Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

A salicylaldoximate-based AIE probe for the detection of a nerve agent simulant DCP

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1 UV-Vis spectra of TPE-D with DCP in different f_w water/acetonitrile solutions.

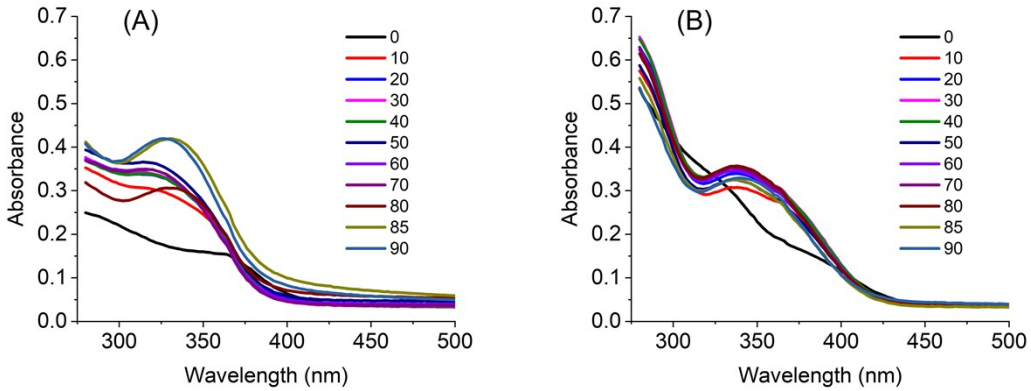


Fig. S1. UV-Vis spectra of TPE-D (40 μM) with (A) and without (B) DCP (200 μM) in water/acetonitrile solutions with increased water fractions (f_w, 0-90%).

2 Selectivity of TPE-D from compounds with low activity when detecting DCP.

In addition, three compounds with low activity, triethyl phosphate (TEP), tributyl phosphate (TBP), and 2-chloroethyl ethyl sulfide (CEES, a sulphur mustard mimic) were chosen to evaluate the probe's selectivity. As we expected, no obvious fluorescence emission (EX: 336nm) appeared after TEP, TBP and CEES were added to TPE-D detection solutions separately (Fig. S2). The results indicated that TPE-D shows a good selectivity to prevent from the interference of other compounds with low activity when it detects DCP.

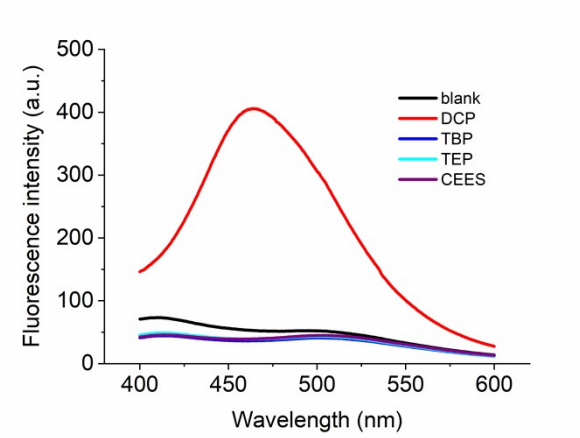


Fig. S2. Fluorescence spectra of probe TPE-D (40 μM) with DCP (200 μM), TBP (200 μM), TEP (200 μM), CEES (200 μM) in the presence of DBU. EX 336 nm.

3 The structural confirmation of the probe TPE-D by MS and NMR analysis.

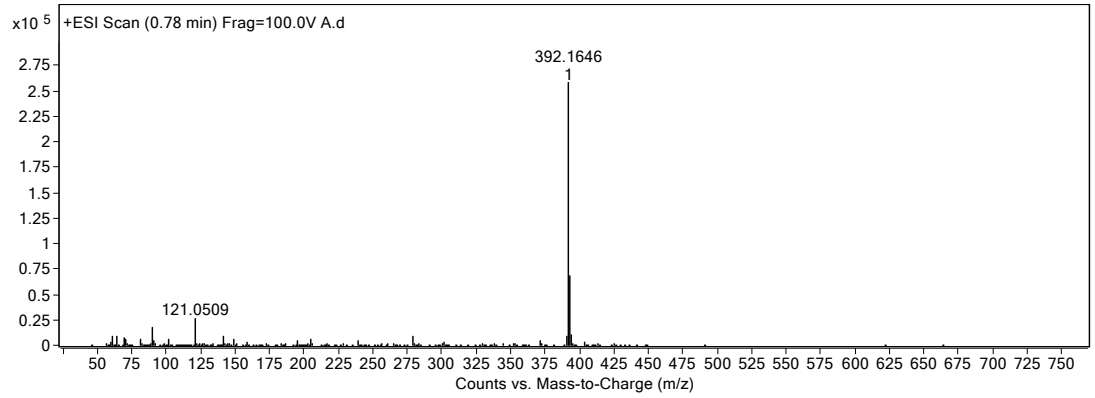


Fig. S3. High-resolution mass spectrum of TPE-D.

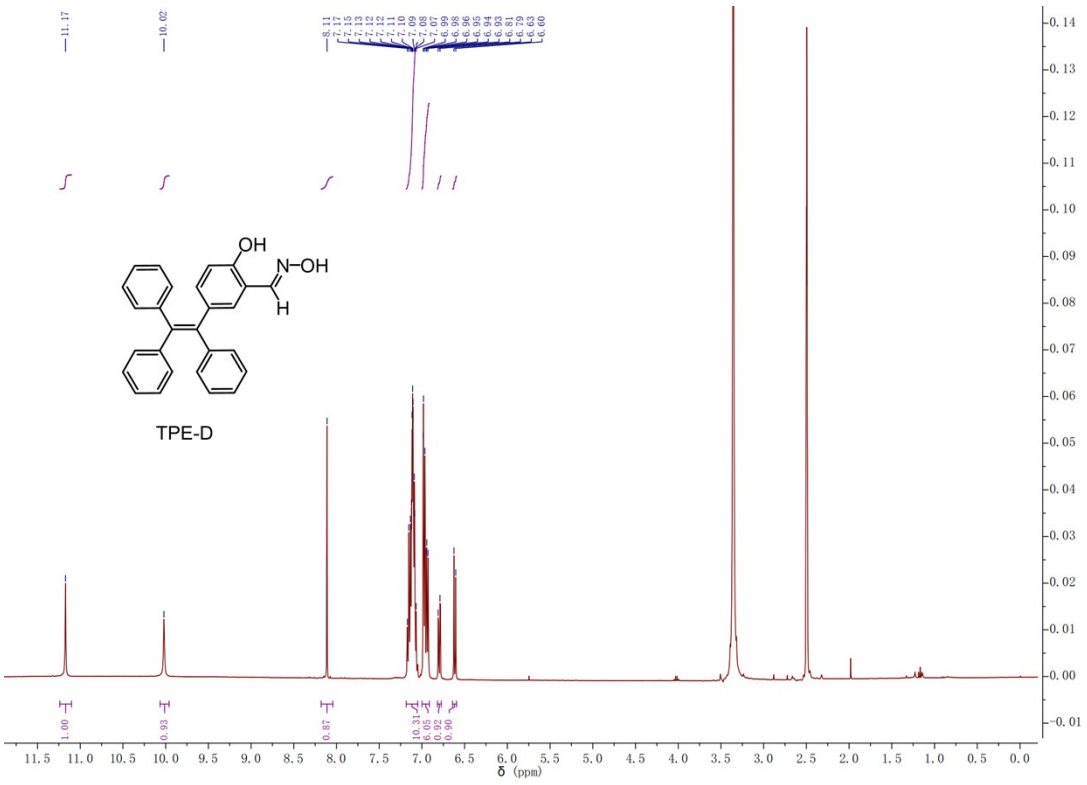


Fig. S4. ^{1}H NMR (400 MHz) spectra of TPE-D.

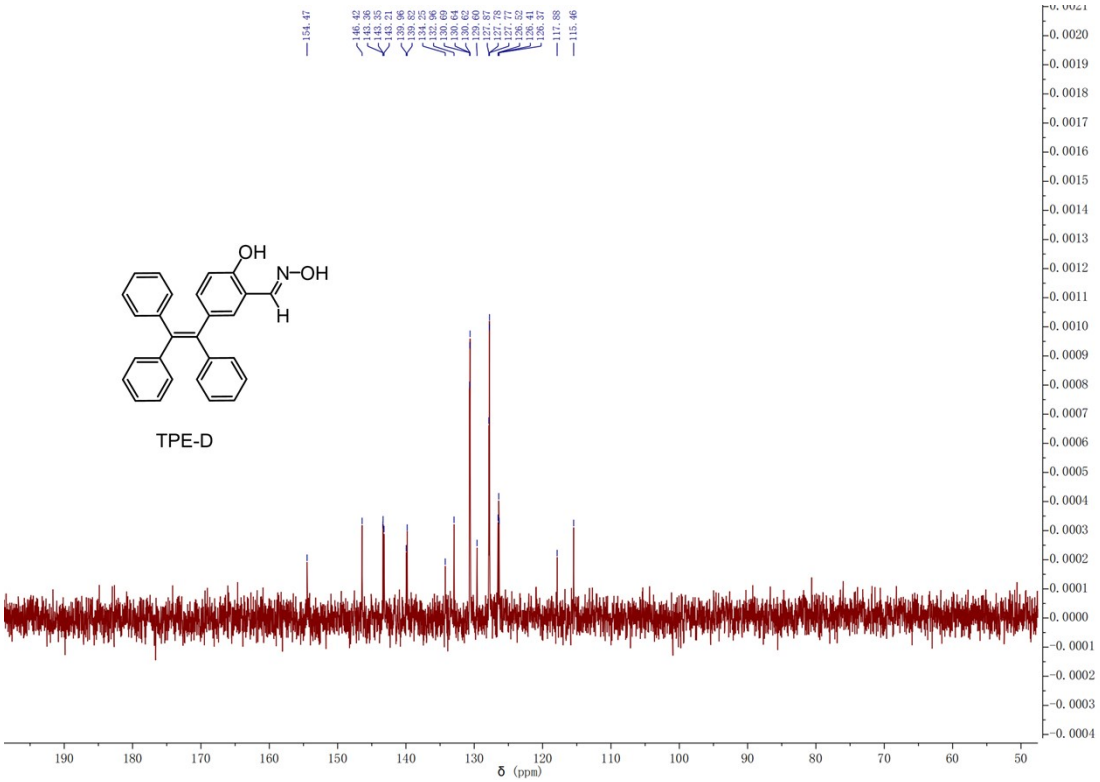


Fig. S5. ^{13}C NMR (101 MHz) spectra of TPE-D.

4 The structural confirmation of the intermediate TPE-OH during the detection of TPE-D for DCP by MS and NMR analysis.

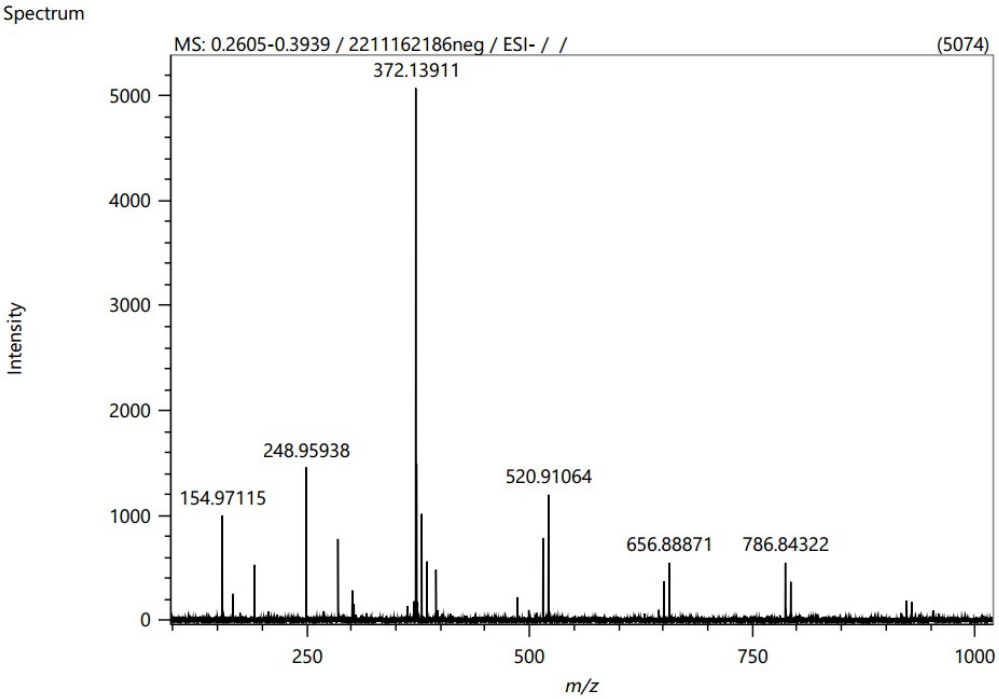


Fig. S6. High-resolution mass spectrum of TPE-OH.

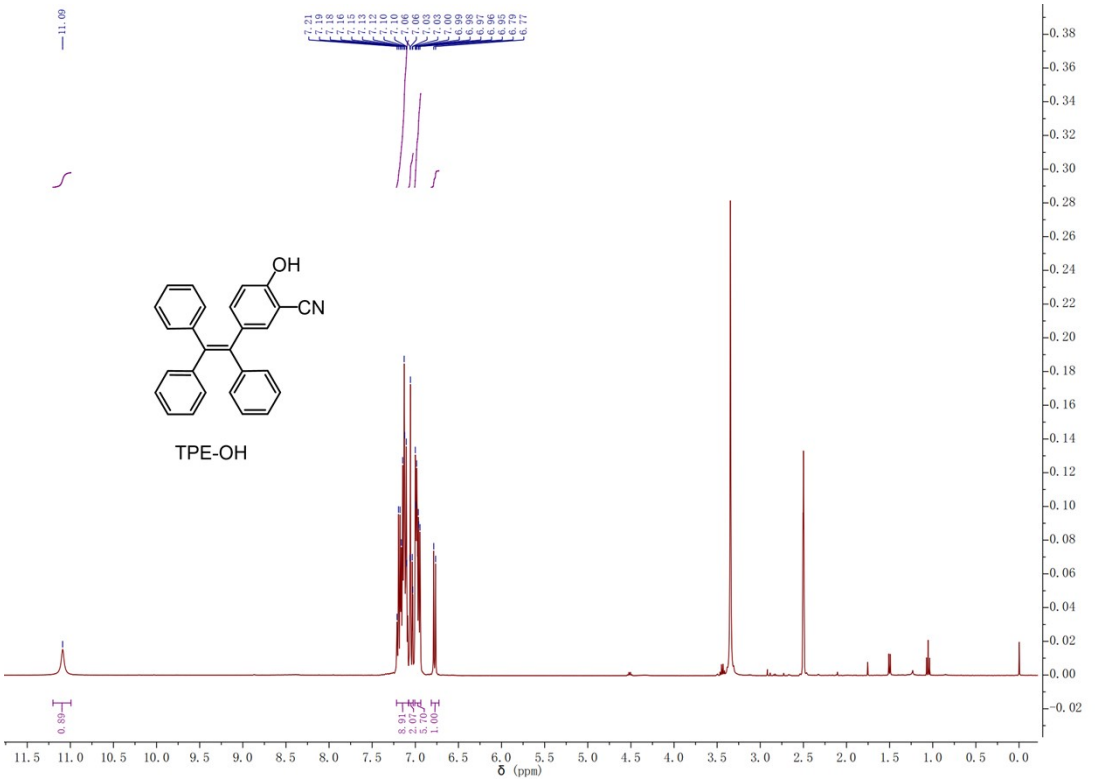


Fig. S7. ^{1}H NMR (400 MHz) spectra of TPE-OH.

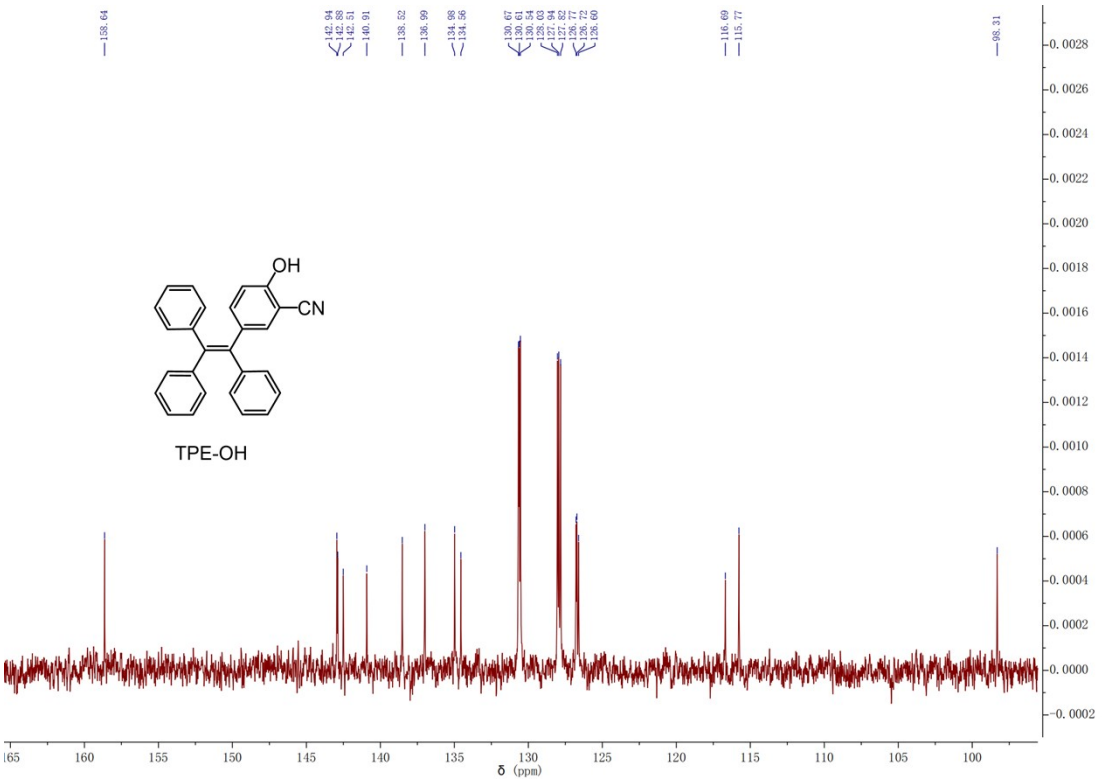


Fig. S8. ^{13}C NMR (101 MHz) spectra of TPE-OH.

5 The structural confirmation of the final product TPE-OP during the detection of TPE-D for DCP by MS and NMR analysis.

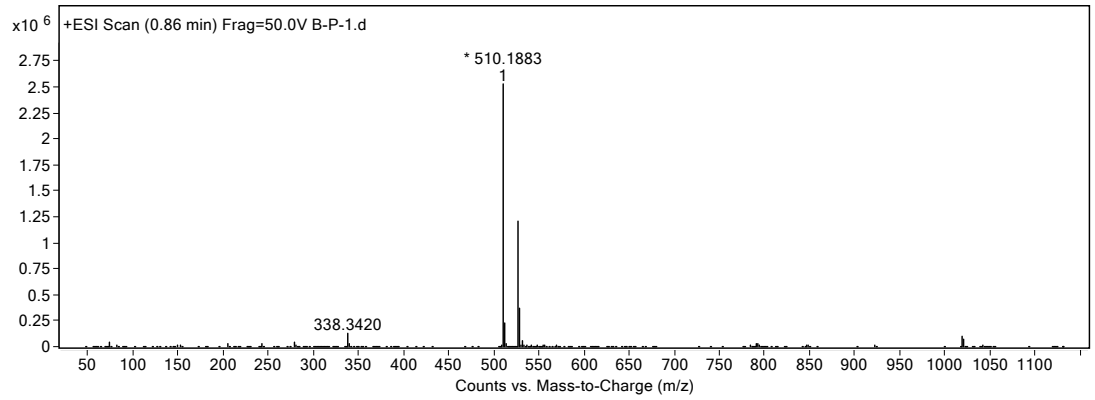


Fig. S9. High-resolution mass spectrum of TPE-OP.

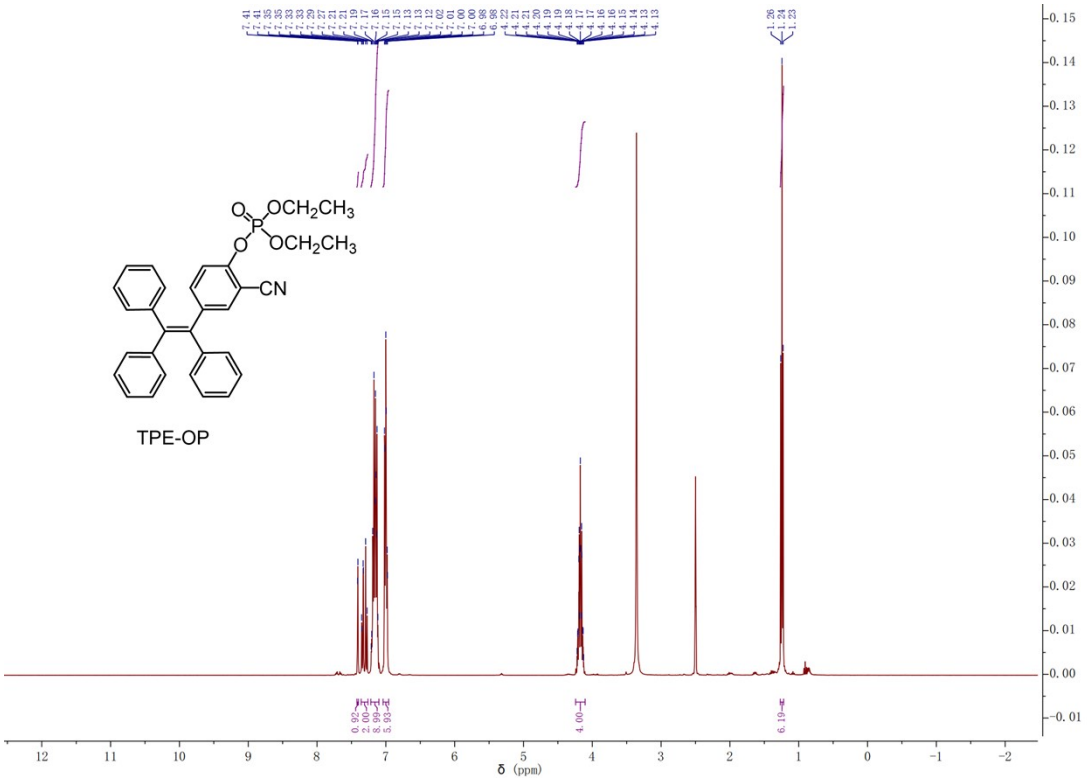


Fig. S10. ^{1}H NMR (400 MHz) spectra of TPE-OP.

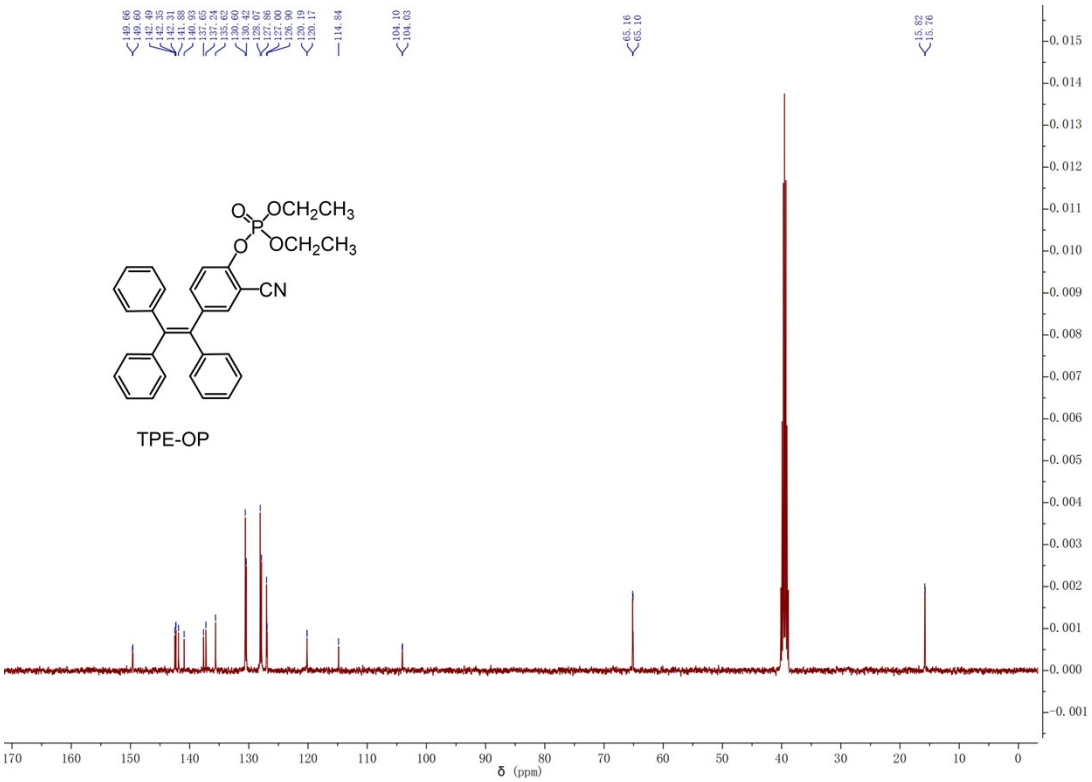


Fig. S11. ^{13}C NMR (101 MHz) spectra of TPE-OP.

6 TPE-D detected and distinguished DCP and DCNP.

Fluorescence measurement was performed after DCNP was added to the probe detection system. The resultant solution exhibited a significant emission fluorescent signal (Fig. S12), which suggested that the probe could also detect DCNP, the simulant of Tabun.

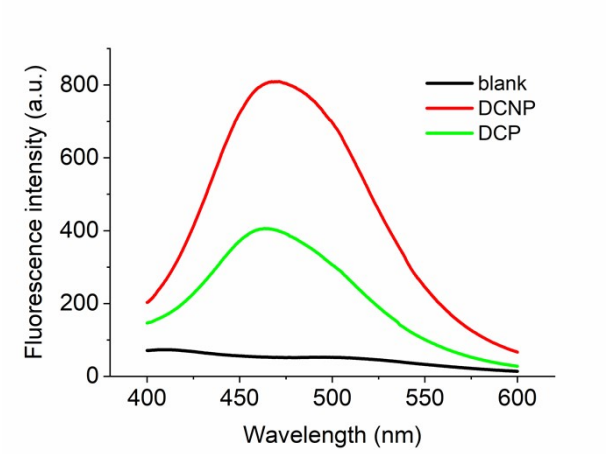


Fig. S12. Fluorescence emission spectra of TPE-D (40 μM) with DCNP (200 μM) and DCP (200 μM) in the presence of DBU. EX 336 nm.

Analysis with MS was carried out to confirm the product(s) of TPE-D with DCNP in the

presence of DBU. For the sample of TPE-D with DCNP at the ratio of DCNP to TPE-D less than 1, a clear major peak of 372.1 appeared in negative ion mode (Fig.S13), which matched the calculated molecular weight of the product TPE-OH (372.1, $[M-H]^-$, $C_{27}H_{18}NO^-$). When the ratio of DCNP to TPE-D was more than 1, peaks located at 510.1 and 532.1 were observed in positive ion mode (Fig. S14), which matched the calculated molecular weight of the product TPE-OP (510.1, $[M+H]^+$, $C_{31}H_{29}NO_4P^+$, and 532.1 $[M+Na]^+$, $C_{31}H_{28}NO_4PNa^+$). Therefore, the reaction of probe with DCNP generated the same products as its reaction with DCP.

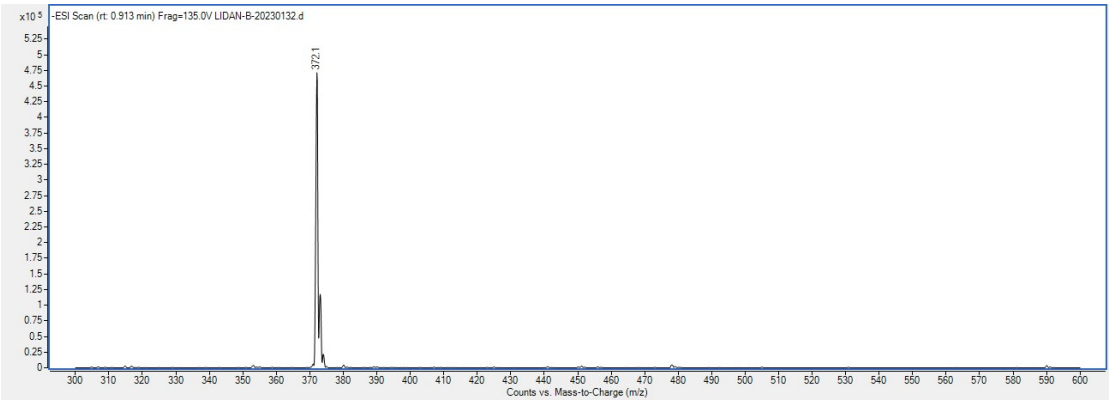


Fig. S13. MS analysis of the sample of TPE-D with DCNP when the ratio of DCNP to TPE-D was less than 1.

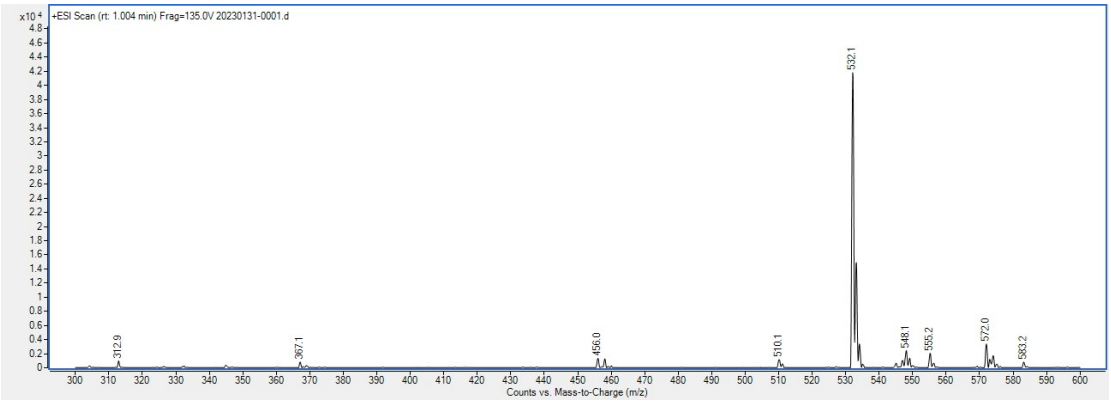


Fig. S14. MS analysis of the sample of TPE-D with DCNP when the ratio of DCNP to TPE-D was more than 1.

However, we noticed that the reaction of TPE-D with DCNP was faster than that of TPE-D with DCP, which might be due to the probe's different reactivity to the two nerve agent mimics. Therefore, as the referee suggested, the probe of TPE-D may have the potential to distinguish them. There is a possibility that the probe can exhibit clearly different reactivity to the two nerve agent mimics in the presence of different bases.

Two organic bases, DBU and triethylamine (TEA), were chosen to evaluate the reactivity of TPE-D with the two nerve agent mimics. As shown in Fig. S15, the two samples of TPE-D with DCP and DCNP in the absence of an organic base showed very weak fluorescence signals, which indicated that TPE-D had low reactivity to DCP and DCNP without the help of organic bases. But with the assistance of the stronger base DBU, both reactions of TPE-

D with DCP and DCNP were accelerated. The two samples of TPE-D with DCP and DCNP in the presence of DBU exhibited clear and strong emission fluorescence peaks, which suggested the TPE-D was not able to distinguish DCP and DCNP with the help of DBU. On the other side, with the assistance of the weaker base TEA, there was a big difference between the reactions of TPE-D with DCP and DCNP. The sample of TPE-D with DCP in the presence of TEA showed a slightly higher fluorescence signal than that of the sample without organic bases, which was consistent with our preliminary experiment result. TEA could hardly accelerate the reaction of TPE-D with DCP, which did not meet the need of rapid detection. However, the sample of TPE-D with DCNP in the presence of TEA showed a very strong fluorescence signal which was the highest among all samples. It indicated that TEA had a great capacity of accelerating the reaction of TPE-D with DCNP. Intriguingly, the sample of TPE-D with DCNP in the presence of TEA had much higher fluorescence signal than that of the sample in the presence of DBU. Considering that DBU is a stronger base than TEA, the basicity of an organic base should not be the determinant factor for promoting the reaction rate of TPE-D with DCNP. Therefore, TPE-D can distinguish DCP and DCNP by utilizing its different reactivity to the two nerve agent mimics in the presence of TEA and DBU. The method was illustrated in Scheme S1.

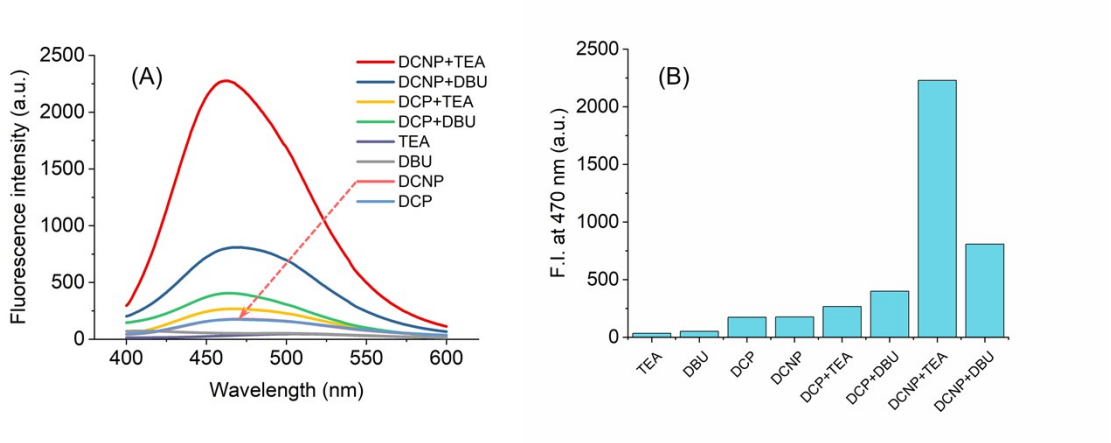
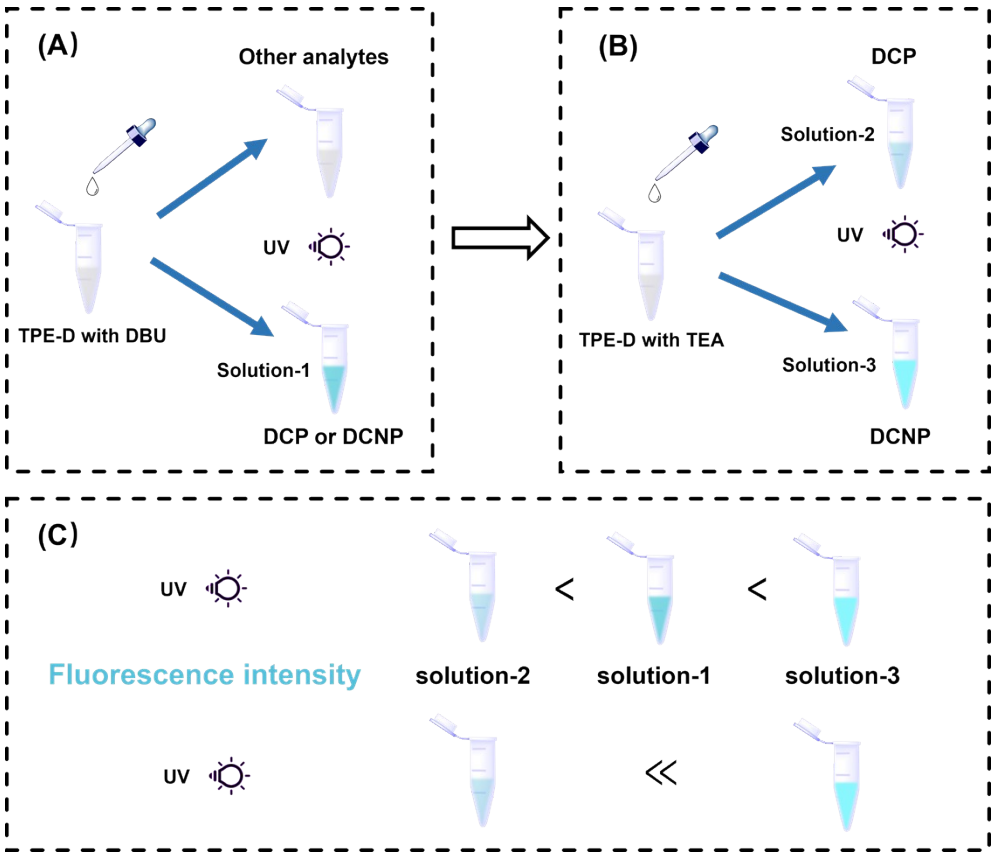


Fig. S15. (A) Fluorescence emission spectra and (B) fluorescence intensities (at 470 nm) of TPE-D (40 μM) with or without DCNP (200 μM) or DCP (200 μM) in the presence of two organic bases (200 μM, TEA and DBU). EX 336 nm.



Scheme S1. Method of (A) detecting and (B) distinguishing DCP and DCNP via different fluorescence behaviours (C) in the presence of DBU or TEA.

7 Comparison of fluorescence behaviours of TPE-OH and TPE-OP.

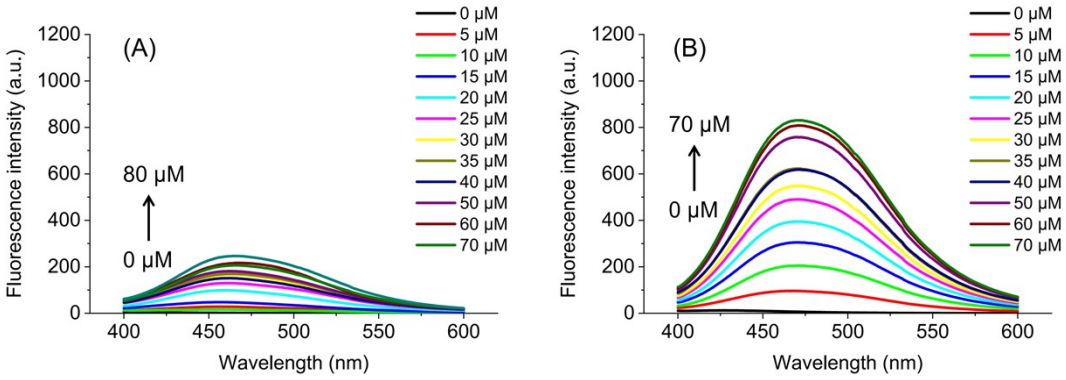


Fig. S16. Fluorescence spectra of TPE-OH (A) and TPE-OP (B) with increasing concentration without the addition of DBU (f_w=85%). EX 336 nm.

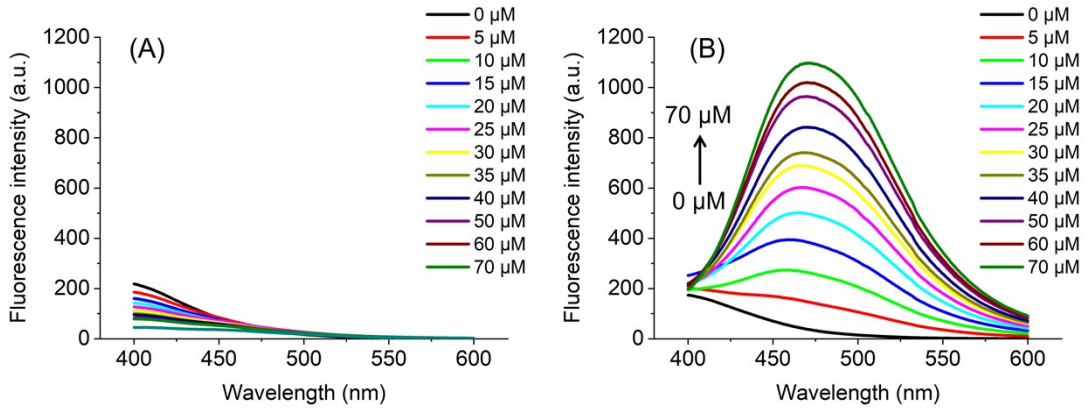


Figure S17. Fluorescence spectra of TPE-OH (A) and TPE-OP (B) with increasing concentration with the addition of DBU (f_w=85%). EX 336 nm.

8 The LOD of TPE-D detecting DCP by reducing the initial probe concentration.

Three initial probe concentrations (1, 5 and 10 μM) were chosen. However, after addition of different amounts of DCP, the positive fluorescence signal only appeared for the samples with the probe concentration of 10 μM (Fig. S18). Therefore, the initial probe concentration was lowered from 40 μM to 10 μM to obtain a LOD for DCP. The calculated detection of limit (LOD) was 18.73 μM (10 + 8.73 μM) based on the 3σ criterion, which was lower than the LOD of 43.94 μM (40 + 3.94 μM) by using initial probe concentration at 40 μM.

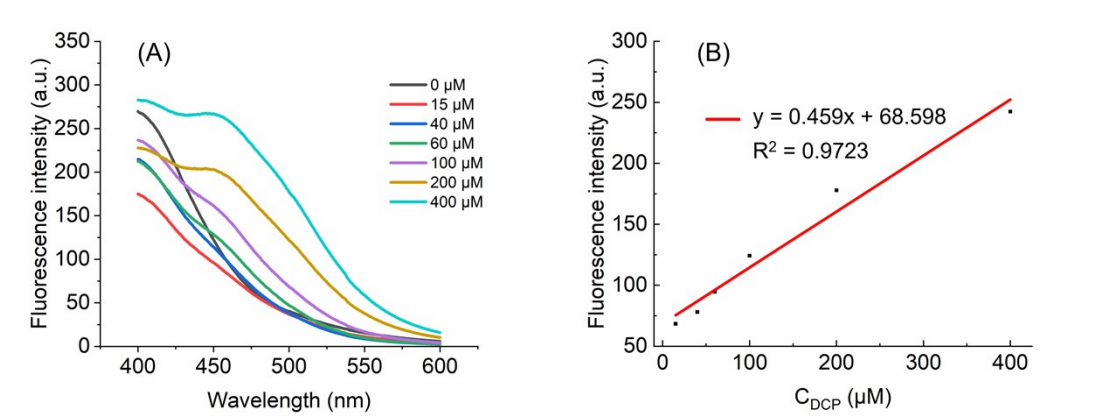


Fig. S18. (A) Fluorescence spectra of probe TPE-D (10 μM) in water/acetonitrile solution (f_w = 85%) with DCP at different concentrations (0–400 μM); (B) Linear relationships of emission intensity at 470 nm versus concentration of DCP (15–400 μM) in the detection solution. EX: 336 nm.