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Novel near-infrared fluorescent probe with a large Stokes shift for sensing hypochlorous acid in mitochondria

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Contents

Synthesis of MXSO:

Upon addition of the *m*-CPBA (1 mmol, 172 mg) to compound **MXS** (1 mmol, 430 mg) in dry dichloromethane under ice bath, the temperature was naturally raised to room temperature, and the reaction was carried out for 8 hours under vigorous stirring. After removing the solvent under vacuum, the crude product was purified by silica gel column to afford a pure red solid product **MXSO** (272 mg, 61 % yield). HRMS m/z = 446.1790 calcd for $C_{27}H_{28}NO_3S^+$ $[M]^+$, found: 446.1796. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 16.3 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.30-7.28 (m, 2H), 7.17-7.14 (m, 2H), 6.85 (s, 1H), 4.01 (s, 3H), 3.71 (s, 4H), 2.88 (s, 3H), 1.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.70, 158.88, 158.64, 158.23, 157.47, 156.56, 154.97, 144.24, 144.07, 138.33, 132.22, 130.00, 129.38, 124.81, 121.17, 117.35, 116.89, 116.22, 115.41, 114.21, 113.38, 100.64, 96.65, 56.76, 46.78, 42.47, 30.92, 29.69, 27.93.

Table S1 Spectral data of **MXS** in different solvents.

Solvents	λ_{abs} (nm)	λ_{em} (nm)	ε (mol^{-1}cm^{-1}L)	Φ[a]
DCM	532	662	26000	0.168
EtOH	530	661	19000	0.113
DMSO	538	674	20000	0.064
PBS	524	654	20100	0.028
MeCN	528	669	23600	0.054
DMF	533	664	8900	0.085

[a] Relative fluorescence quantum yield estimated by using Nile Blue (Φ_B = 0.27 in ethanol)[1] as a fluorescence standard.

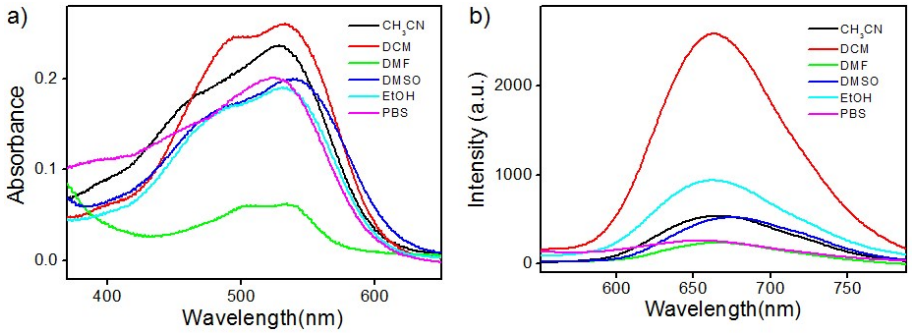
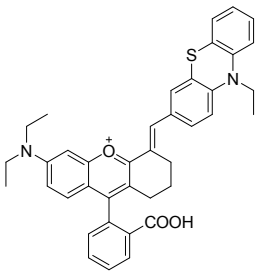
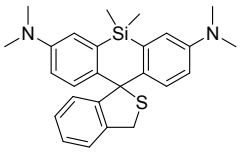
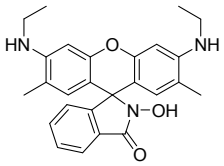
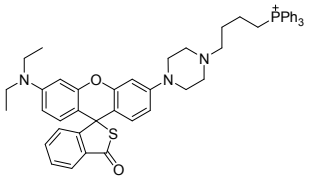
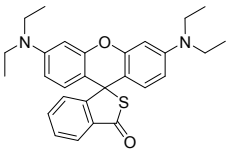
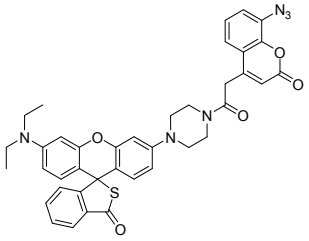
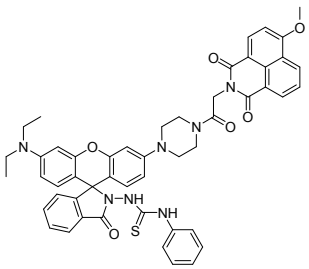
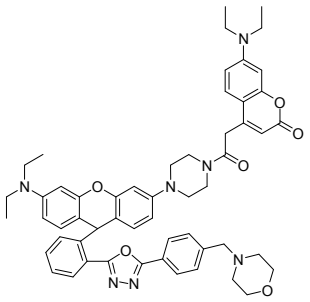
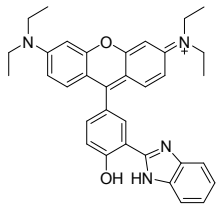
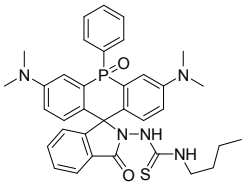
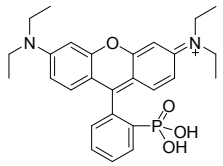
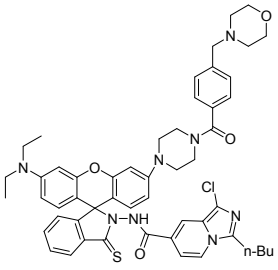
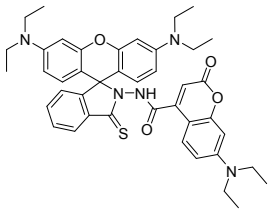
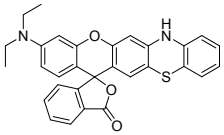
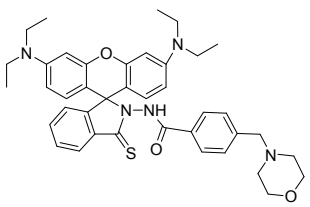
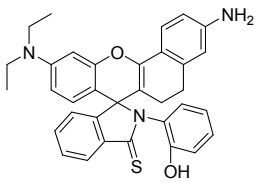
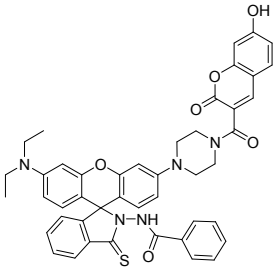
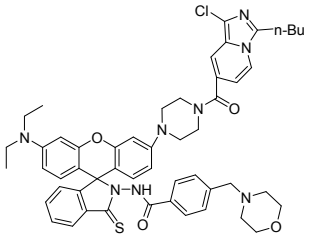
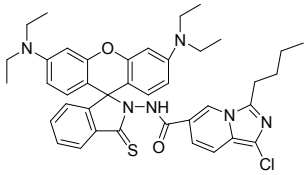
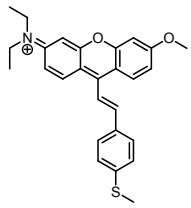


Fig. S1. Absorption and fluorescence spectra of **MXS** in different solvents.

Table S2. Comparison of **MXS** with reported probes.

Structure	Stokes shifts (nm)	Emission (nm)	LOD (nM)	Reference
	97	672	92	*Org. Biomol. Chem., 2019, 17, 108–114*
	18	670	-	*J. Am. Chem. Soc. 2011, 133, 5680–5682*
	17	547	25	*Org. Lett., 2009, 859-861,*
	27	580	9	*Chem. Sci., 2015, 6, 4884-4888*
	18	579	300	*Sensors and Actuators B, 2010, 150, 774–780*
	35	580	192.1	Anal. Chem. 2018, 90, 7510-7516
	50	618	4.5	Tetrahedron, 2020, 76, 131291

	12	582	12	*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2019, 223, 117355*
	18	581	52	*Sensors and Actuators B: Chemical, 2020,304, 127299*
	20	730	10	*Sensors & Actuators: B. Chemical, 2020, 307, 127652*
	20	570	52	*Sensors & Actuators: B. Chemical, 2019, 291, 207–215*
	19	589	10.2	*Analytica Chimica Acta, 2019, 1052, 124-130*
	22	590	140	*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2019, 219, 232–239*
	97	730	2.3	*Dyes and Pigments, 2019, 160, 989–994*
	24	592	71.5	*Analytica Chimica Acta, 2019, 1046, 185-191*

	40	630	40	*Talanta, 2019, 192, 128–134*
	20	585	42	*Talanta, 2018, 186, 65–72*
	23	588	27	*Sensors and Actuators B, 2018, 263, 252–257*
	19	587	2080	*Dyes and Pigments, 2018, 148, 206-211*
	**130**	**654**	**72**	***This work***

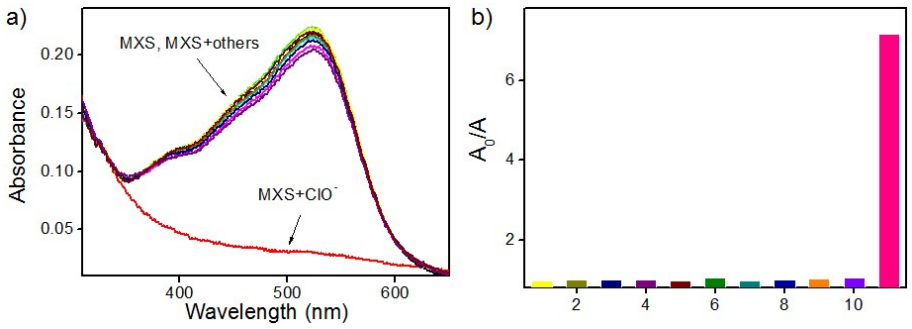


Fig. S2. Absorption responses of **MXS** (10 μM) in the presence of different relevant analytes (5 equiv.) in PBS (10 mM, pH = 7.4), 1: $^1O_2$, 2: H_2O_2, 3: blank, 4: NO, 5: NO_2^-, 6: NO_3^-, 7: O_2^-, 8: •OH, 9: $ONOO^-$, 10: TBHP, and 11: ClO^-.

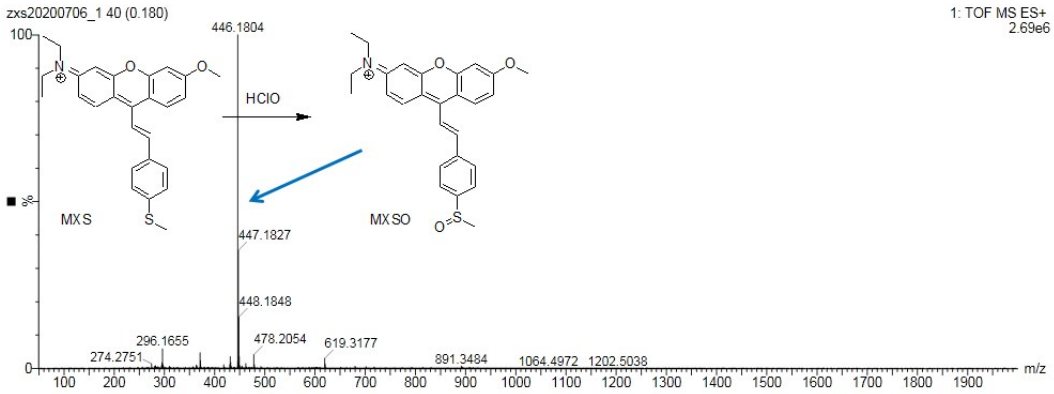


Fig. S3. HRMS spectra of **MXS** upon addition of OCl^-.

Table S3 Spectral data of **MXSO** in different solvents.

Solvents	λ_{abs} (nm)	λ_{em} (nm)	ε ($mol^{-1}cm^{-1}L$)	Φ[a]
DCM	533	570, 626	8900	0.082
EtOH	530	573, 628	6800	0.067
DMSO	536	631	6800	0.036
PBS	504	649	5700	0.018
MeCN	530	632	8300	0.031
DMF	533	578, 633	3300	0.053

[a] Relative fluorescence quantum yield estimated by using Nile Blue (Φ_B = 0.27 in ethanol)[1] as a fluorescence standard.

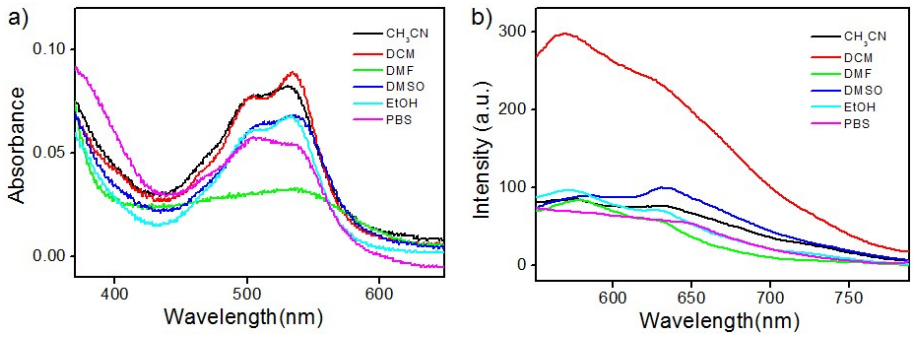


Fig. S4. Absorption and fluorescence spectra of **MXSO** in different solvents.

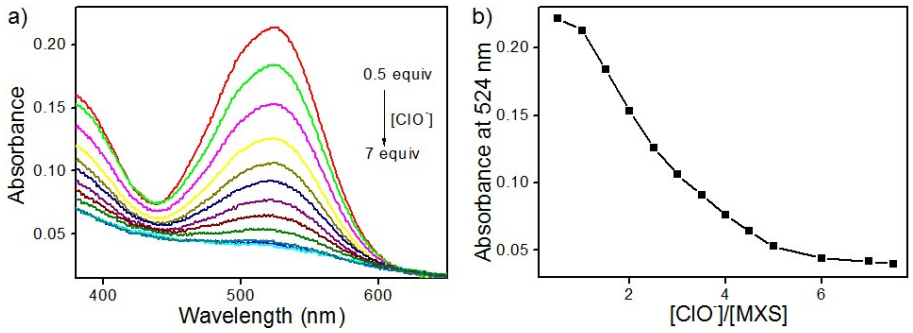


Fig. S5. (a) The absorption changes of **MXS** (10 μM) treated with increasing concentrations of OCl^- (0.5 – 7 equiv.) in PBS (10 mM, pH = 7.4). (b) The plot of the fluorescence intensities at 524 nm versus the equivalents of OCl^-.

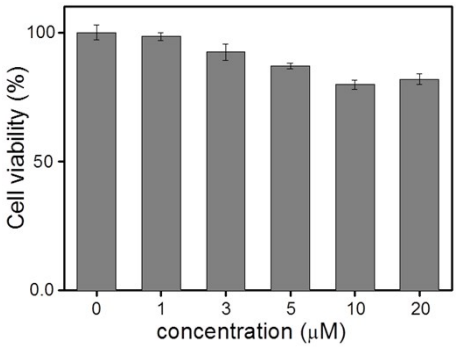


Fig. S6 MTT assay of **MXS**.

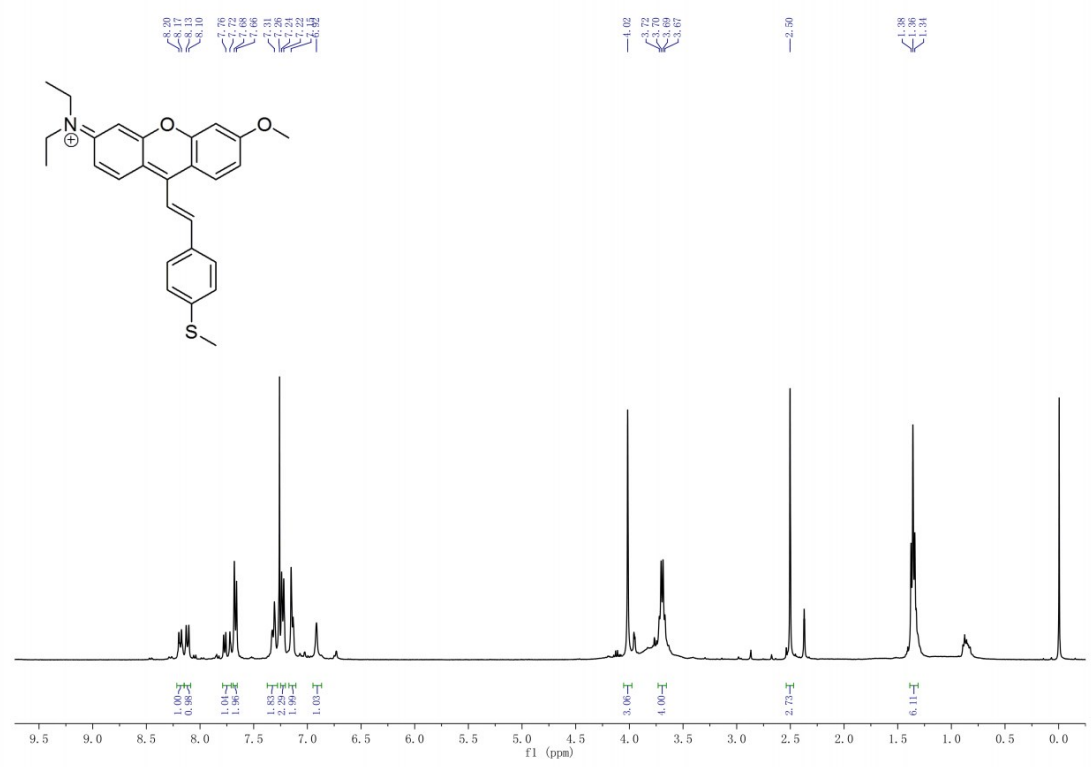


Fig. S7 ^1H NMR spectra of **MXS** in $CDCl_3$

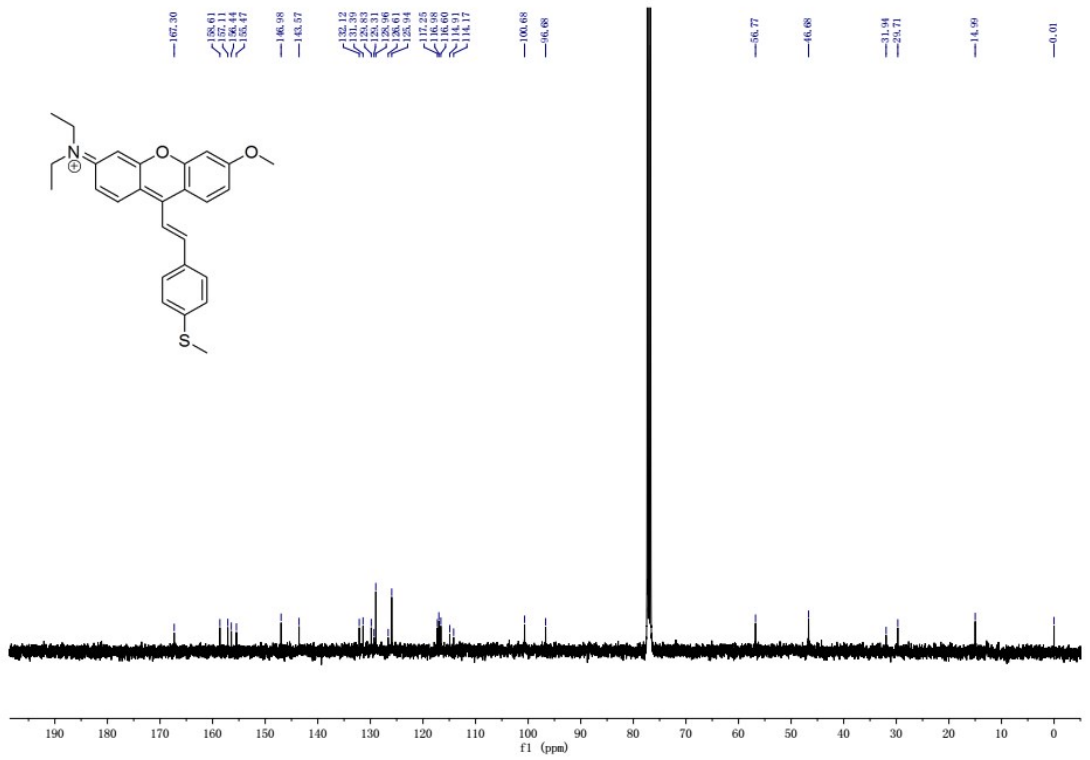


Fig. S8 ^{13}C NMR spectra of **MXS** in $CDCl_3$

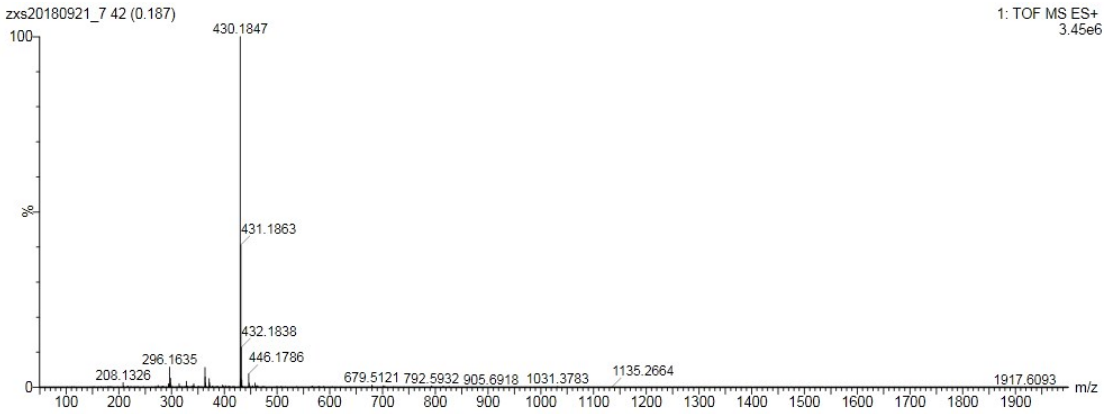


Fig. S9 HRMS spectra of **MXS**

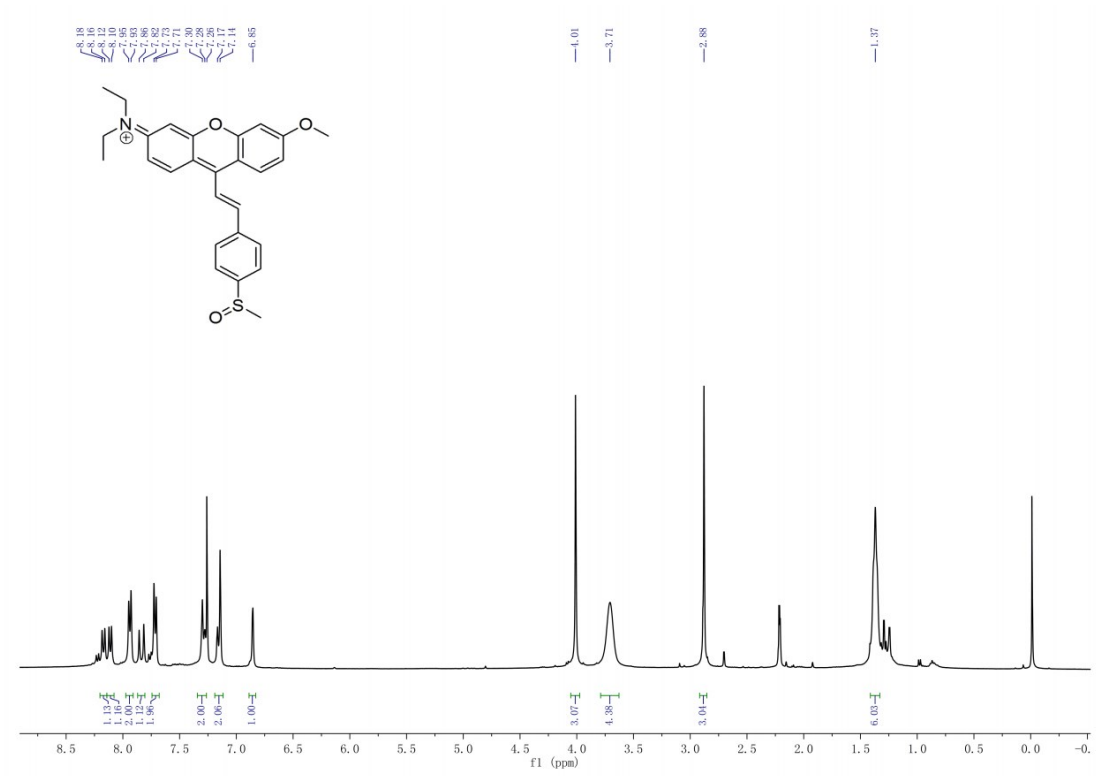


Fig. S10 ^{1}H NMR spectra of **MXSO** in $CDCl_3$ (400 MHz).

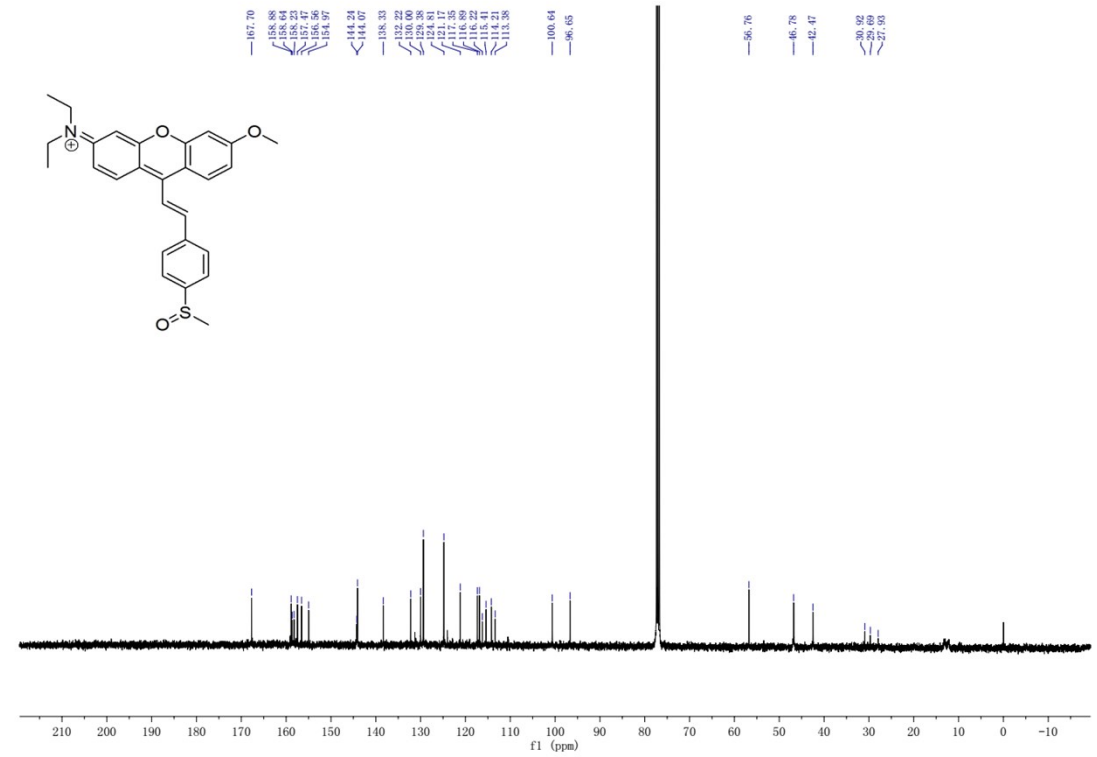


Fig. S11 ^{13}C NMR spectra of **MXSO** in $CDCl_3$ (100 MHz).

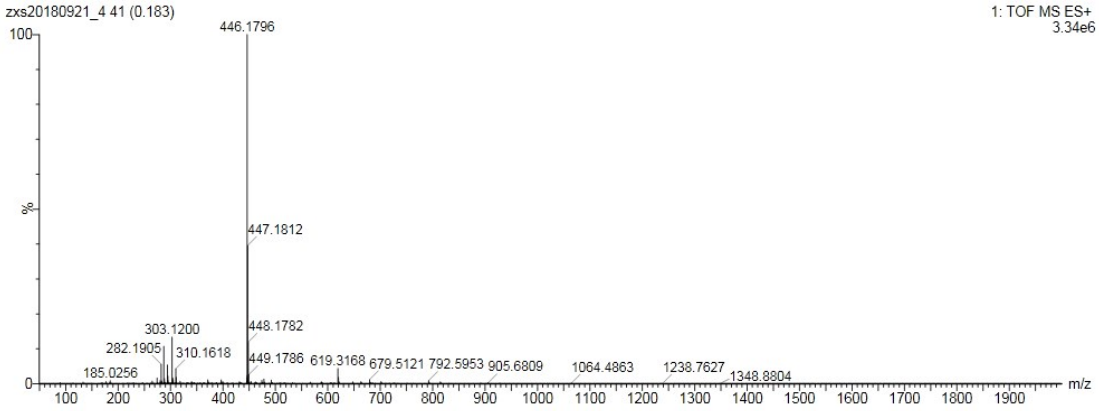


Fig. S12 HRMS spectra of **MXSO**.

References:

1. R. Sens, K. H. Drexhage, *J. Luminesc.*, 1981, **24**, 709.