Supplementary Information

Fluorescent probes based on oxonium-coumarin scaffold for the detection of SO_2 derivatives

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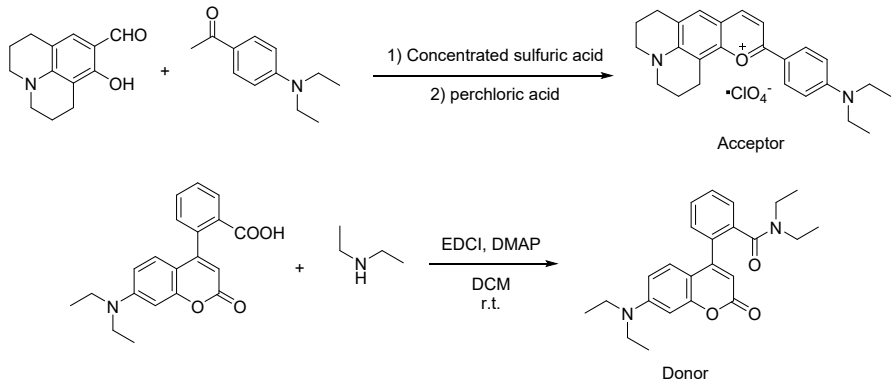
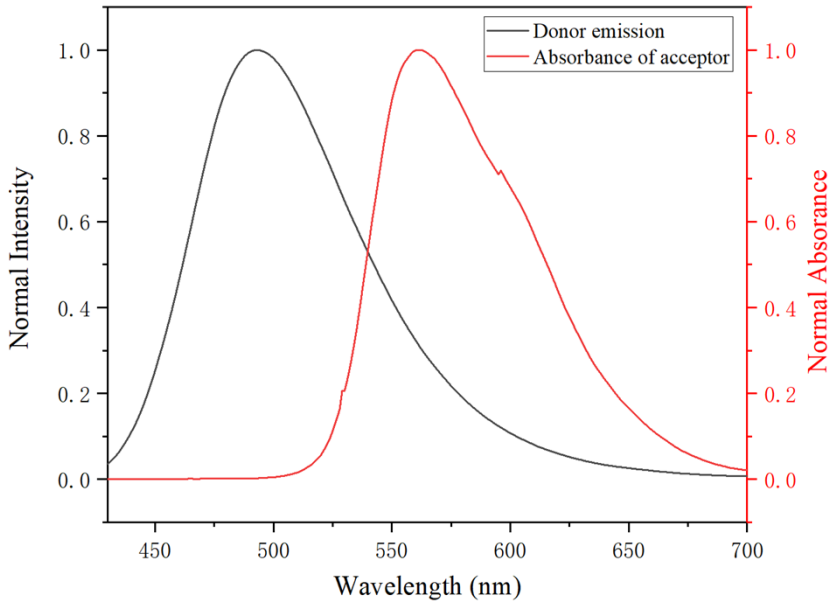
(a)



(b)



Scheme S1. (a) Synthesis route of **acceptor** and **donor**; (b) Normalized fluorescence emission spectrum of **donor** and normalized UV-vis absorption spectrum of **acceptor**.

Synthesis of acceptor and donor

Acceptor was synthesized according to the synthetic route of intermediate 1 (390 mg, yield = 0.79). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 (s, 1H), 8.05 (s, 2H), 7.72 (t, J = 7.2 Hz, 1H), 7.52 – 7.35 (m, 1H), 6.91 (d, J = 8.6 Hz, 2H), 3.53 (p, J = 6.2, 5.5 Hz, 8H), 2.97 (d, J = 6.2 Hz, 2H), 2.82 (s, 2H), 2.12 - 1.87 (m, 4H), 1.18 (t, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.88, 152.69, 152.53, 151.09, 145.78, 130.71, 127.14, 126.33, 116.17, 112.64, 106.97, 104.89, 50.63, 50.14, 44.90, 27.42, 20.35,

19.49, 19.34, 12.94. HRMS (ESI+): m/z calculated 373.2274, found 373.22859.

Donor was synthesized according to previous work[1].

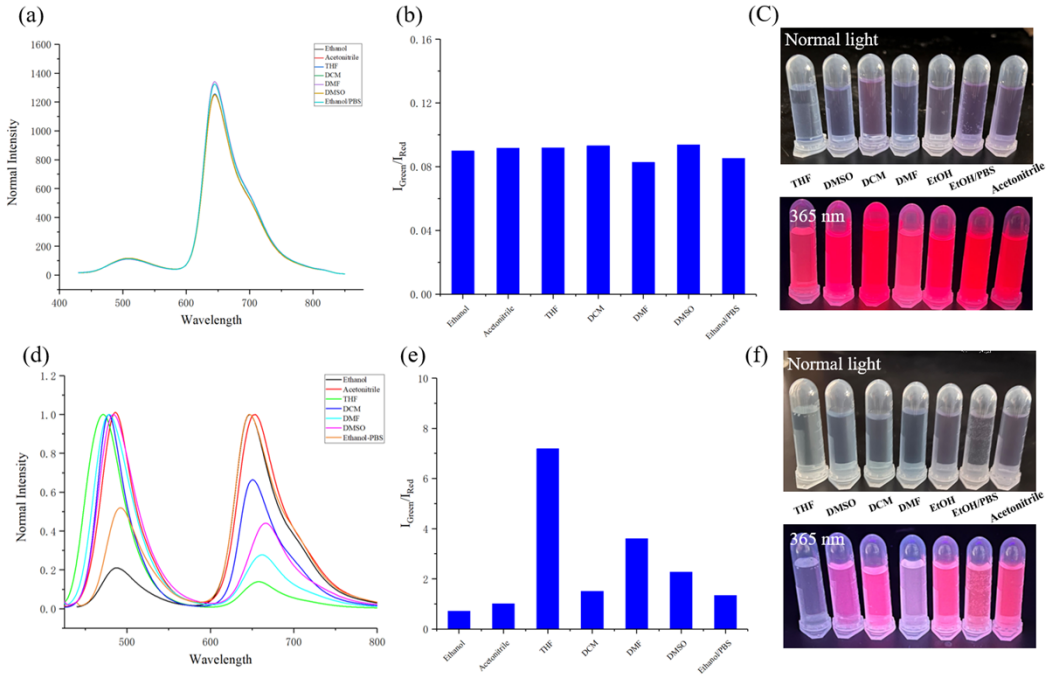


Fig. S1. Fluorescence responses of probes in different solvents. (a) Fluorescence spectrum of CPO1; (b) Fluorescence ratio of CPO1; (c) Images of CPO1 under normal light and 365 nm UV light; (d) Fluorescence spectrum of CPO2; (e) Fluorescence ratio of CPO2; (f) Images of CPO2 under normal light and 365 nm UV light;

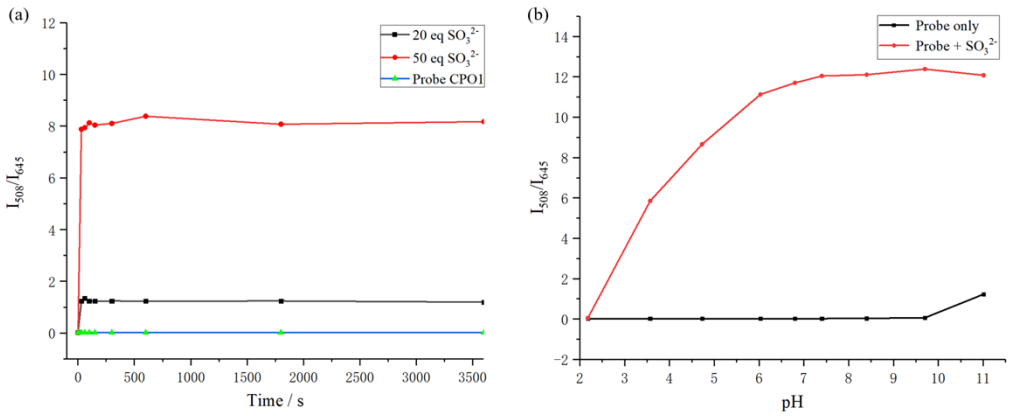


Fig. S2. (a) . Time-dependent experiment of CPO1 (10 μM) in the presence of Na_2SO_3 (20 eq and 50 eq). (b) The effect of pH values on the ratio of fluorescence intensity (I_{508}/I_{645}) of CPO1 (10 μM) in the absence and presence of Na_2SO_3 (100 eq).

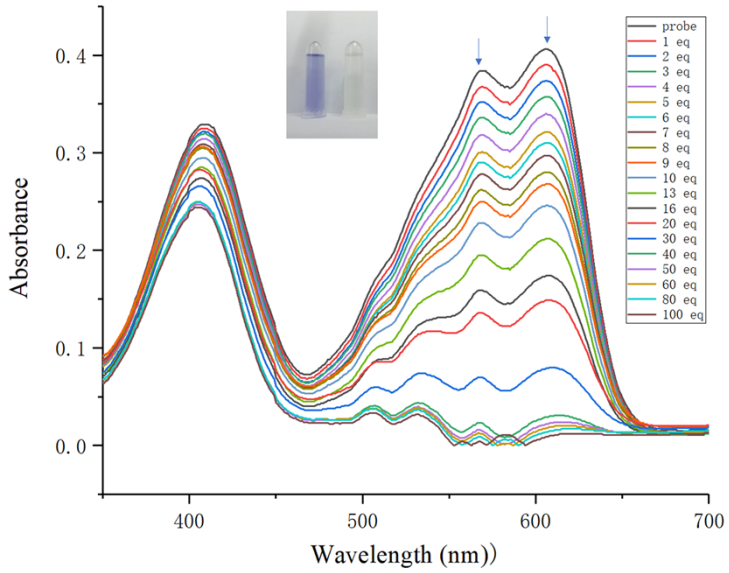


Fig. S3. UV-Vis spectrum of CPO1 (10 μM) in the presence of Na_2SO_3 (0 - 100 eq). Inset: color changes of CPO1 with or without Na_2SO_3 under normal light.

Fig. S4. HRMS of probe CPO1-HSO_3.

Fig. S5. ^{1}H NMR titration experiment of probe CPO1 towards SO_3^{2-}.

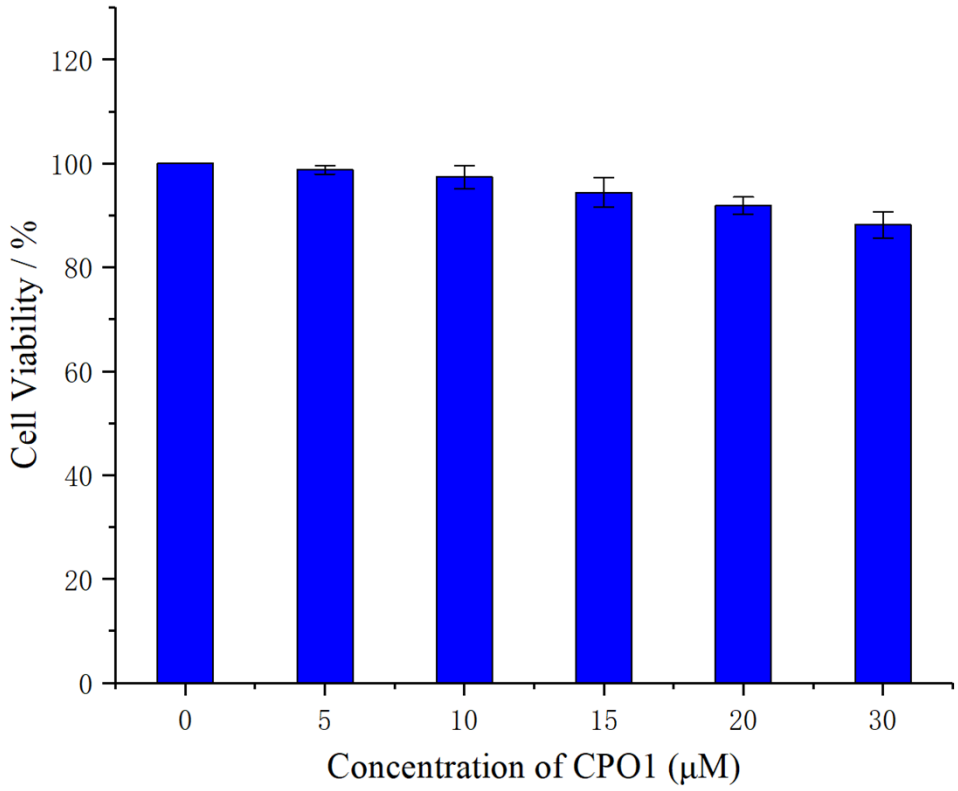


Fig. S6. MTT assay of HepG-2 cells with probe CPO1 at different concentration (0 - 30 μM) for 24 h.

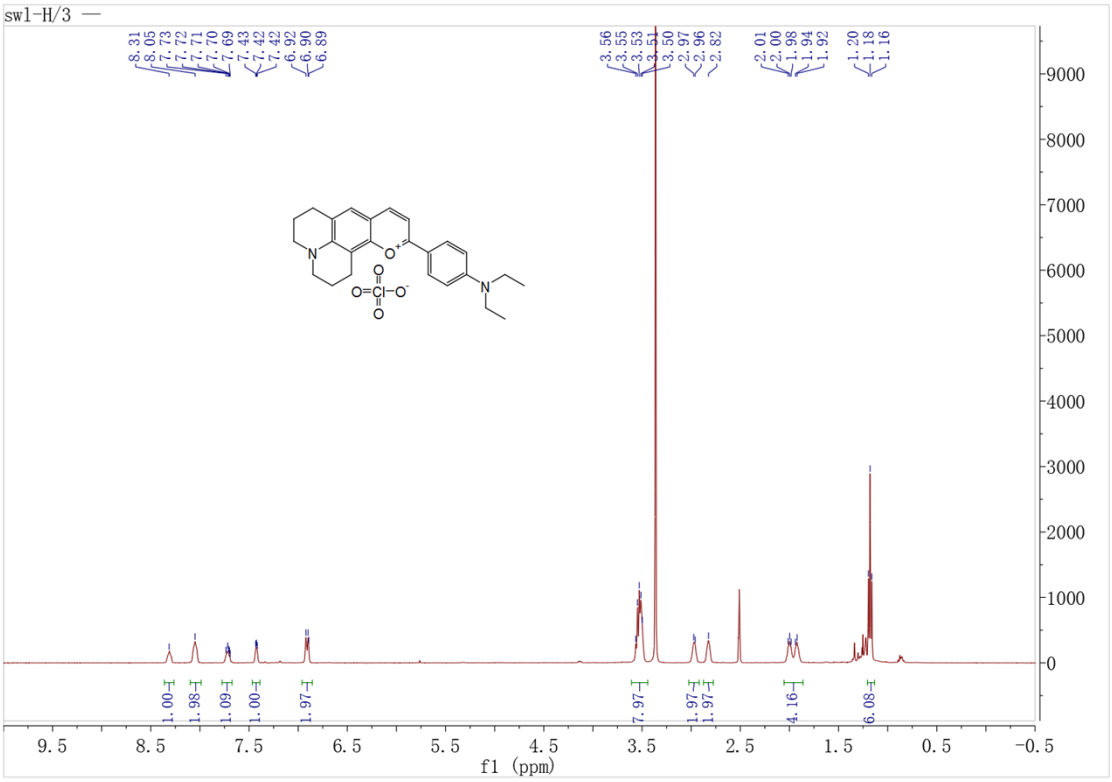


Fig. S7. ^{1}H NMR for Acceptor.

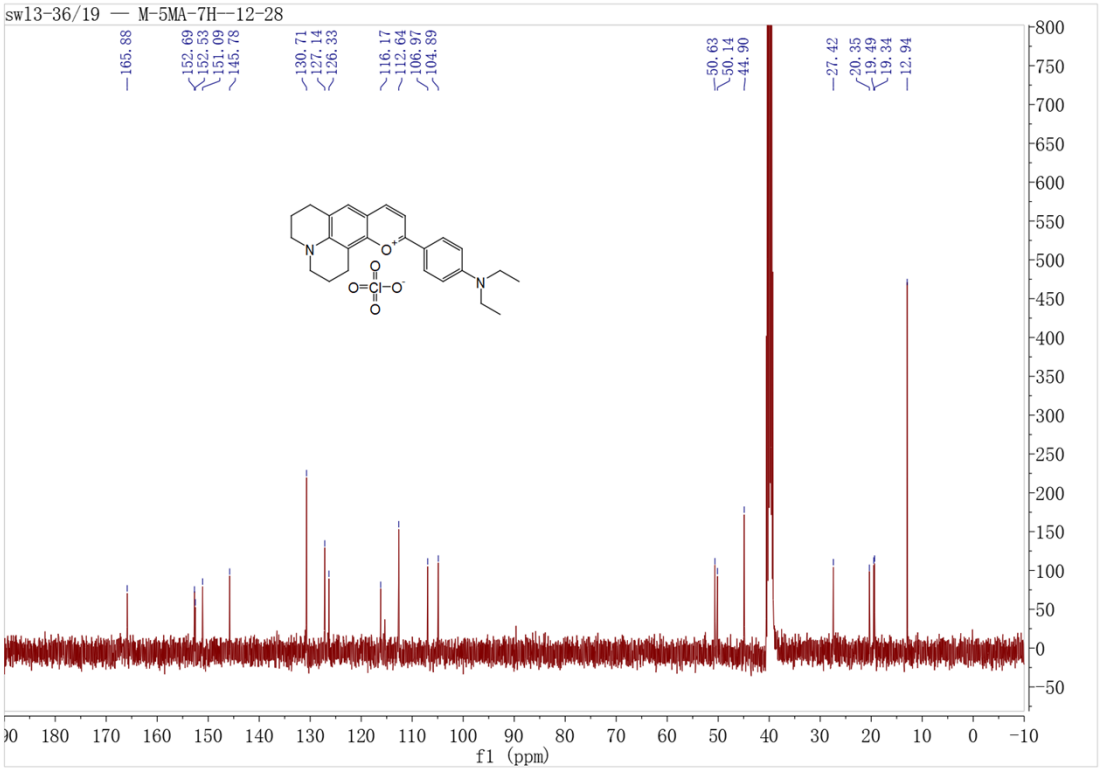


Fig. S8. ^{13}C NMR for Acceptor.

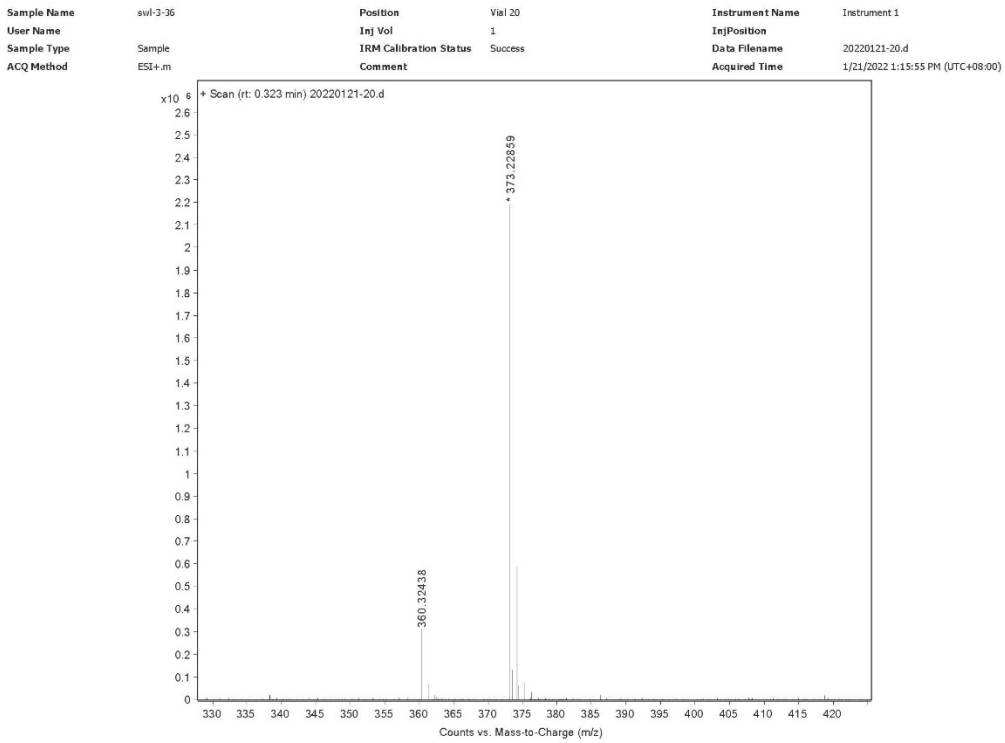


Fig. S9. HRMS for Acceptor.

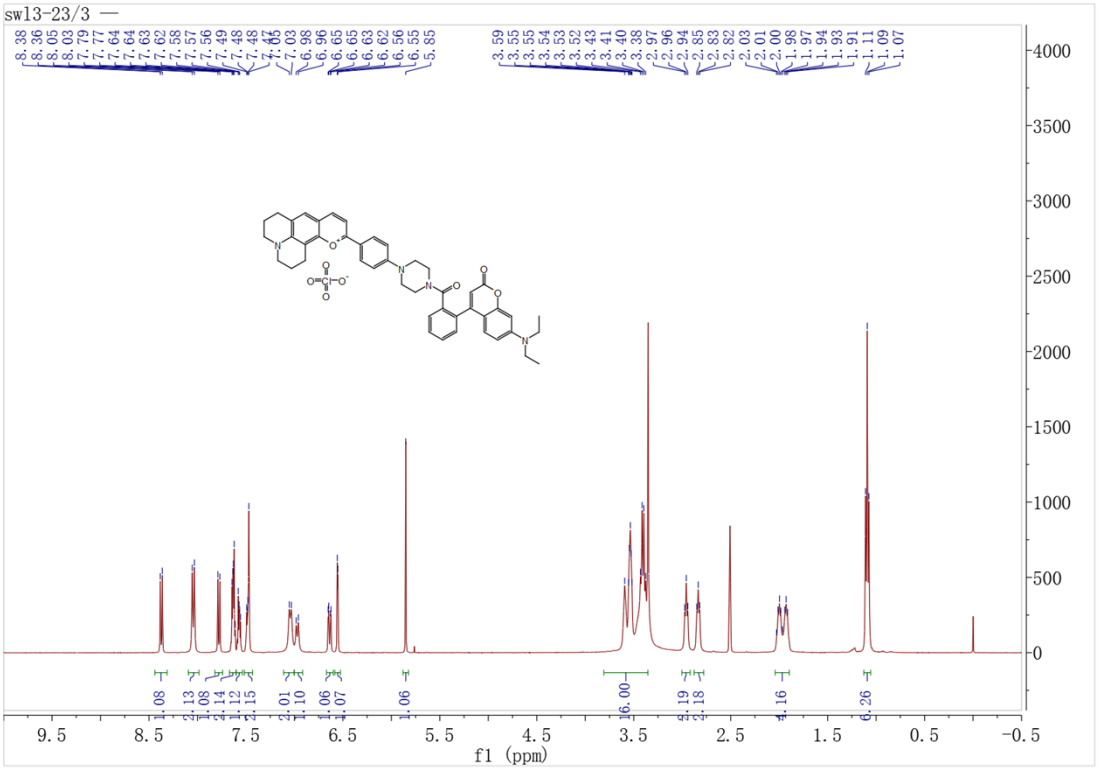


Fig. S10. ^{1}H NMR for probe CPO1.

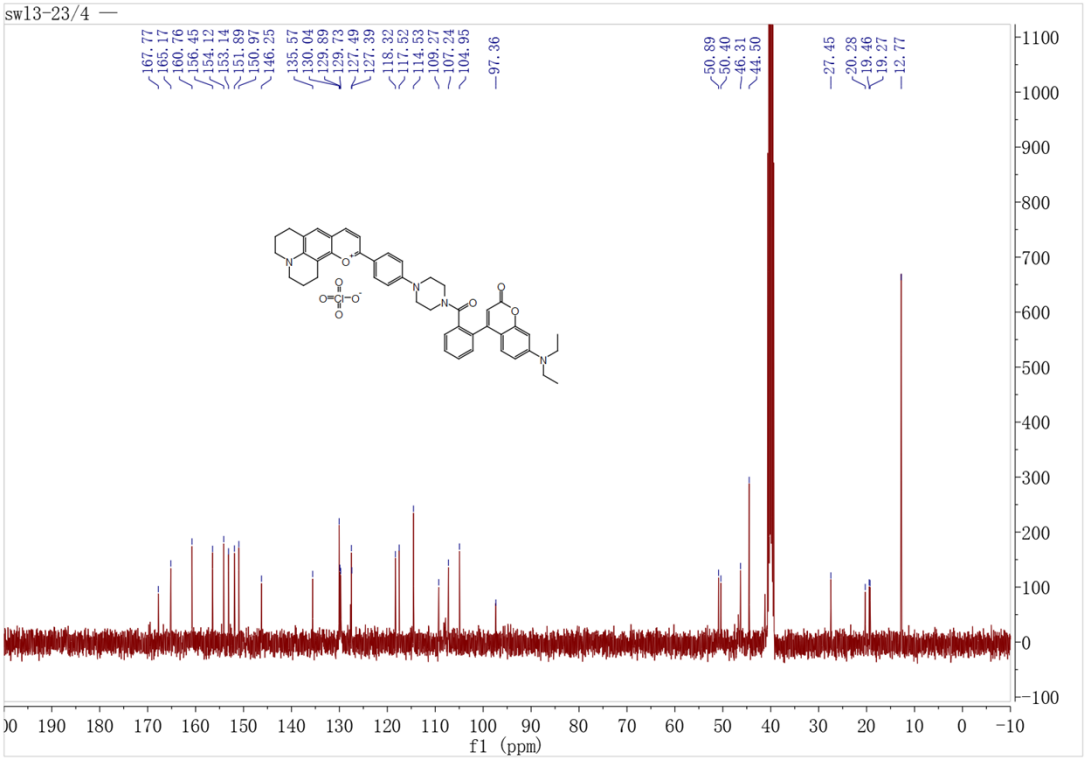


Fig. S11. ^{13}C NMR for probe CPO1.

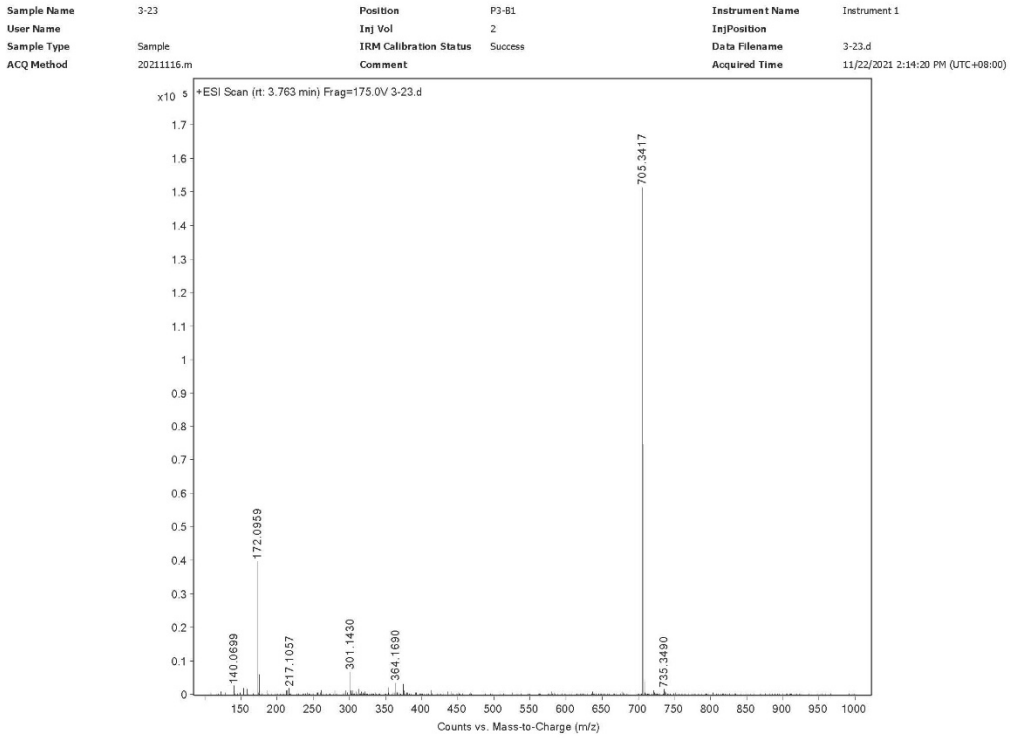


Fig. S12. HRMS for probe CPO1.

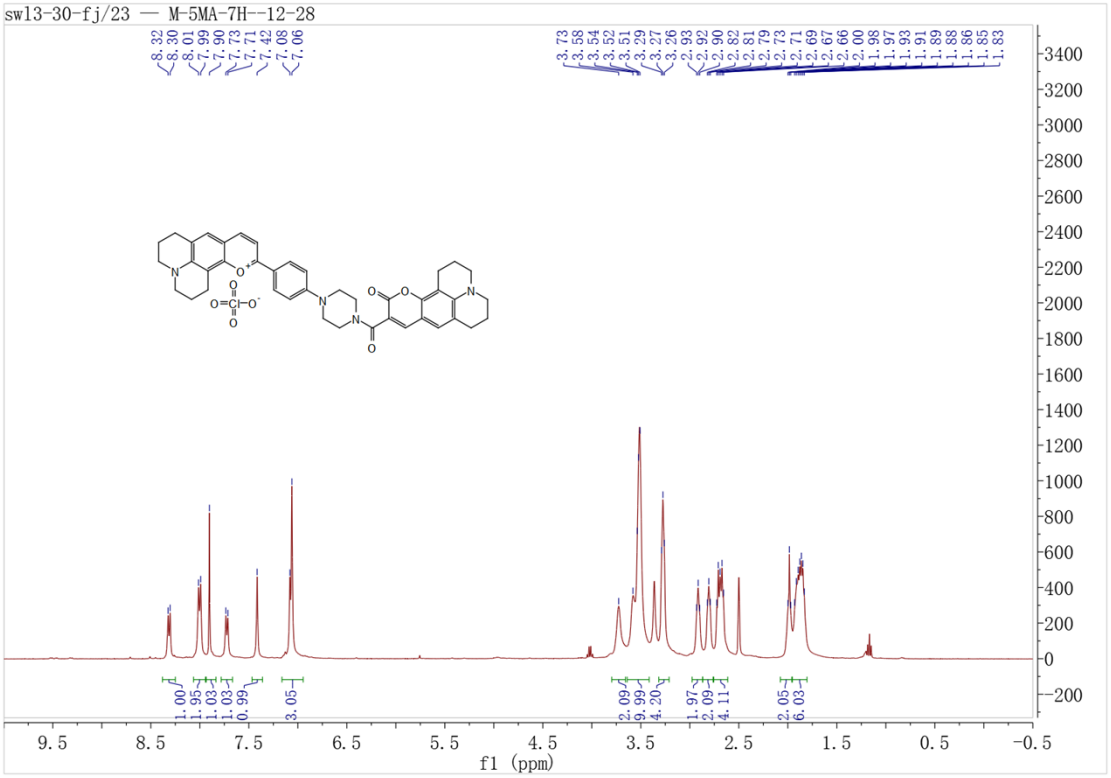


Fig. S13. ^{1}H NMR for probe CPO2.

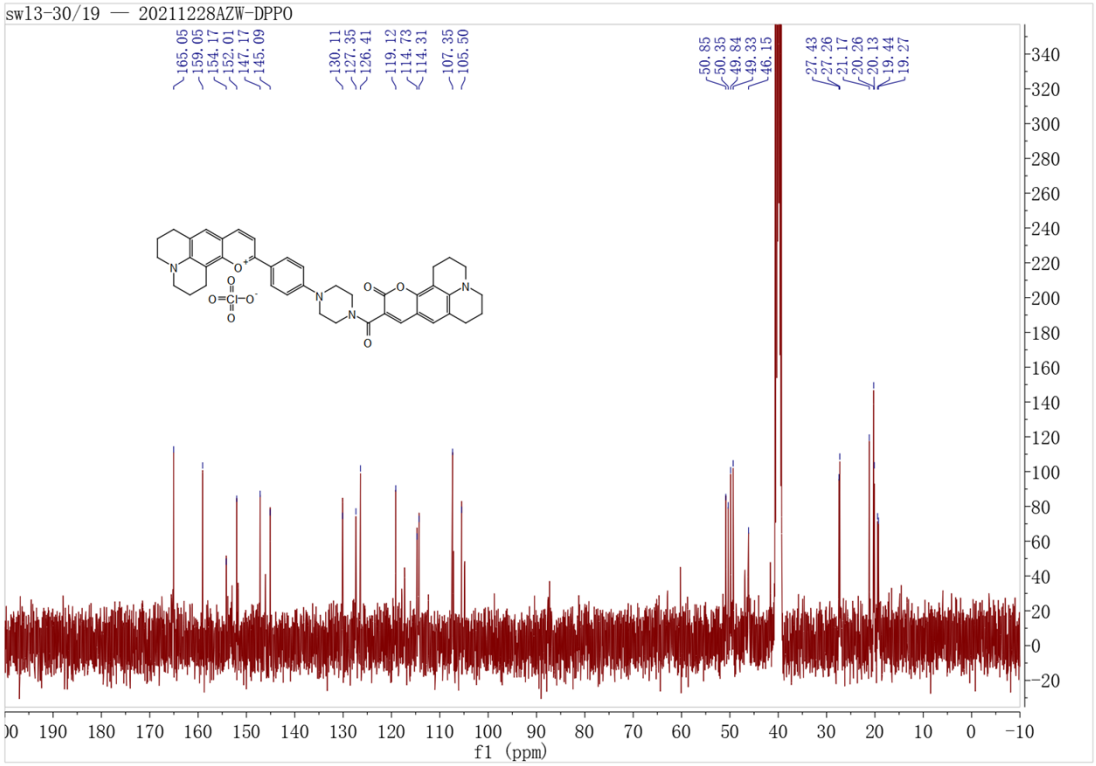


Fig. S14. ^{13}C NMR for probe CPO2.

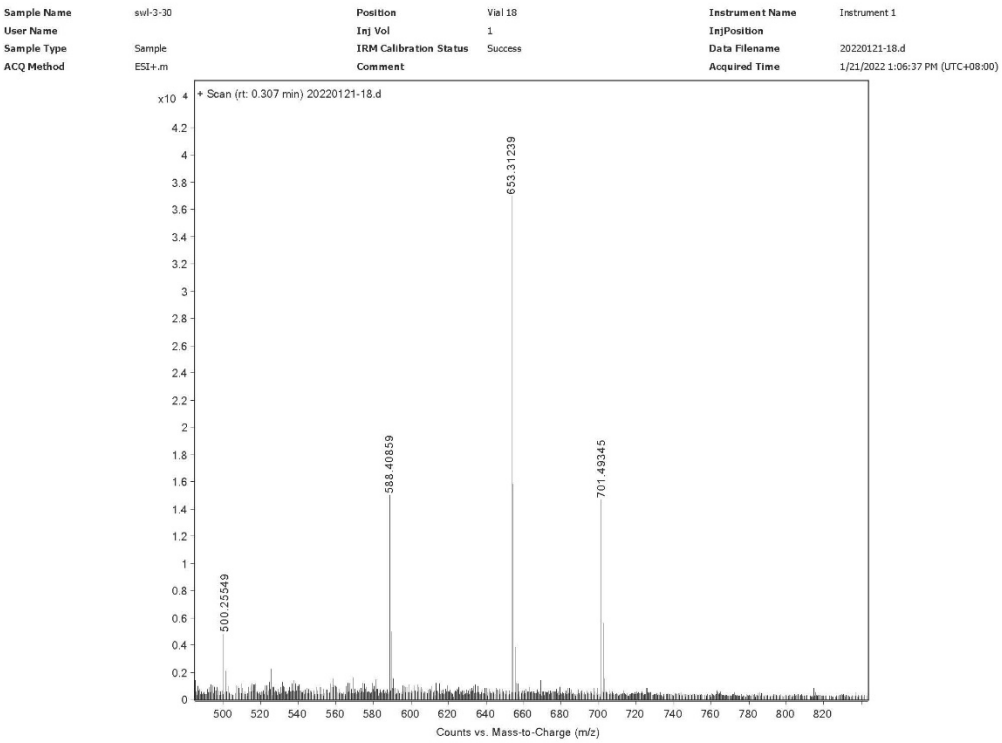


Fig. S15. HRMS for probe CPO2.

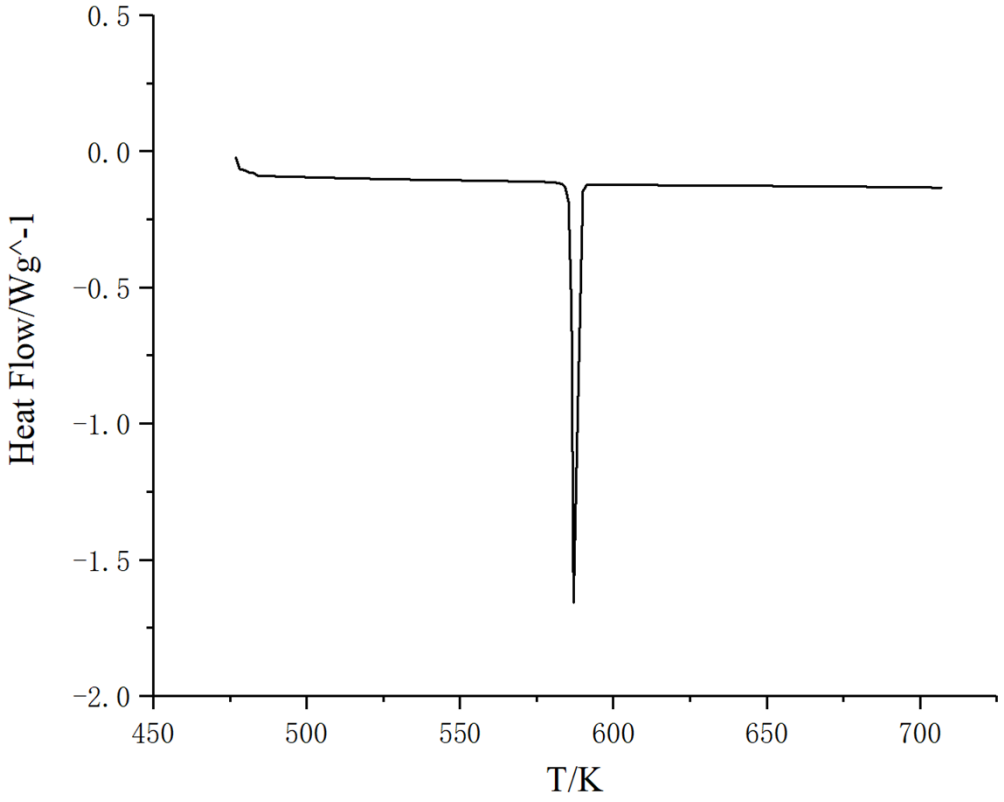
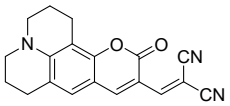
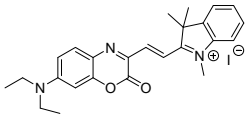
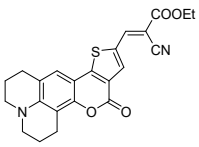
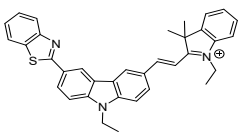
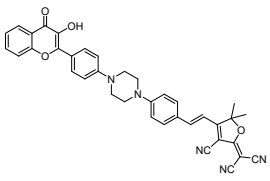
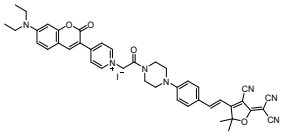
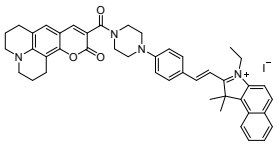
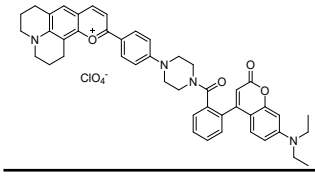


Fig. S16. Thermal analysis (DSC) of CPO1.

Table S1. Comparison of probe CPO1 with other probes.

Probe	Response time	Emission window gap λ_{em} (nm)	λ_{ex} and λ_{em} (nm)	LOD (μM)	Targeted subcellar	Quantitative detection interval	Ref.
	5 min	No ratio	440 488	0.87	No	0 - 200 μM	[2]
	30 s	157	500 560/717	0.087	No	0 - 4 μM	[3]
	160 s	221	410/540 715/494	0.055	No	0 - 55 μM	[4]
	3 min	138	350 458/596	1.76	Mitochondria	3 - 7 μM	[5]

	30 min	111	345 530/641	0.017	Mitochondria	0 - 20 μM	[6]
	15 min	80	435 568/648	0.080	Lipid droplets	0 - 5 μM	[7]
	230 s	116	440 492/608	0.013	Mitochondria	0 - 100 μM	[8]
	< 30 s	137	410 508/645	0.06	Mitochondria	50 - 400 μM	This work

Reference:

[1] W. Shen, H. Xu, J. Feng, W. Sun, G. Hu, Y. Hu, W. Yang, A ratiometric and colorimetric fluorescent probe designed based on FRET for detecting SO3(2-)/HSO3(-) in living cells and mice, Spectrochim Acta A Mol Biomol Spectrosc 263 (2021) 120183-120191.

[2] Y. Yang, B. Bai, W. Xu, Z. Xu, J. Zhang, W. Li, A highly sensitive fluorescent probe for the detection of bisulfite ion and its application in living cells, Dyes and Pigments 136 (2017) 830-835.

[3] M. Li, W. Feng, H. Zhang, G. Feng, An aza-coumarin-hemicyanine based near-infrared fluorescent probe for rapid, colorimetric and ratiometric detection of bisulfite in food and living cells, Sensors and Actuators B: Chemical 243 (2017) 51-58.

[4] Z. Peng, L. Shi, X. Zeng, S. Yang, J. Xiao, S. Gong, H. Xiang, G. Shao, Rational design of the ratiometric fluorescent probes for sulfur dioxide derivatives and the study on the sensing performance of cyano-containing groups, Dyes and Pigments 186 (2021) 108972-78.

[5] W. Gao, Y. Ma, W. Lin, A mitochondria-targeted and deep-red emission ratiometric fluorescent probe for real-time visualization of SO2 in living cells, zebrafish and living mice, Analyst 144(16) (2019) 4972-4977.

[6] D.-P. Li, X.-J. Han, Z.-Q. Yan, Y. Cui, J.-Y. Miao, B.-X. Zhao, A far-red ratiometric fluorescent probe for SO 2 derivatives based on the ESIPT enhanced FRET platform with improved performance, Dyes and Pigments 151 (2018) 95-101.

[7] W.-X. Sun, N. Li, Z.-Y. Li, Y.-C. Yuan, J.-Y. Miao, B.-X. Zhao, Z.-M. Lin, A mitochondria-targeted ratiometric fluorescence probe for detection of SO2 derivatives in living cells, Dyes and Pigments 182 (2020).

[8] W. Shen, G. Hu, H. Xu, W. Sun, Y. Hu, W. Yang, Construction and evaluation of ratiometric fluorescent probes based on a 7-aminocoumarin scaffold for the detection of SO2 derivatives, Dyes and Pigments 198 (2022) 109971-109979.