Supporting Information for

Optical detection of sulfur mustard contaminated surface based on sprayable fluorescence probe

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Synthesis and characterization of DPXT for sulfur mustard
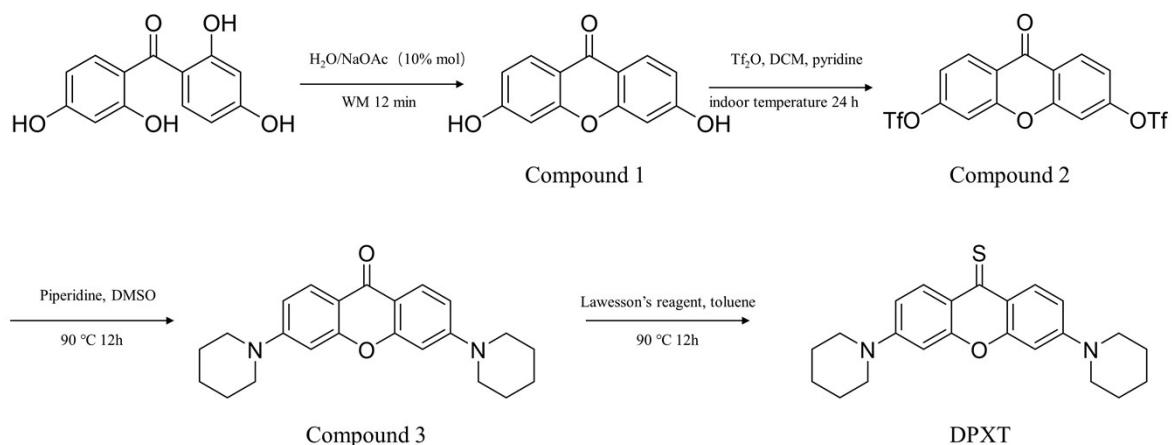
Scheme S1 Synthetic Route for DPXT Probe.

Synthesis 3,6-Dihydroxy-9H-xanthen-9-one (Compound 1)

In the presence of NaOAc as a base catalyst, the cyclization of hydroxybenzophenone 2,2,4,4-tetrahydroxybenzophenone to hydroxyxanthone Compound 1 under microwave irradiation at 100 °C in

water as solvent was accomplished in 12 min.[1] 2,2,4,4-tetrahydroxybenzophenone (2.46 g, 10.0 mmol) and NaOAc (0.082 g, 1 mmol, 10% mol) in water (40 mL) was introduced in the cavity of the microwave reactor and irradiated for 12 min in PTFE microwave digestion tank. After cooling to room temperature, the reaction mixture was collected by Büchner funnel and washed with water (3×30 mL), hexane (3×30 mL) and dried, Compound 1 was obtained as a white solid (2.166 g, 95%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.99 (d, J = 8.7 Hz, 2H), 10.82 (s, 2H), 6.87 (dd, J = 8.7, 2.2 Hz, 2H), 6.83 (d, J = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 174.39, 163.83, 157.94, 128.24, 114.46, 114.13, 102.56.
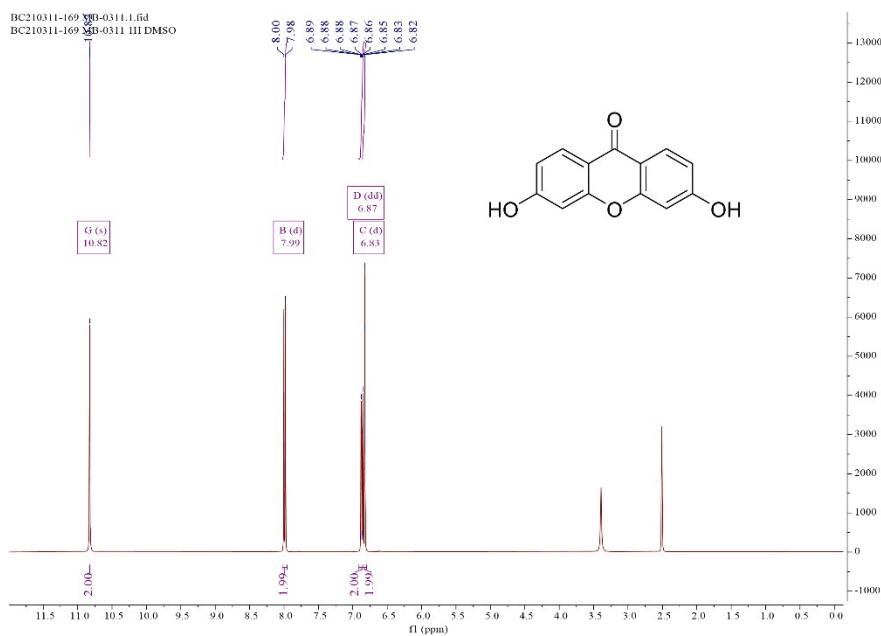
Fig. S1 ^{1}H NMR spectrum of Compound 1 (DMSO-d_6, 400 MHz).
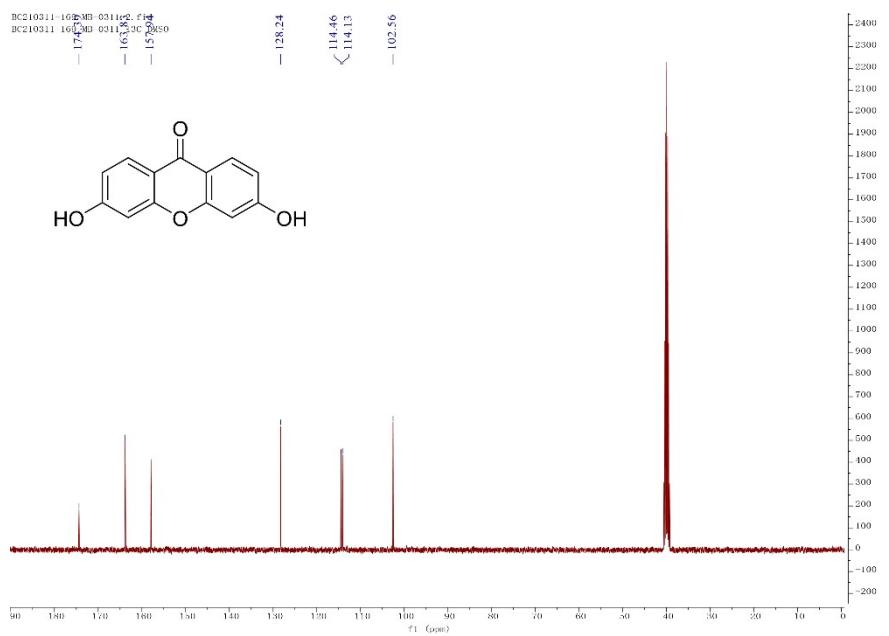
**Fig. S2** ^{13}C NMR spectrum of Compound 1 (DMSO-d$_6$, 100 MHz).

Synthesis of 3,6-Di(piperidin-1-yl)-9H-xanthene-9-thione (DPXT)

After the compound 1 was obtained, DPXT was synthesized according to a reported method.[2] The ^{1}H NMR, ^{13}C NMR and ESI-MS spectrum were shown below.
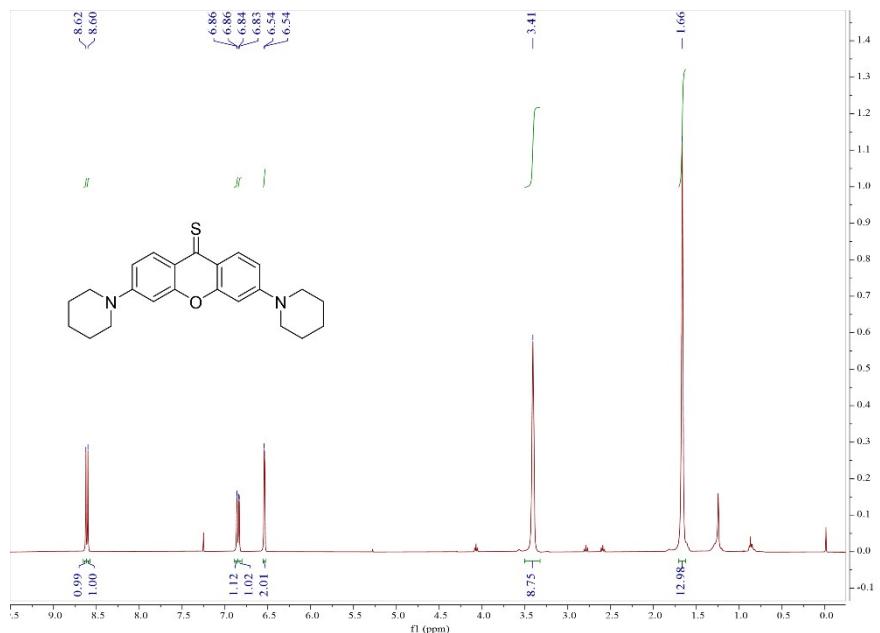
Fig. S4 ^{13}C NMR characterization results of DPXT (CDCl$_3$, 400 MHz).
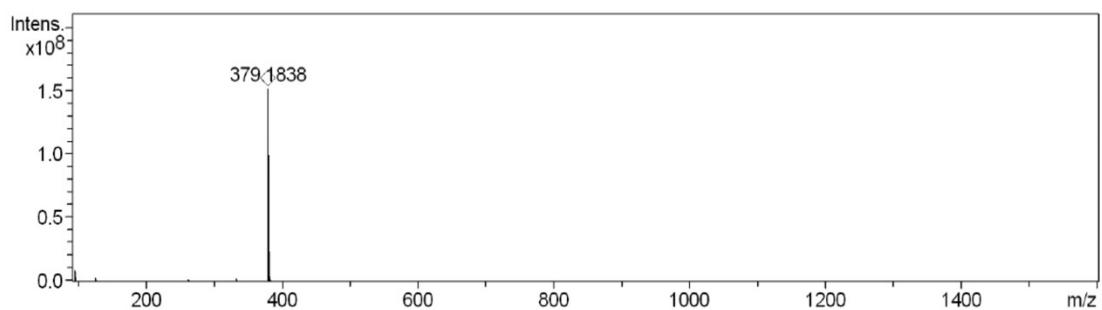
Fig. S5 ESI-MS spectrum of DPXT.
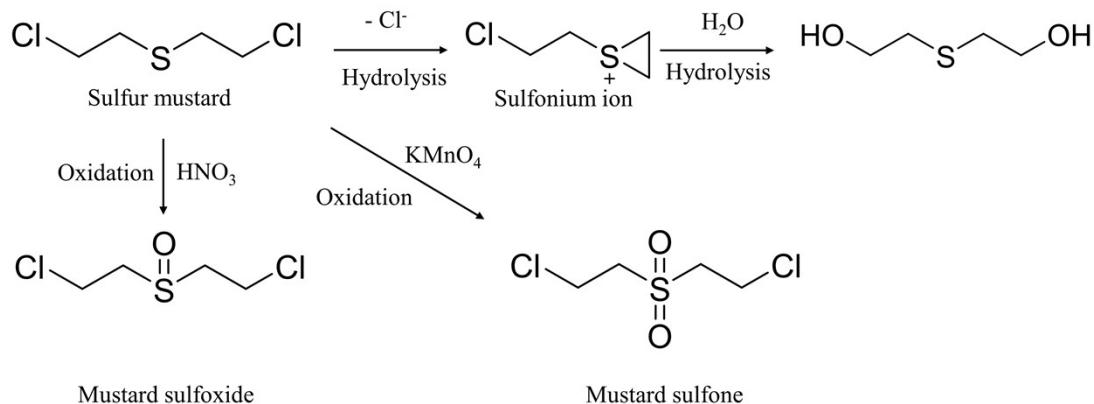
Scheme S2 The primary hydrolysis and oxidation pathways of HD
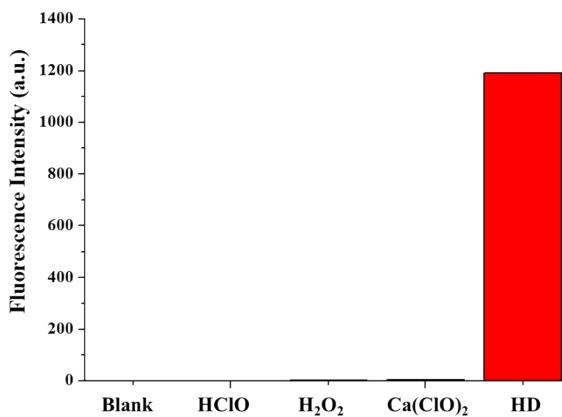
Fig. S6 Fluorescence responses (615 nm) of DPXT (10 μM) toward HD (1 mM) and common oxidizing substances (2 mM) in sodium bicarbonate buffer (pH=7.2, 30% ACN).

DTF Calculations

Geometric optimizations and energy level calculations were performed in the gas phase at the B3LYP 6-31 G (d, p) level of theory, using the Gaussian 09 software pachage. Absolute energies in Hartrees are given without additional corrections.

Table S1 Cartesian coordinates of DPXT in the ground state.

(Energy: -1475.0844 hartrees)

Center Number	Atom	Coordinates (ground state)		
		X	Y	Z
1	C	-3.6632	1.4839	0.0058
2	C	-3.6056	0.0632	0.0315
3	C	-2.3305	-0.5279	0.0430
4	C	-1.1853	0.2602	0.0242
5	C	-1.2247	1.6697	-0.0098
6	C	-2.5125	2.2443	-0.0169
7	O	-0.0051	-0.4309	0.0239
8	C	1.1766	0.2543	-0.0045
9	C	1.2265	1.6606	-0.0199
10	C	0.0039	2.4545	-0.0261
11	C	2.3202	-0.5451	0.0046
12	C	3.5943	0.0396	-0.0185
13	C	3.6626	1.4617	-0.0411
14	C	2.5214	2.2293	-0.0400
15	S	0.0104	4.1322	-0.0502
16	N	-4.7568	-0.7242	0.0107
17	N	4.7626	-0.7227	-0.0681
18	C	-4.8150	-1.9416	0.8323
19	C	-5.7821	-2.9741	0.2478
20	C	-7.1758	-2.3655	0.0577
21	C	-7.0734	-1.0847	-0.7768
22	C	-6.0638	-0.0940	-0.1821
23	C	5.9065	-0.3239	0.7669
24	C	7.2284	-0.8407	0.1948
25	C	7.1815	-2.3614	0.0097
26	C	5.9608	-2.7456	-0.8328
27	C	4.6620	-2.1708	-0.2527
28	H	-4.6175	1.9932	0.0363
29	H	-2.1959	-1.6018	0.0245
30	H	-2.5718	3.3273	-0.0233
31	H	2.1760	-1.6158	0.0574
32	H	4.6254	1.9547	-0.1045
33	H	2.5860	3.3115	-0.0732
34	H	-3.8177	-2.3703	0.9193
35	H	-5.1385	-1.6779	1.8558
36	H	-5.3933	-3.3206	-0.7179
37	H	-5.8219	-3.8428	0.9151
38	H	-7.8519	-3.0833	-0.4196
39	H	-7.6072	-2.1297	1.0408
40	H	-6.7562	-1.3363	-1.7964

41	H	-8.0479	-0.5891	-0.8540
42	H	-5.9497	0.7455	-0.8697
43	H	-6.4536	0.3088	0.7707
44	H	5.9318	0.7616	0.8530
45	H	5.7715	-0.7214	1.7894
46	H	7.4136	-0.3543	-0.7711
47	H	8.0446	-0.5532	0.8675
48	H	8.1024	-2.7245	-0.4597
49	H	7.1161	-2.8461	0.9941
50	H	6.0855	-2.3630	-1.8534
51	H	5.8623	-3.8348	-0.9053
52	H	3.8430	-2.3759	-0.9454
53	H	4.4225	-2.6768	0.7009

Table S2 Cartesian coordinates of product for DPXT reaction with sulfur mustard in the ground state.

Center Number	Atom	Coordinates (ground state)		
		X	Y	Z
1	C	-2.3421	3.1659	-0.6812
2	C	-3.4902	2.5401	-0.1477
3	C	-3.4299	1.1467	0.0593
4	C	-2.2840	0.4341	-0.2462
5	C	-1.1193	1.0416	-0.7875
6	C	-1.2041	2.4363	-0.9920
7	O	-2.3415	-0.9180	-0.0041
8	C	-1.2630	-1.7191	-0.2883
9	C	-0.0650	-1.1865	-0.8229
10	C	0.0248	0.2237	-1.0757
11	C	-1.4271	-3.0678	0.0043
12	C	-0.3896	-3.9839	-0.2420
13	C	0.8114	-3.4751	-0.7928
14	C	0.9638	-2.1296	-1.0658
15	N	-4.6747	3.2405	0.1381
16	N	-0.5288	-5.3621	-0.0061
17	C	-5.3056	3.0136	1.4475
18	C	-6.7850	3.4060	1.4337
19	C	-6.9573	4.8582	0.9745
20	C	-6.2569	5.0663	-0.3720
21	C	-4.7890	4.6255	-0.3183
22	C	0.5438	-6.0349	0.7431
23	C	0.5408	-7.5442	0.4900
24	C	-0.8301	-8.1468	0.8174
25	C	-1.9276	-7.3947	0.0567
26	C	-1.8577	-5.8839	0.3106

27	H	-2.3254	4.2376	-0.8355
28	H	-4.2851	0.5926	0.4274
29	H	-0.3371	2.9449	-1.3988
30	H	-2.3684	-3.3702	0.4445
31	H	1.6160	-4.1568	-1.0454
32	H	1.8856	-1.7739	-1.5131
33	H	-5.1979	1.9635	1.7203
34	H	-4.7794	3.6005	2.2239
35	H	-7.3247	2.7359	0.7529
36	H	-7.2036	3.2603	2.4363
37	H	-8.0190	5.1197	0.9020
38	H	-6.5163	5.5310	1.7237
39	H	-6.7693	4.4825	-1.1466
40	H	-6.3003	6.1185	-0.6763
41	H	-4.3549	4.6968	-1.3184
42	H	-4.2218	5.3140	0.3370
43	H	1.5045	-5.6060	0.4568
44	H	0.4203	-5.8453	1.8261
45	H	0.7850	-7.7286	-0.5637
46	H	1.3272	-8.0109	1.0946
47	H	-0.8539	-9.2146	0.5728
48	H	-1.0133	-8.0660	1.8983
49	H	-1.8159	-7.5731	-1.0199
50	H	-2.9211	-7.7577	0.3447
51	H	-2.5881	-5.3769	-0.3249
52	H	-2.1335	-5.6727	1.3617
53	C	2.5415	1.1187	-0.2055
54	H	2.0331	1.8039	0.4771
55	H	2.6231	0.1399	0.2736
56	C	6.4973	2.4529	0.1297
57	H	6.8569	1.7191	-0.5970
58	H	6.2893	3.3910	-0.3923
59	S	1.5089	0.9366	-1.7421
60	C	3.9166	1.6526	-0.5935
61	H	3.8275	2.6291	-1.0797
62	H	4.4136	0.9648	-1.2847
63	S	4.9528	1.8311	0.9182
64	C	7.5416	2.6749	1.2119
65	H	7.7876	1.7490	1.7329
66	H	7.2206	3.4236	1.9369
67	Cl	9.0918	3.2883	0.4859

Based on DFT, the excitation energy and oscillator strength (f) of the probe molecule in dichloromethane solvent and the measured values of fluorescence probe molecule in dichloromethane solvent are shown in Table S3 and Fig. S7 . It can be seen from Fig. S7 that the calculated maximum absorption peak is basically consistent with the experimental value. The calculated electron transition orbits $101 \rightarrow 102$ corresponding to λ_{max}= 449 nm are molecular Homo orbital and LUMO orbital. The absorption at 378 nm is the transition from HOMO-1 and HOMO-3 to LUMO.

Table S3 Calculated optical transitions for probe

Absorption observed in experiment	Calculated excitation energy (EV)	Transition orbit	Oscillator strength (f)
449 nm	2.8405 eV (436.48 nm)	99→102	0.0018
	2.9728 eV (417.06 nm)	101→102	0.7936
378 nm	3.3256 eV (372.82 nm)	98→102 100→102	0.2418

Fig. S7 The commercially available pump to spray fluorescent material.

Reference

1.   X. J. Zhang and Q. D. You, *Cheminform*, 2012, **42**, 2952-2958.
2.   H. Wang, J. Guan, X. Han, S.-W. Chen, T. Li, Y. Zhang, M.-S. Yuan and J. Wang, *Talanta*, 2018, **189**, 39-44.