Supporting Information

A Turn-on Fluorescent Probe for Detection of Sub-ppm level of a Sulfur Mustard Simulant with High Selectivity

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Table of contents

Figure S6. Partial ^{1}H NMR (400 MHz) characterization results of DPXT probe and the thiopyronin product in CD_2Cl_2.

Figure S7. ^{1}H NMR characterization result of the DPXT probe ($CDCl_3$, 400 MHz)

Figure S8. ^{13}C NMR characterization result of the DPXT probe ($CDCl_3$, 100 MHz)

Figure S9. MALDI-MS characterization result of the DPXT probe.

Figure S10. ^{1}H NMR characterization result of thiopyronin derivative ($CDCl_3$, 400 MHz)

Figure S11. ^{13}C NMR characterization result of thiopyronin derivative (DMSO-d_6, 150 MHz)

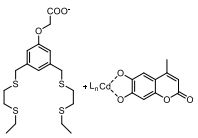
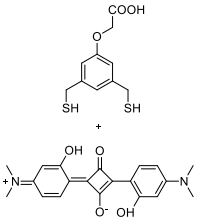
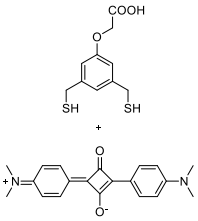
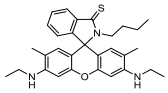
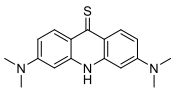
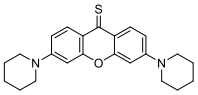
Figure S12. MALDI-MS characterization result of thiopyronin derivative.

Figure S13. ^{1}H NMR characterization result of XTT ($CDCl_3$, 400 MHz)

Figure S14. ^{13}C NMR characterization result of XTT ($CDCl_3$, 100 MHz)

Figure S15. MALDI-MS characterization result of XTT

Table S1. Summary of merits of representative fluorescent probes for sulfur mustard (simultant) sensing.

Probe structure	Response time (2-CEES)	Signal enhancement	Limit of detection (LOD)	Test condition	Gas detection	Ref.
	1 min (2-CEES)	~ 4 fold	200 μM (2-CEES)	80℃，pH=9	No	[1]
	1 min (2-CEES)	~ 27 fold	10 μM (2-CEES)	80℃+K_2CO_3	Yes	[2]
	1 min (2-CEES)	~ 6 fold	18 μM (SM)	80℃+K_2CO_3	Yes	[3]
	>1 h (SM in solution), 10 min (gaseous SM)	~ 100 fold	4.75 μM (SM in solution), 6.25 ppm /10 min (SM gas)	room temperature	Yes	[4]
	1 min (SM in solution)	~ 25 fold	31.6 μM (0.005 mg/mL) (SM in solution)	50-60℃，KOH, MeOH	No	[5]
	> 1 h (2-CEES in solution), 2 min (2-CEES vapor)	850 fold (in solution)	1.2 μM (2-CEES in solution), 0.5 ppm/ min (2-CEES gas)	room temperature	Yes	This work

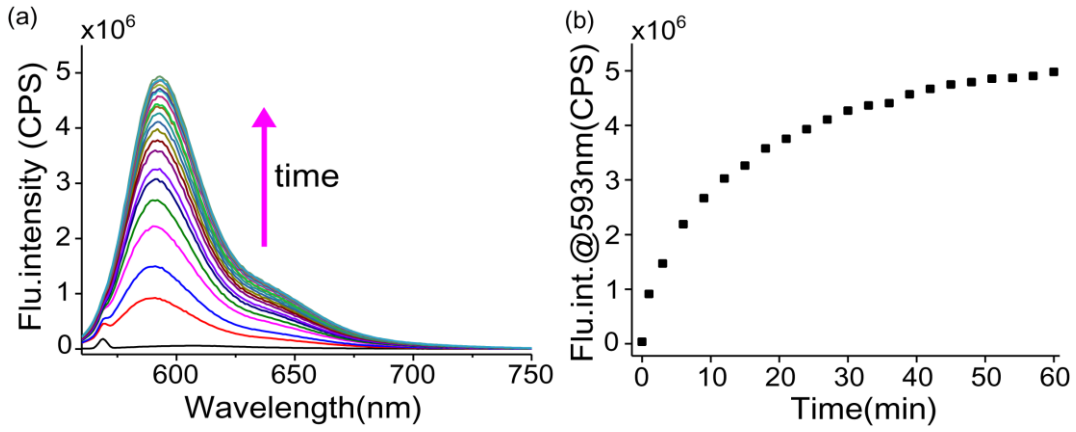


Figure S1. (a) Fluorescence responses of DPXT (10 μM) to 2-CEES (100 equiv.) recorded at 2 min interval; (b) time-dependent fluorescence responses recorded at 593 nm. λ_{ex} = 465 nm

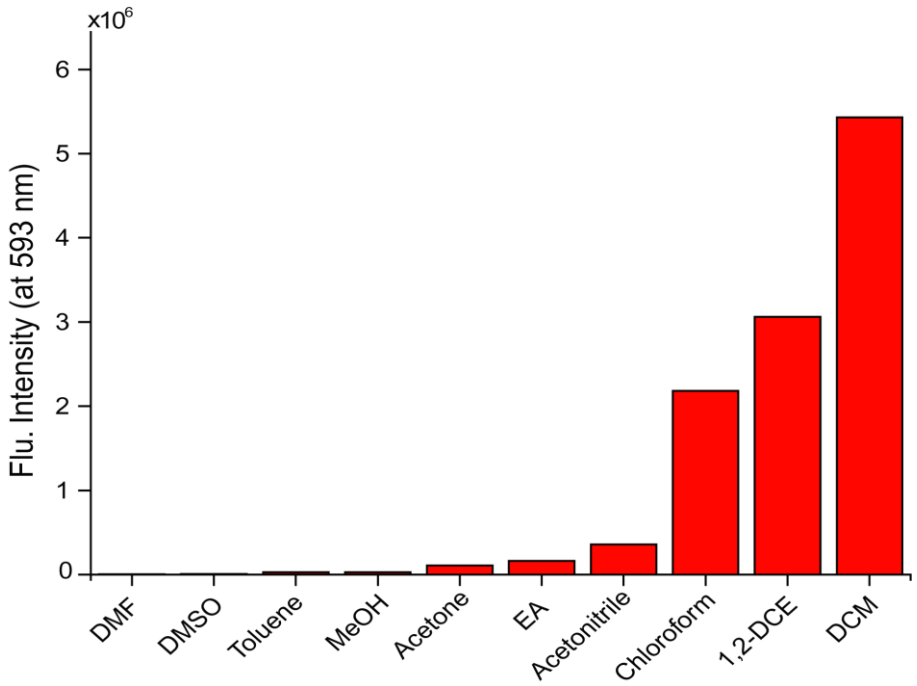


Figure S2. Fluorescence intensity (at 593 nm) enhancement of DPXT in various solvents (10 μM) upon addition of 100 equiv. of 2-CEES. λ_{ex} = 570 nm. Each spectrum was recorded 1 h after the addition of 2-CEES.

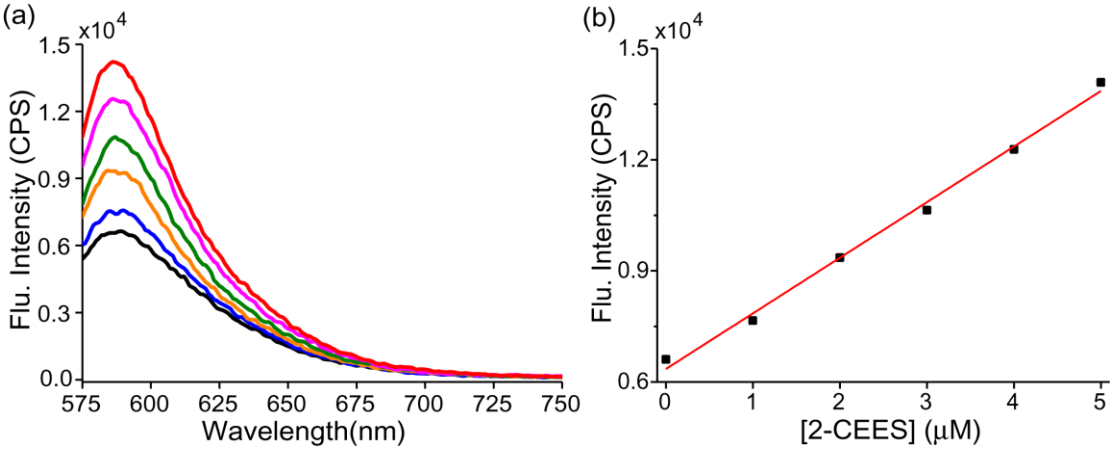


Figure S3. (a) Fluorescence emission spectra of DPXT/DCM solution upon gradually increasing the concentration 2-CEES (0-5μM). (b) A plot of the fluorescence intensity (at 593 nm) as a function of 2-CEES concentration. The red line is a linear fit to the experimental data (R^2 = 0.993).

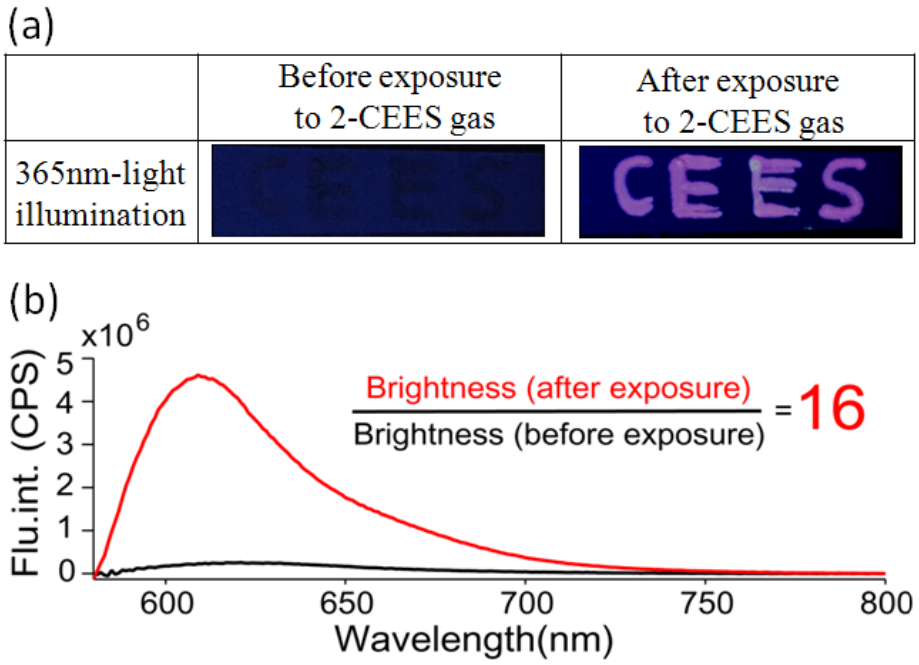


Figure S4. (a) Photographs of a TLC plate patterned with "CEES" using DPXT/DCM solution acquired before and after exposure to 2-CEES vapor with concentration of 0.5 ppm upon illumination of 365-nm light. (b) Fluorescence emission spectra of the abovementioned TLC plate before (black curve) and after (red curve) exposure to 2-CEES vapor (λ_{ex} = 570 nm).

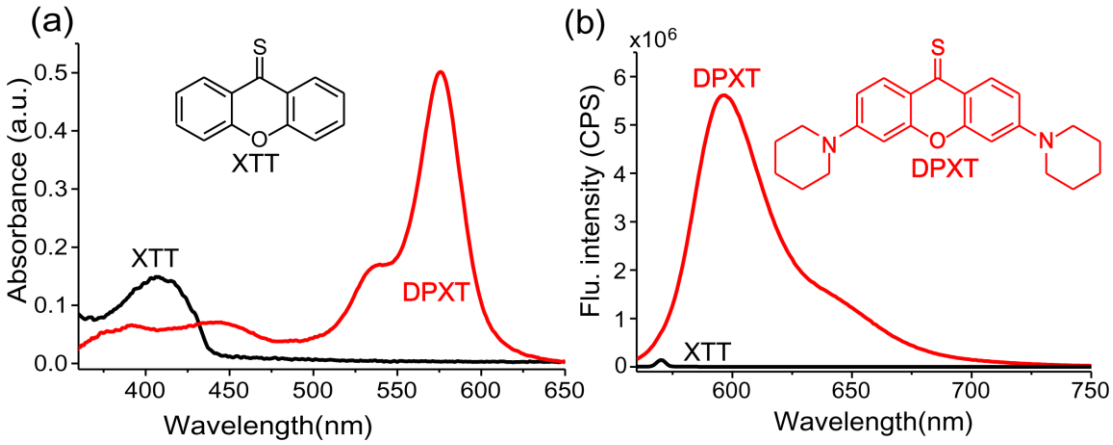


Figure S5. UV-vis absorption (a) and fluorescence emission spectra (b) of DPXT/DCM solution and the DCM solution containing the reference compound xanthene-9-thione (XTT), respectively, in the presence of 100 equiv. of 2-CEES.

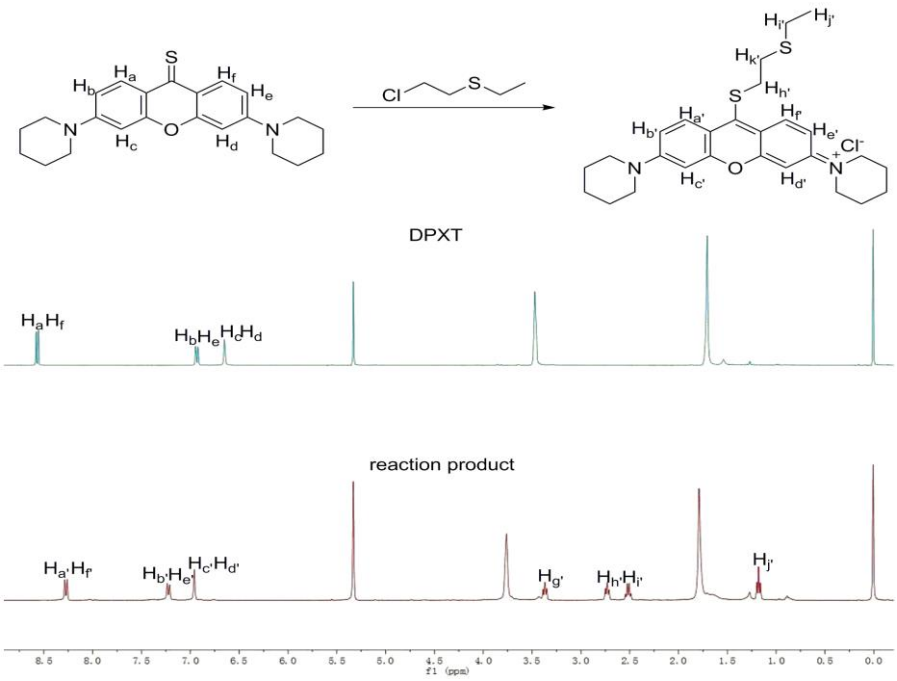


Figure S6. Partial ^{1}H NMR (400 MHz) characterization results of DPXT probe and the thiopyronin product in CD_2Cl_2

To gain a deeper insight into the underlying mechanism that DPXT underwent, the comparative analysis of the ^{1}H NMR measurement results of DPXT and the reaction product confirmed the molecular structure of the latter and presented a clue to the underlying mechanism that DPXT underwent. In the presence of CEES, the new signals at 3.37 ($H_{g'}$), 2.73($H_{h'}$), 2.52($H_{i'}$), 1.18($H_{j'}$) ppm in the ^{1}H NMR spectrum

attributable to reaction between DPXT and CEES. Hydrogen signals H_a, H_f (8.55 pm) shifted to $H_{a'}$, $H_{f'}$ (8.29 ppm) due to the shielding effect, it attribute to the disappearance of the electron-withdrawing thiocarbonyl groups after the reaction of DPXT with CEES. Due to the de-shielding effect of the nitrogen ionization in the piperidyl group, hydrogen signals H_b, H_e (6.95 pm) and H_b, H_e (6.65 pm) which are adjacent to piperidyl group shift to the low field $H_{b'}$, $H_{e'}$ (7.24 ppm) and $H_{b'}$, $H_{e'}$ (6.96ppm). At the same time, the hydrogen signals in the piperidyl group carbon also moves to the low field significantly. In addition, the proposed mechanism of DPXT probe for 2-CEES sensing also found support from the MALDI-MS characterization results of the DPXT probe sample in the absence and presence of 2-CEES. Specifically, the adduct product of the probe upon addition of 2-CEES displayed characteristic mass-to-charge ratios at 467.2186 (MALDI-MS, $[M]^+$), which is in well agreement with the calculated m/z values of the structures of reaction product. Definitely, the ^{1}H NMR and MALDI-MS characterization results validated the abovementioned proposed sensing mechanism of the as-prepared DPXT probe.

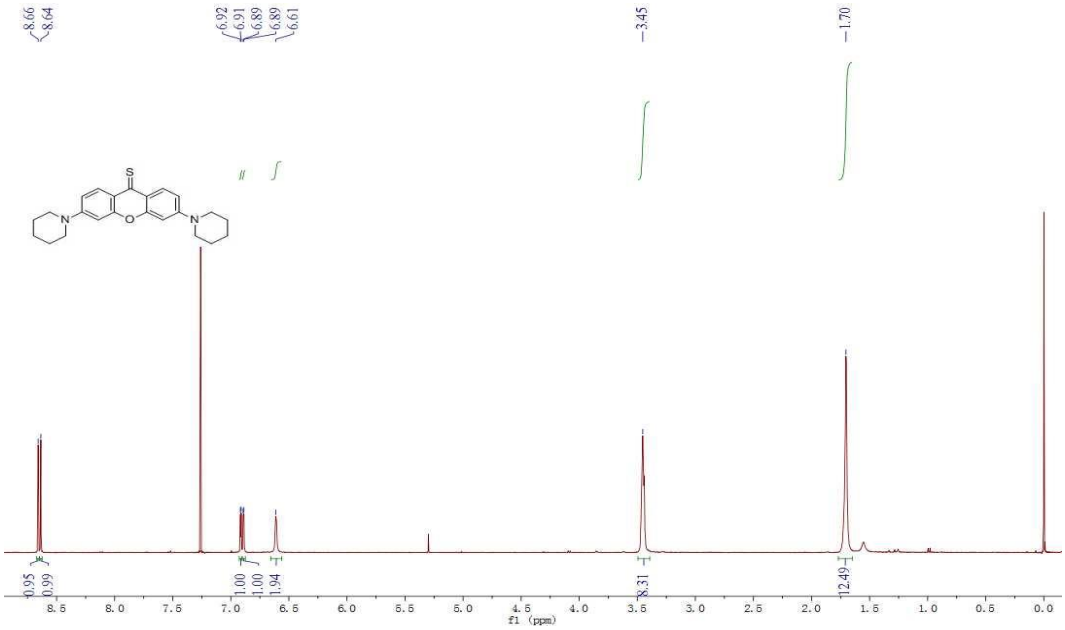


Figure S7. ^{1}H NMR characterization result of the DPXT probe ($CDCl_3$, 400 MHz)

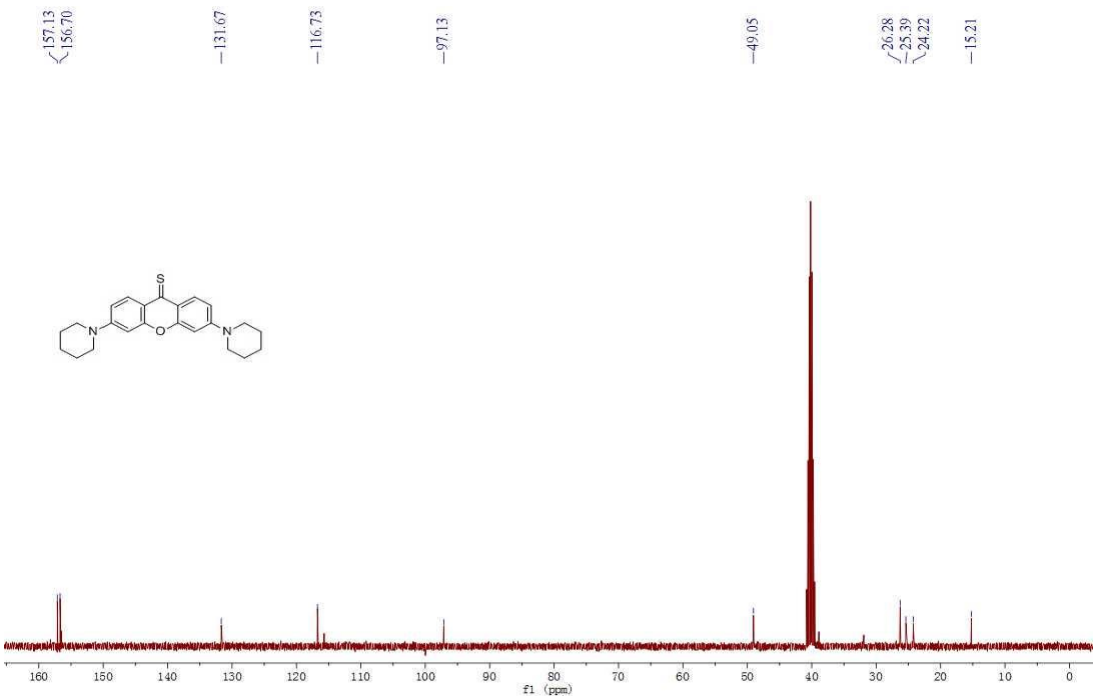


Figure S8. ^{13}C NMR characterization result of the DPXT probe ($CDCl_3$, 100 MHz)

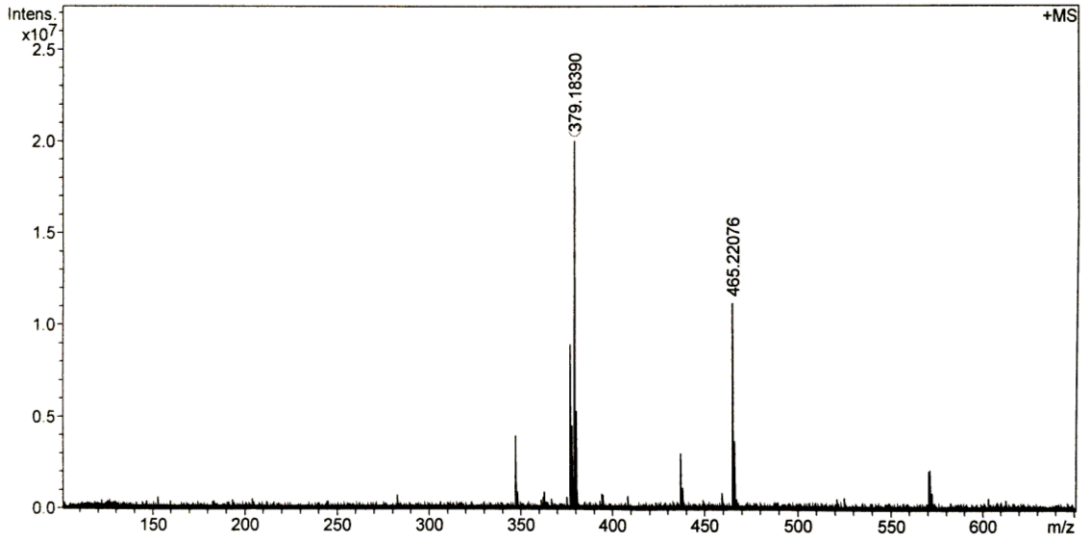


Figure S9. MALDI-MS characterization result of the DPXT probe.

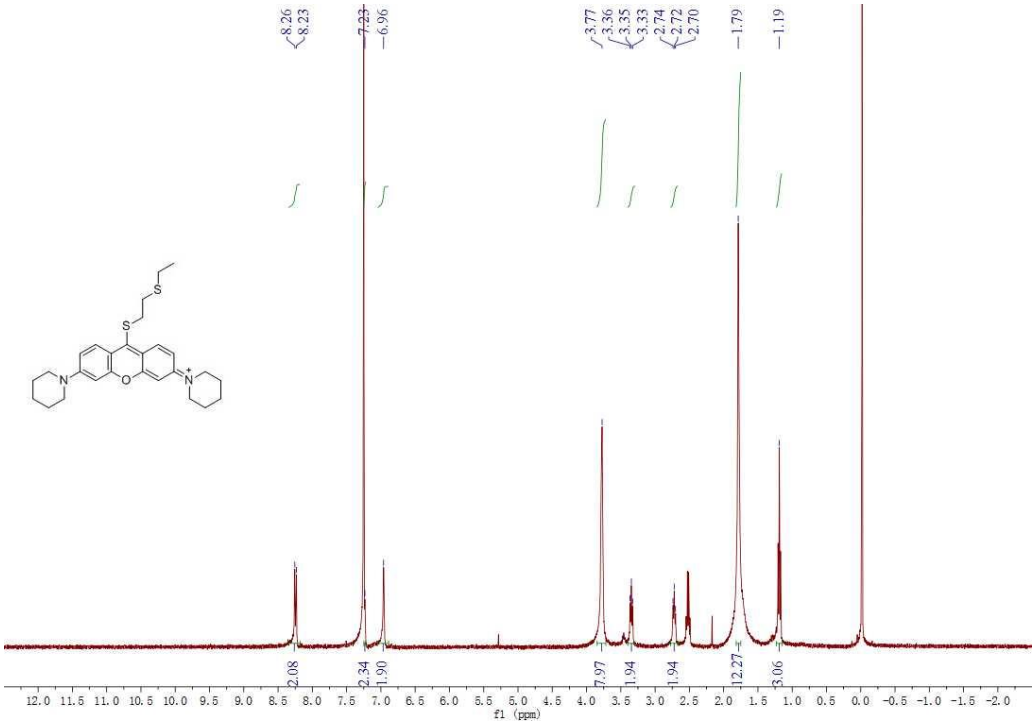


Figure S10. ^{1}H NMR characterization result of thiopyronin derivative ($CDCl_3$, 400 MHz)

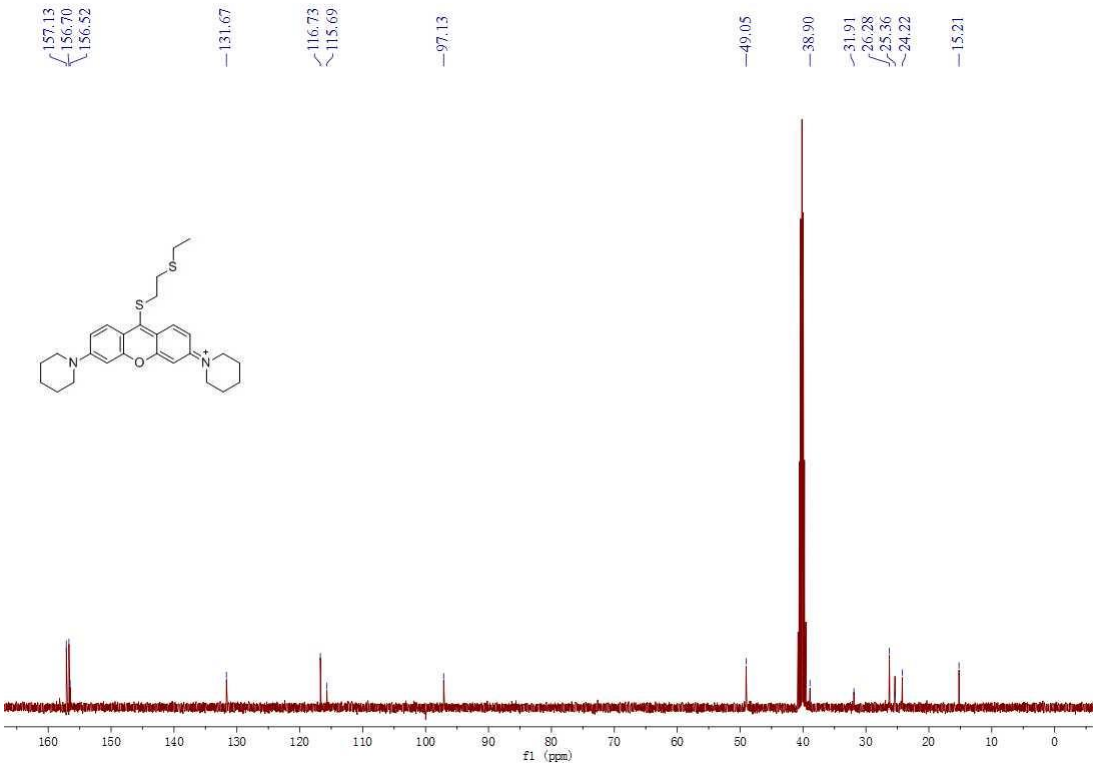


Figure S11. ^{13}C NMR characterization result of thiopyronin derivative (DMSO-d_6, 150 MHz)

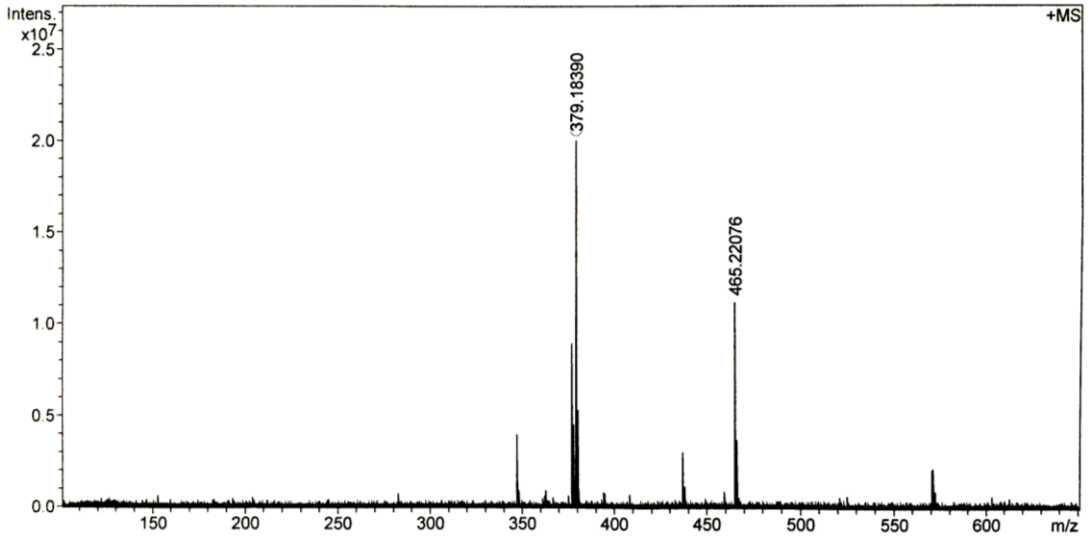


Figure S12. MALDI-MS characterization result of thiopyronin derivative.

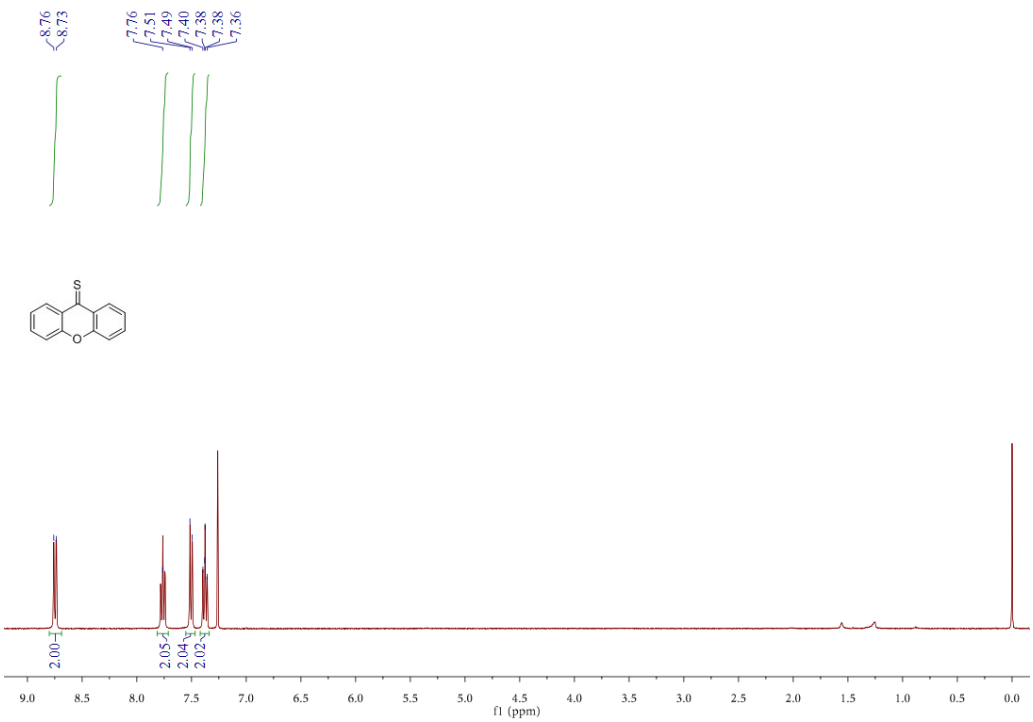


Figure S13. ^{1}H NMR characterization result of XTT ($CDCl_3$, 400 MHz).

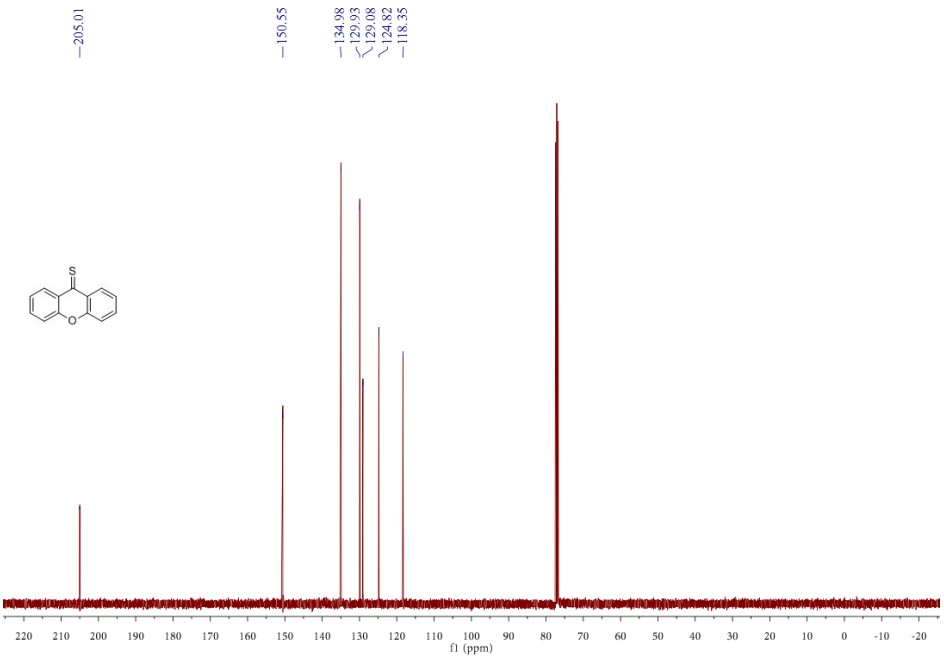


Figure S14. ^{13}C NMR characterization result of XTT ($CDCl_3$, 400 MHz).

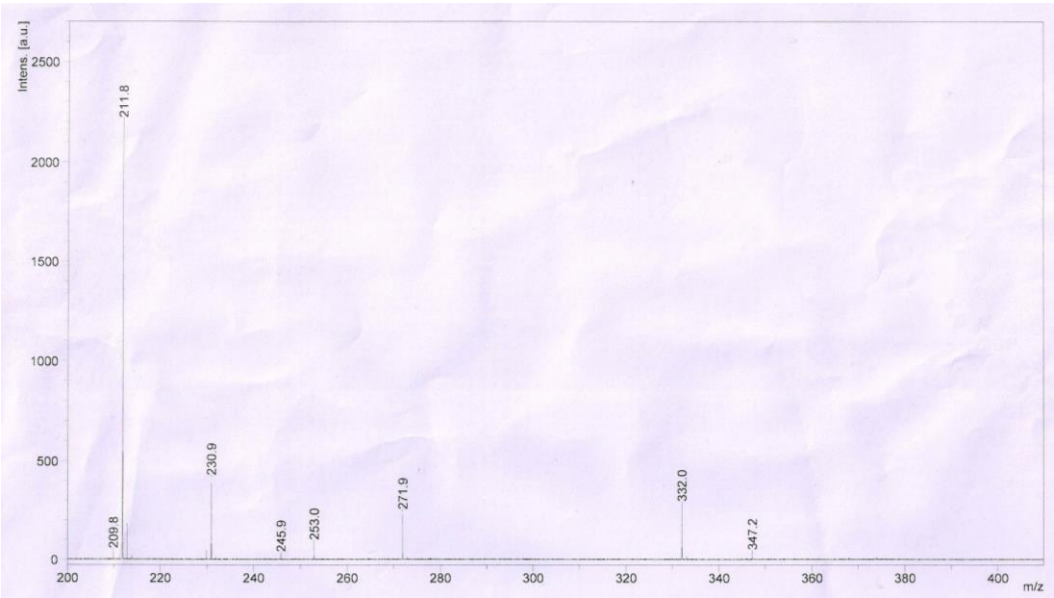


Figure S15. MALDI-MS characterization result of XTT.

References

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(3) Kumar, V.; Rana, H. *RSC Adv.* **2015**, *5*, 91946-91950.

(4) Goud, D. R.; Purohit, A. K.; Tak, V.; Dubey, D. K.; Kumar, P.; Pardasani, D. *Chem. Commun.* **2014**, *50*, 12363-12366.

(5) Kumar, V.; Rana, H.; Raviraju, G.; Gupta, A. K. *Anal. Chem*. 2018, 90, 1417-1422.