW-67	Position	Vial 1	Instrument Name	Instrument 1	User Name	
Inj Vol	0	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	LW-01.d	ACQ Method		Comment		Acquired Time	10/10/2014 2:38:04 PM

Fig. S7 HRMS(ESI<sup>+</sup>) of probe 1a.Fig. S8 <sup>1</sup>H-NMR of probe 1b.

Fig. S9 <sup>13</sup>C-NMR of probe 1b.

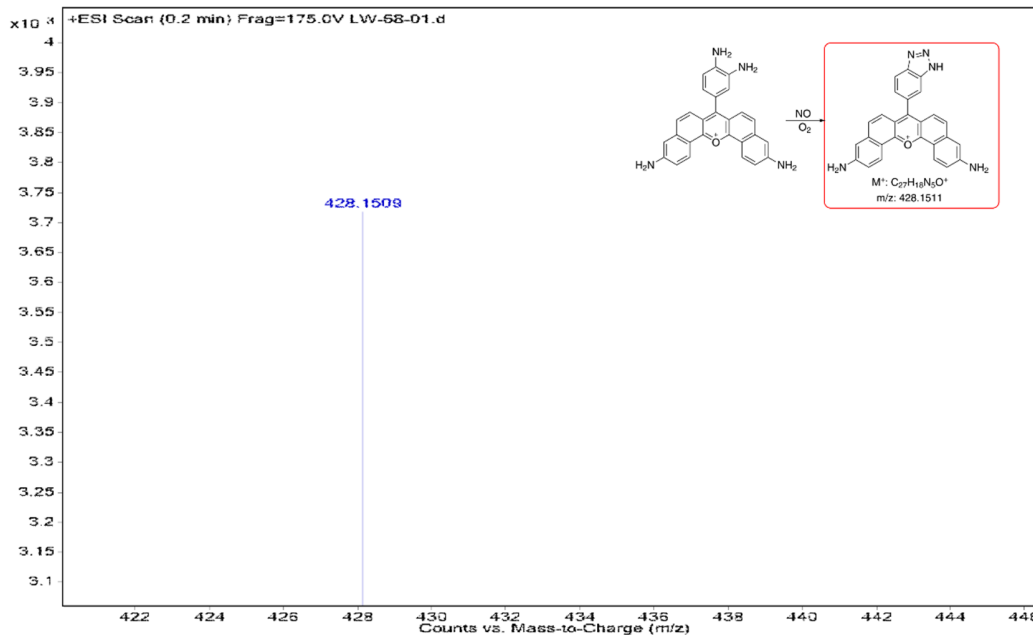
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Fig. S10 HRMS(ESI<sup>+</sup>) of probe 1b.

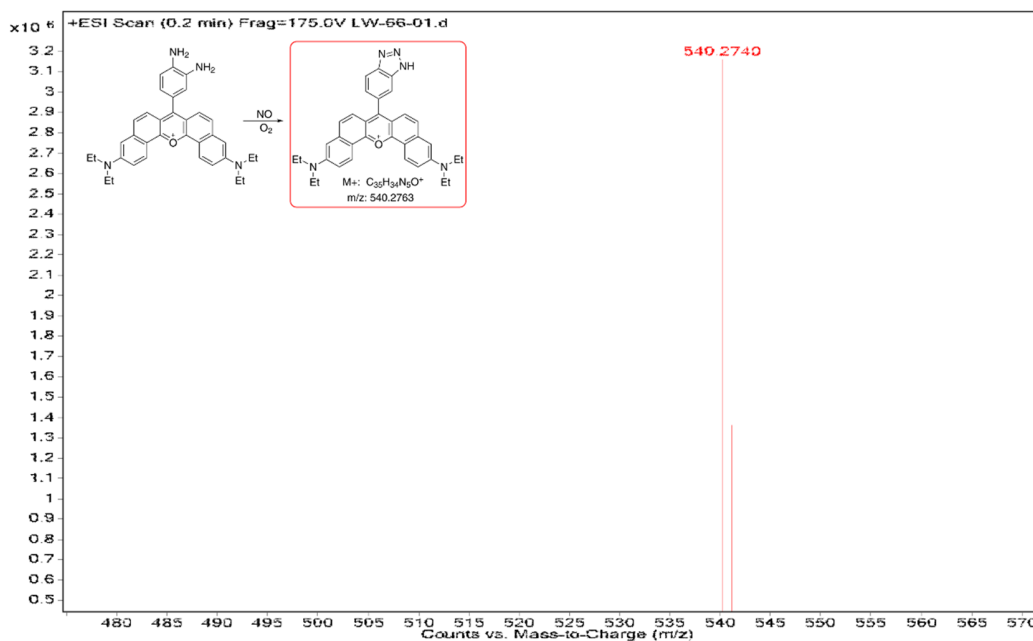


## Supporting Information

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**Fig. S11** HRMS(ESI<sup>+</sup>) of probe **1a** + NO donor.

Sample Name	LW-66	Position	Vial 1	Instrument Name	Instrument 1	User Name	
Inj Vol	0	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	LW-66-01.d	ACQ Method		Comment		Acquired Time	7/2/2014 10:06:11 AM

**Fig. S12** HRMS(ESI<sup>+</sup>) of probe **1b** + NO donor.