Supporting information

An AIE fluorescent sensor for rapid and selective detection of phosgene

1 Experimental

Column chromatography was performed on silica gel (300-400 mesh). Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) were recorded on a Varian NMR System 600 spectrometer (600 MHz). Electrospray ionization mass spectra (ESI-MS) were recorded on an Angilent 6520 Q-TOF mass spectrometer and an Thermo fisher Positive UHPLC(Ultimate 3000)-QE Focus mass spectrometer. The fluorescent spectra measurements were investigated by Hitachi F-4600 fluorescence at RT using an 1-cm pathlength quartz cell. UV-Vis absorption spectra were obtained using a Beijingpuxi TU-1901 UV/Vis spectrophotometer. The probe TPE-phos was routinely synthesized. Its ability to detect phosgene in solutions and in gaseous phase was evaluated.

1.1 Synthesis of probe TPE-phos

4-(1,2,2-triphenylvinyl)benzaldehyde (360 mg, 1 mmol) and hydroxylamine hydrochloride (139 mg, 2 mmol) were dissolved in 25 mL ethanol aqueous solution (4:1, v/v). Then, sodium carbonate (0.212 g, 2 mmol) was added into the solution and the resultant solution stirred at room temperature overnight. After that, the pH of the reaction solution was adjusted to 6.0 with acetic acid. The solution was extracted with ethyl acetate (50 mL×3) and the organic extracts were combined. Then the organic phase was washed with water and brine respectively. The resultant solution was dried with Na_2SO_4 overnight. The solvent was further evaporated under vacuo. The obtained residue was purified by silica gel flash column chromatography (petroleum ether/ ethyl acetate, 5/1) to afford TPE-phos as a pale green solid (308 mg, 0.82 mmol, yield: 82.0%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.46 (s, 1H), 7.31 (d, J = 6.0 Hz, 2H), 7.12 – 7.08 (m, 9H), 7.05 – 7.01 (m, 8H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 150.26, 145.74, 143.43, 143.38, 143.30, 141.79, 140.18, 131.72, 131.32, 131.28, 131.27, 129.90, 127.80, 127.75, 127.65, 127.52, 126.70, 126.60, 126.58, 126.53, 126.36. ESI-HRMS: m/z calcd for $C_{27}H_{21}NO$ $[M+1]^+$: 376.1623, found: 376.1700.

1.2 Synthesis of TPE-CN

The probe TPE-phos (75 mg, 0.2 mmol) was dissolved in anhydrous acetonitrile (20 mL). Then, 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU, 40 μL) and triphosgene (594 mg, 2 mmol) were successively added into the mixture, and the solution was stirred for 4 h. The solvent was further evaporated under vacuo, and the crude product was purified by silica gel flash column chromatography (petroleum ether/ ethyl acetate, 5/1) to afford the product TPE-CN (57 mg, 0.16 mmol, yield: 80.0%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 6.0 Hz, 2H), 7.17 – 7.05 (m, 11H), 7.02 – 6.97 (m, 6H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 148.83, 143.35, 142.82, 142.72, 142.58, 139.14, 131.94, 131.49, 131.23, 131.15, 128.01, 127.76, 127.18, 126.98, 119.02, 109.82. ESI-MS: m/z calcd for $C_{27}H_{19}N$ $[M+1]^+$: 358.1517, found: 358.1586.

1.3 Detection of phosgene in solutions using fluorescence

The probe TPE-phos (5.6 mg, 15.0 mmol) was dissolved in anhydrous acetonitrile (1 mL) as the probe stock solution (solution A), and triphosgene (17.8 mg, 60.0 mmol) was dissolved in anhydrous acetonitrile (1 mL) as the triphosgene stock solution (solution B). The 20 μL solution A and 2 μL DBU were successively added into a certain volume of anhydrous acetonitrile at room temperature, then a certain volume of solution B was added into the mixture to obtain 1 mL reaction system (solution C, 300 μM TPE-phos). Then portions of solution C (120 μL) were added into a series of mixtures of anhydrous acetonitrile and water to obtain 1200 μL fluorescence detection solutions (30 μM TPE-phos) with different water fraction (f_w, 0-90%). The fluorescence spectra (λ_{ex} = 354 nm, slit width: d_{ex} = 5 nm; d_{em} = 5 nm) of the detection solutions were then measured by a Hitachi F-4600 fluorescence spectrophotometer and the visual detection by the naked eye was performed with a handy UV lamp. Portions of solution C (120 μL) were added into a series of mixtures of anhydrous acetonitrile and water to obtain 3000 μL absorption detection solutions (10 μM TPE-phos) with different water fraction (f_w, 0-85%). UV-Vis absorption spectra (200-600 nm) were obtained by using a Beijingpuxi TU-1901 UV/Vis spectrophotometer.

In addition, TPE-phos in water/acetonitrile solution was directly used to detect phosgene. Firstly, portions of solution A (20 μL) and DBU (2 μL) were successively added into the mixed solutions of water and acetonitrile respectively, and then a certain volume of solution B was added to each of the above mixed solutions to produce a series of TPE-phos detection solutions (30 μM) with different water fraction (f_w, 0-90%). Fluorescence spectra of the detection solutions were then measured.

1.4 Gaseous phosgene detection with test strips

Some 1.5×6 cm cut filter papers were dotted with solution A and 0.2% DBU, and then dried naturally. Gaseous phosgene detection was tested with the TPE-phos-loaded strips. Firstly, 0.1 g triphosgene was placed at the bottom of a sealed conical flask (250 mL), and heated at 60°C for 5 min. Then the test strips were hanged and fixed in the sealed conical flask for 30 s. The visual detection by the naked eye was performed with a handy UV lamp. Photos were collected by a digital camera.

2 NMR and HR-MS data of TPE-phos

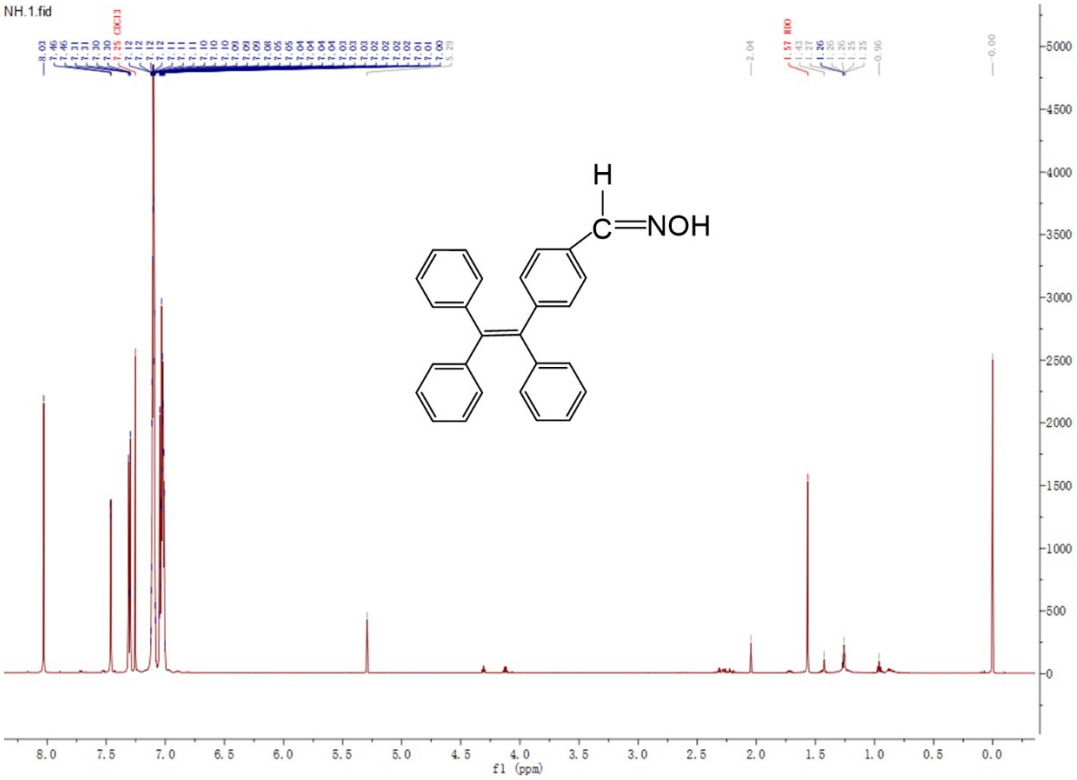


Fig. S1. ^{1}H NMR (600 MHz) spectra of TPE-phos

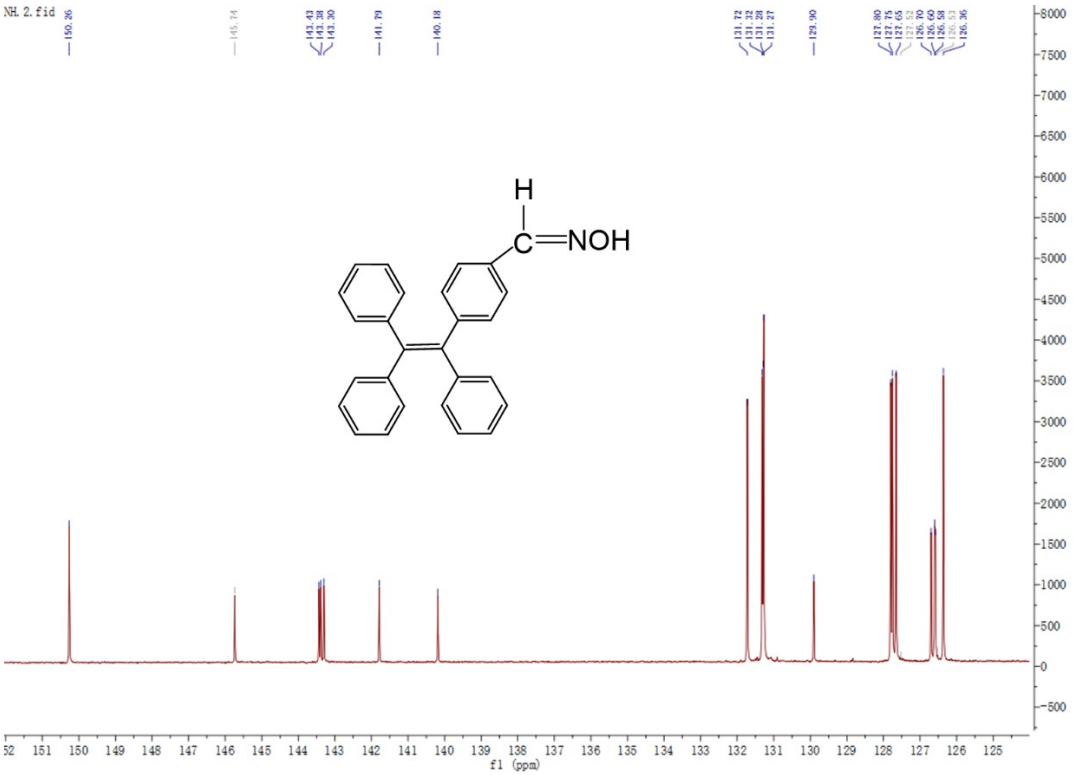


Fig. S2. ^{13}C NMR (600 MHz) spectra of TPE-phos

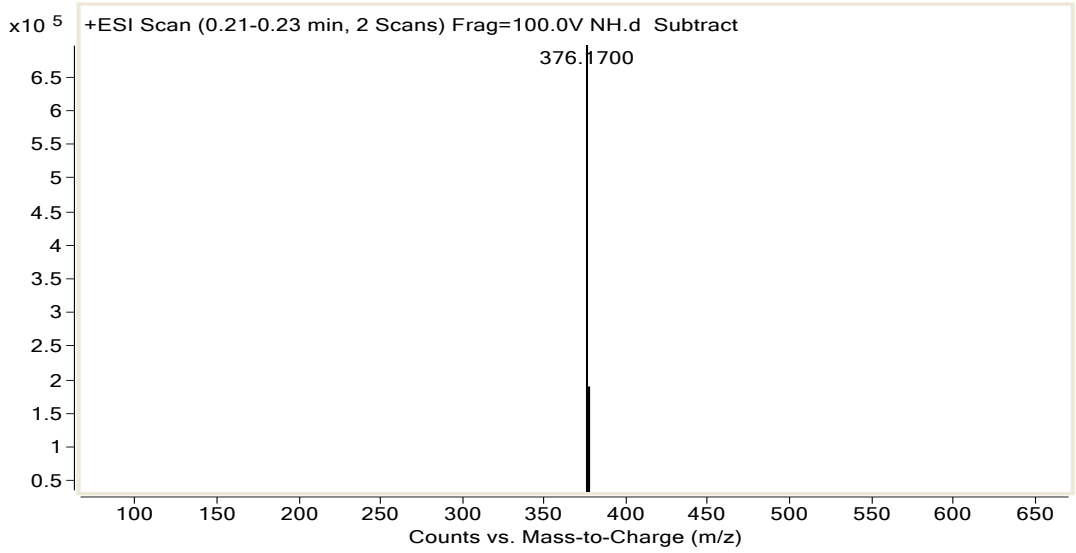


Fig. S3. High resolution mass spectrum of TPE-phos

3 NMR and HR-MS data of TPE-CN

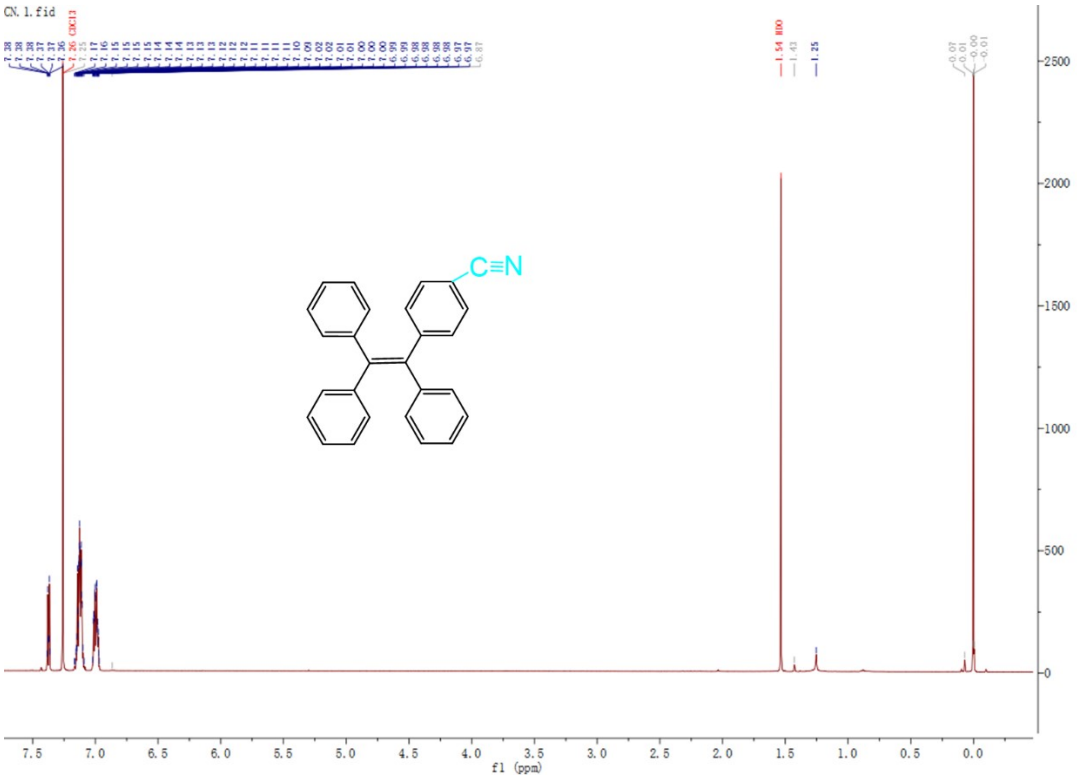


Fig. S4. ^{1}H NMR (600 MHz) spectra of TPE-CN

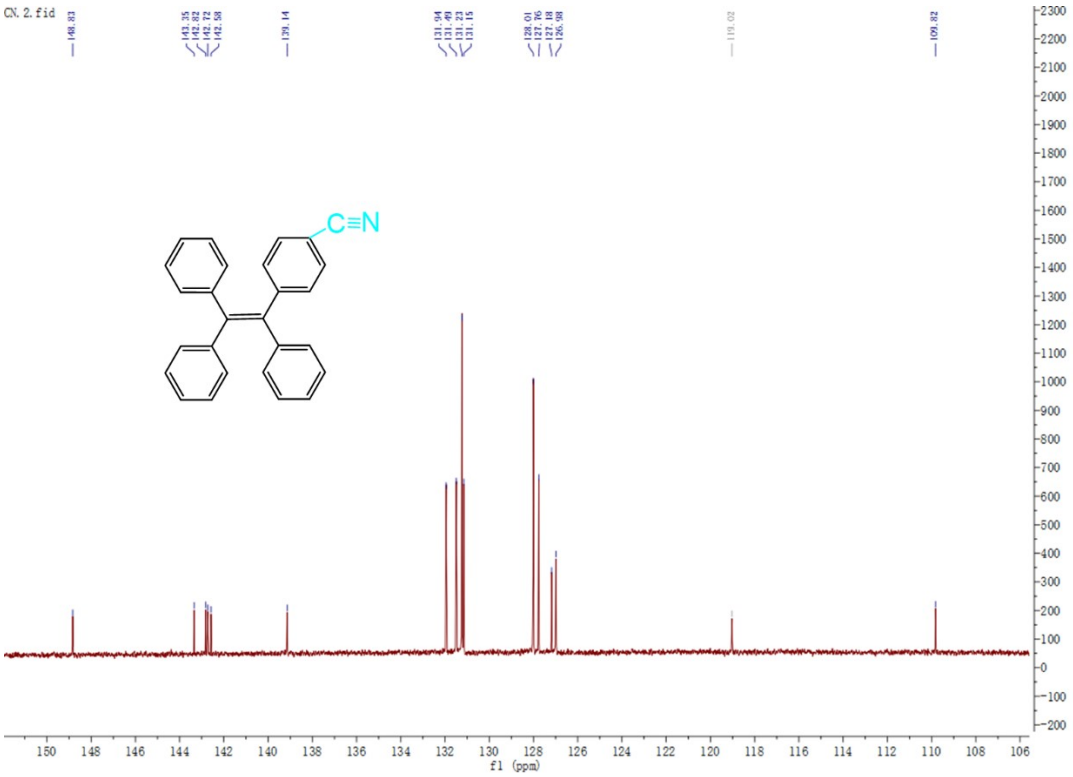


Fig. S5. ^{13}C NMR (600 MHz) spectra of TPE-CN

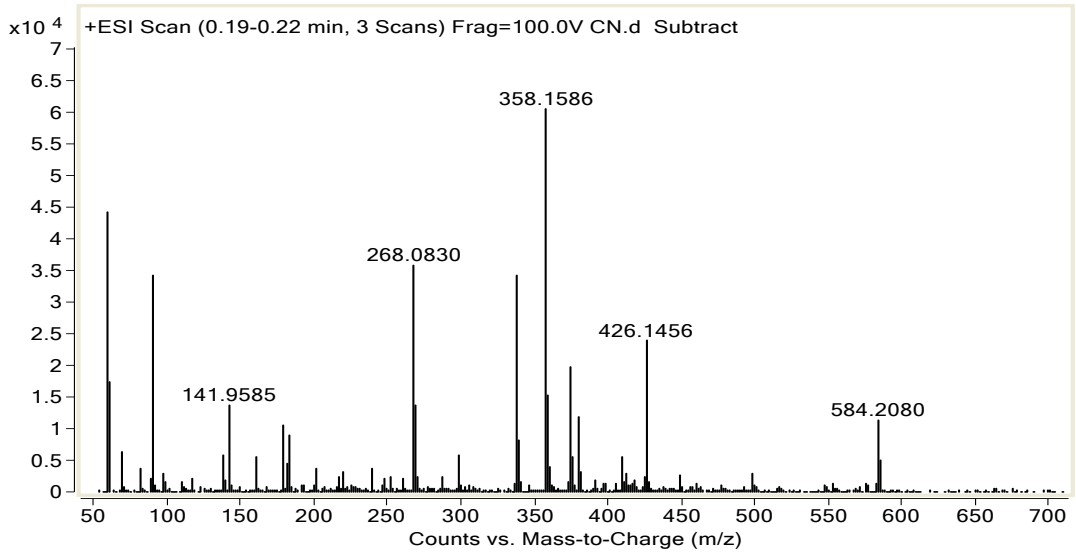


Fig. S6. High resolution mass spectrum of TPE-CN

4 the UV absorption spectra of TPE-phos and TPE-CN

The absorption spectra of TPE-phos and TPE-CN were measured. TPE-phos showed an UV absorption in the near UV-range (200-400 nm) with a very weak peak centred at 325 nm (Fig. S7A). When a water fraction was increased, the peak was virtually unchanged. In contrast, TPE-CN, namely TPE-phos with phosgene also showed an UV absorption in the near UV-range with the absorption peak centred at 316 nm (Fig. S7B), and the absorbance peak at 316 nm was much stronger than that of TPE-phos at 325 nm. Moreover, when water fractions changed, the absorbance of the TPE-CN peak changed. Therefore, The UV absorption spectra of TPE-CN exhibited a characteristic absorption peak at about 316 nm. When f_w was increased from 0 to 50%, the peak at 316 nm rose gradually and arrived at its maximum at f_w of 50%. When the water fraction was increased from 50% to 70%, there was a gradual decrease in absorbance at 316 nm. Intriguingly, when the f_w reached 75% of AIE appearance, the increase in absorbance at 316 nm occurred again, which may be caused by the Mie effect of the nanoaggregate suspensions in the solvent mixtures[1]. The result showed that the obvious difference between absorption spectra of TPE-phos and TPE-CN can be used to verify the generation of TPE-CN.

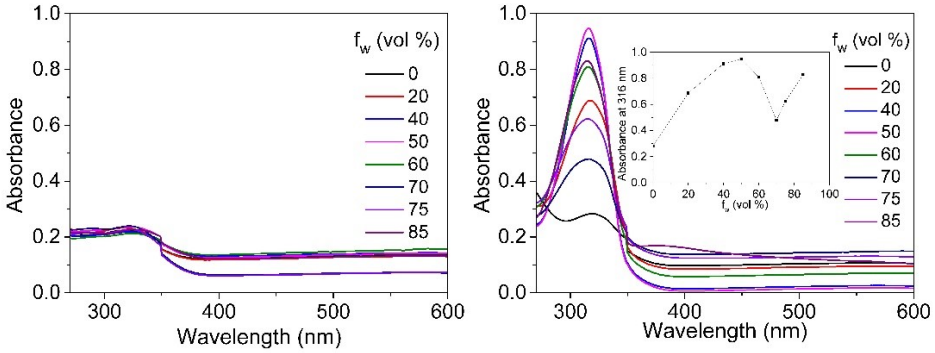


Fig. S7. UV/Vis spectra of (A) TPE-phos and (B) TPE-CN in different water/acetonitrile solution from 0% to 85%. [TPE-phos]=10 μM.

5 The possibility for TPE-phos to detect DCP in a different water-containing solution.

The rate of TPE-phos reacting with DCP is much slower than that of TPE-phos with phosgene. The product of TPE-phos with DCP was observed by thin-layer chromatography after a half of hour. Therefore, analysis with MS was carried out after DCP reacted with the probe TPE-phos for a half of hour. The peaks of 512.19805, 534.17990 and 557.25573 appeared (Fig. S8), which are in accordance with the nucleophilic substitution product of TPE-phos to DCP (the theoretical molecular weight is 512.19124 ($C_{31}H_{31}NO_4P^+$), 534.18101 ($C_{31}H_{30}NNaO_4P^+$) and 557.17078 ($C_{31}H_{30}NNa_2O_4P^+$) respectively). Therefore, it was confirmed that DCP reacts with the sensor.

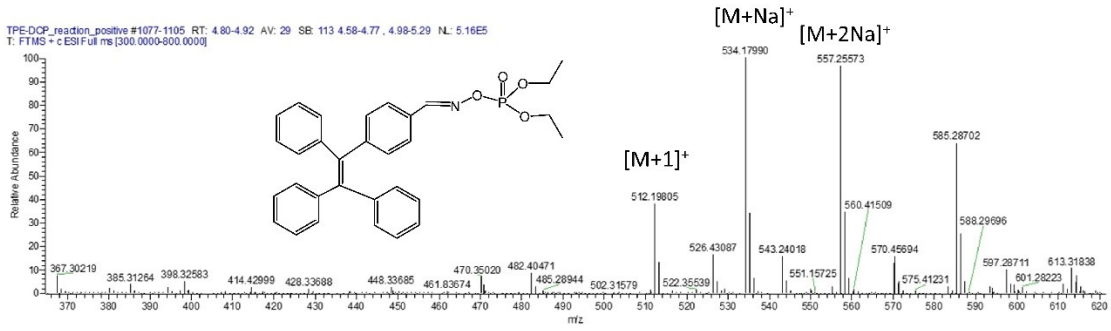


Fig. S8. High resolution mass spectrum of the product of TPE-phos with DCP

Then we investigated the possibility of TPE-phos to detect DCP in a different water-containing solution. Our previous result showed that TPE-phos in water/acetonitrile solution (f_w, 75%) with phosgene will give an AIE signal while the detection solution with DCP shows no fluorescence changed. Thus, we measured the fluorescence spectra of the TPE-phos with or without DCP in water/acetonitrile solution with f_w above 75%. The emission of TPE-phos alone remained unchanged as the f_w increased from 75% to 79%, while a slight fluorescence signal appeared when the f_w arrived at 80% (Fig. S9A), which is consistent with our previous result. TPE-phos with DCP also showed no fluorescence signal change as the f_w increased from 75% to 78%. However, the slight fluorescence signal appeared obviously when the f_w arrived at 79% (Fig. S9B), which is different from the samples of TPE-phos alone and TPE-phos with phosgene. Moreover, the product of TPE-phos with DCP was purified by flash chromatography and then dissolved in different water-containing solutions. AIE signals appeared in the water-containing solution with f_w above 79% (data not shown). Theoretically, the sensor can be also used to detect DCP in a different water-containing solution (f_w 79%). Nevertheless, the conditions of generating AIE effect for the probe alone (f_w 80%) and the probe with DCP (f_w 79%) are very close. Thus, it is difficult in practice to use the sensor to detect DCP in a water-containing solution.

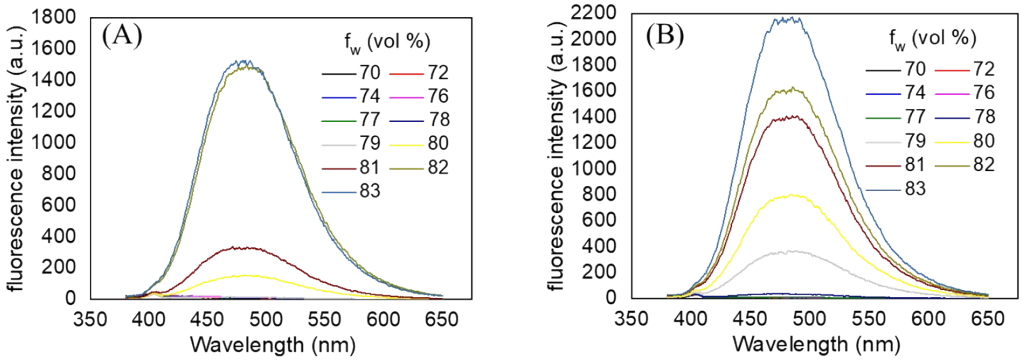
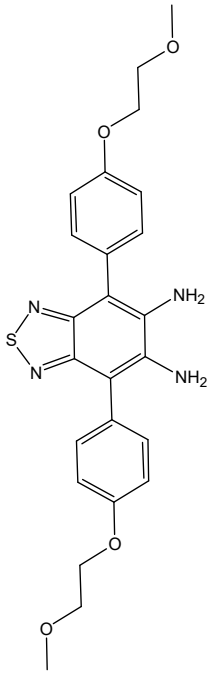
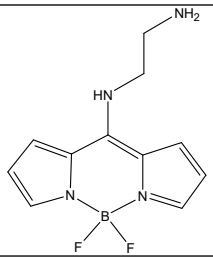
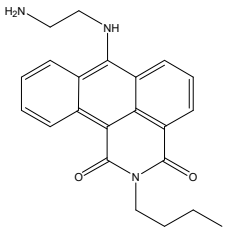
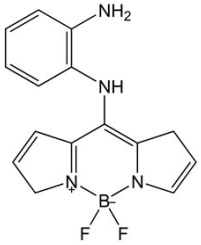
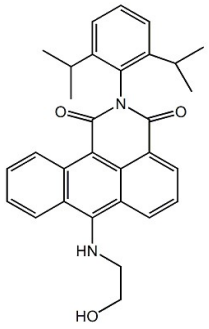
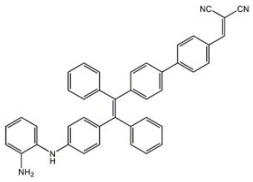
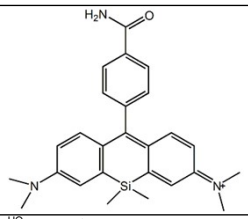
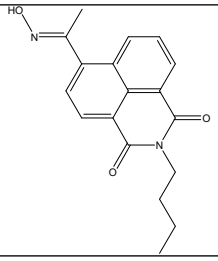
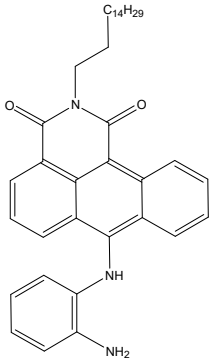
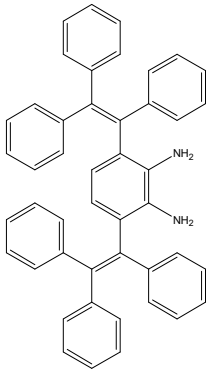


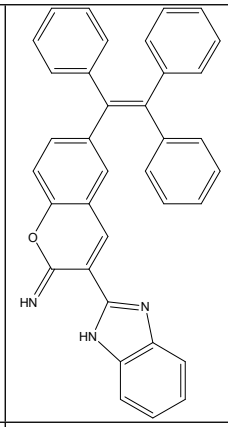
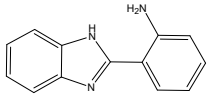
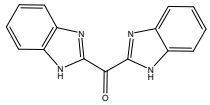
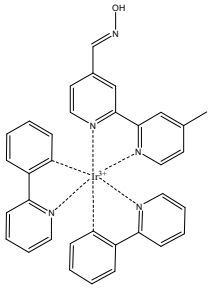
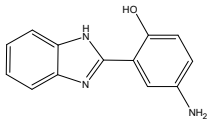
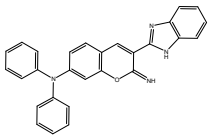
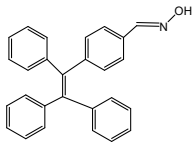
Fig. S9. Fluorescence emission spectra of TPE-phos (30 μM) alone(A) and with DCP (B) in water/acetonitrile solutions with increased water fractions (f_w, 70-85%). EX 354 nm.

6 Comparison of the present probe (TPE-phos) with the reported probes for detection of phosgene.

Table S1 Comparison of TPE-phos with the reported probes for detection of phosgene

References	Structure of probe	Recognition site	Fluorophore moiety	LOD	Response time
1[2]		o-phenylenediamine (OPD)	benzothiadiazole (BTD)	20 nM	2 min
2[3]		ethylenediamine	8-substituted BODIPY	0.12 nM	1.5 s
3[4]		ethylenediamine	anthracene carboximide	0.09 nM	＜20 s
4[5]		o-phenylenediamine	BODIPY unit	2.7 nM	15 s

5[6]		2-hydroxyethyl aniline	anthracene carboxyimides	2.3 nM	＜5 min
6[7]		o-phenylenediamine	tetraphenylethene (TPE)	1.8 ppm (gasous)	2 min
7[8]		amide	Si-rhodamine	8.9 nM	4 min
8[9]		ketoxime	1,8-naphthalimide chromophore	6.3 nM	15 min
9[10]		o-phenylenediamine (OPD)	an anthracene-carboxyimide fluorophore	72 nM	< 2 min
10[11]		ophenylenediamine (OPD)	triphenylethylene (TPE)	21 nM	2 min

11[12]		3-benzo[d]imidazole-chromen-2-imine	tetraphenylethene (TPE)	0.36 μM	6 s
12[13]				1.27 nM	1 min
13[14]		methanone	bis-(1H-benzimidazol-2-yl)	3.3 nM	30 s
14[15]		oxime	iridium(Ⅲ)	2.4 nM	<5 s
15[16]		hydroxyl and imidazole moieties		5.3 nM	50 s
16[17]		diphenylamine (DPA) and 2-imine-3-benzo[d]imidazole	coumarin	0.27 μM	＜8 s
Our work		oxime	tetraphenylethene (TPE)	9.3 nM	＜30 s

Reference

1. B. J. Xu, Z. G. Chi, J. Y. Zhang, X. Q. Zhang, H. Y. Li, X. F. Li, S. W. Liu, Y. Zhang and J. R. Xu, *Chem-Asian J*, 2011, **6**, 1470-1478.
2. X. J. Wang, W. Q. Zhang, K. Cheng, X. Yang, Q. Y. Li, H. Zhang, Z. Ma, H. Lu and H. Wu, *Organic Chemistry Frontiers*, 2017, 10.1039.C1037QO00378A.

3. Yuanlin, Zhang, Aidong, Peng, Xiaoke, Jie, Yanlin, Lv, Xuefei and Wang, *ACS Applied Materials & Interfaces*, 2017, **9**.
4. P. Liu, N. Liu, C. Liu, Y. Jia, L. Huang, G. Zhou, C. Li and S. Wang, *Dyes Pigments*, 2018.
5. X. X. Xia HC, Song QH, *Anal Chem*, 2017, **89**, 4192-4197.
6. Q. Hu, C. Duan, J. Wu, D. Su, L. Zeng and R. Sheng, *Anal Chem*, 2018, **90**, 8686-8691.
7. H. T. Xie, Y. L. Wu, F. Zeng, J.J. Chen and S.Z. Wu, *Chem Comm,* 2017, **53**, 9813-9816.
8. M. Du, B. Huo, J. Liu, M. Li, A. Shen, X. Bai, Y. Lai, L. Fang and Y. yang, *J Mater Chem C*, 2018, **6**, 10472-10479.
9. Y. L. Huang, W. Ye, Y. T. Su, Z. Y. Wu and H. Zheng, *Dyes Pigments*, 2020, **173**.
10. L. Zeng, H. Zeng, L. Jiang, S. Wang, J. T. Hou and J. Yoon, *Anal Chem*, 2019, **91**, 12070-12076.
11. K. Cheng, N. Yang, Q. Y. Li, X. W. Gao and X. J. Wang, *ACS Omega*, 2019, **4**, 22557-22561.
12. Q. Hu, Q. Huang, K. Liang, Y. Wang, Y. Mao, Q. Yin and H. Wang, *Dyes Pigments*, 2020, **176**, 108229.
13. L. Yang, F. Wang, J. Zhao, X. J. Kong, K. Lu, M. Yang, J. Zhang, Z. W. Sun and J. M. You, *Talanta*, 2021, **221**.
14. L. Yang, F. Wang, Z. W. Sun, X. J. Kong and Y. L. Kong, *Anal Methods-Uk*, 2020, **12**, 3123-3129.
15. B. Ma, X. F. Wang, S. Gao, L. H. Qi, Y. Xu, J. X. Yang and G. M. Zuo, *Dyes Pigments*, 2020, **177**.
16. Z. J. Li, W. J. Zhang, W. Z. Bi, Q. J. Ma, S. X. Feng, X. L. Chen and L. B. Qu, *Rsc Adv*, 2021, **11**, 10836-10841.
17. Q. H. Hu, T. Gong, Y. Mao, Q. Yin, Y. Y. Wang and H. Q. Wang, *Spectrochim Acta A*, 2021, **253**.