

## Supportive Information

### **A simple but highly efficient multi-formyl phenol/amine system for fluorescence detection of peroxide explosive vapour**

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## 1. Synthesis

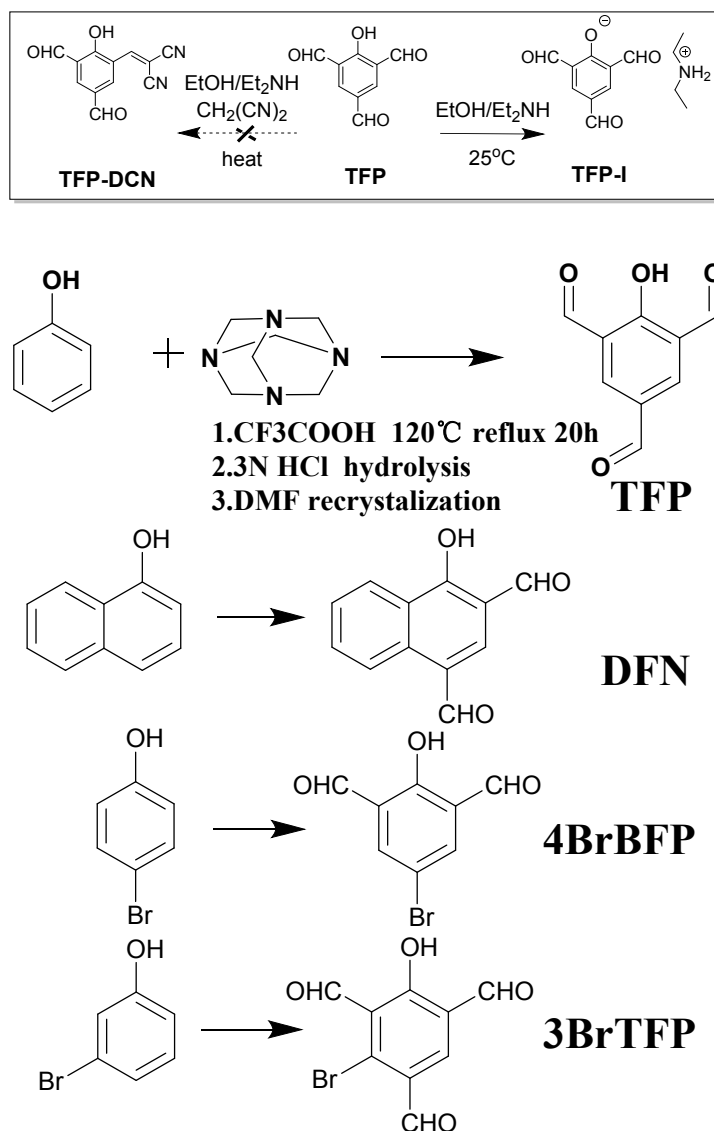
The synthetic route for **TFP** is shown in Scheme S2. 23.1 mg **TFP** was dispersed in 5 mL ethanol. After adding 0.5 mL diethylamine ( $\text{Et}_2\text{NH}$ ), the **TFP** sample was dissolved with an immediate heat release. The excess amine in the solution was evaporated in vacuum to afford 32.1 mg **TFP-I** (yield, 98.5%). Then the solution of **TFP-I** were drop-casted on quartz slides, the sensing performance was tested in several kinds of analytes, such as water, *n*-hexane, ethanol, toluene, THF and peroxide.

The chemical constitution of **TFP-I** has been proved by mass spectra together with  $^1\text{H-NMR}$ . Mass spectra presented that **TFP-I** is consists of cation  $\text{Et}_2\text{NH}^+$  (74.0965 with +1 charge) and anion  $\text{TFP}^-$  (177.0193 with -1 charge). And  $^1\text{H-NMR}$  shows that three hydrogens of aldehyde groups shift to high field from 10.31, 10.00 and 8.52 ppm to 10.22, 9.53 and 7.96 ppm with the introduction of  $\text{Et}_2\text{NH}$ , which proved the existence of anion  $\text{TFP}^-$ .

All solvents and reagents were purchased from commercial sources and used as received except special indication.  $^1\text{H}$  NMR spectra were measured on a Bruker DRX500 instrument, using tetramethylsilane (TMS) as the internal standard substance. A KW-4A Spin Coater (Institute of Microelectronics, CAS) was used to dry the films. Mass spectra were measured on a Bruker Daltonics Inc. APEXII FT-ICR Mass Spectrometry and an Agilent 7890A/5975C Gas Chromatography Mass Spectrometry (GC-MASS). UV-Vis absorption spectra were measured on a Jasco V-670 spectrophotometer while fluorescence spectra and time-course were measured on a Jasco FP 6500 spectrometer. Cyclic voltammetry (CV) measurement were operated with a CH Instruments electrochemical analyzer.

The solvent is tetrahydrofuran (THF) and the concentration for the film fabrication is 2 mg/mL ( $10^{-5}$  M). The solution was deposited on quartz slides in a spin coater at the rotation speed of 2000 r/min. Then the films were further dried under vacuum for 20

minutes and the UV-Vis absorption and fluorescence analysis of the films was conducted.



**Scheme S1** Synthetic route of TFP, DFN, 4BrBFP and 3BrTFP

### 2,4,6-triformyl phenol (TFP):

6.9 g (65 mmol) phenol, 70 mL trifluoroacetic acid (TFA) and 20.1 g (143 mmol) hexamethylenetetramine (HMTA) was added into a flask and the mixed solvent was refluxed at  $120^\circ\text{C}$  for 20 hours. The solvent was heated to  $150^\circ\text{C}$  for 3 hours and cooled back to  $120^\circ\text{C}$ . For initiating the hydrolysis reaction, 100 mL 3N hydrochloric

acid was added into the solvent and the solvent was heated at 102°C for 30 minutes, followed by natural cooling, filtering, washing and drying process. The product was recrystallized in DMF and the yield was 4.28 g (37.3%).

TFP <sup>1</sup>H NMR (500MHz, DMSO-d<sub>6</sub>) δ 10.31(s,2H) 10.00(s,1H) 8.52(s,2H); TFP-I <sup>1</sup>H NMR (500MHz, DMSO-d<sub>6</sub>) δ 10.22(s,2H) 9.53(s,1H) 7.96(s,2H) 6.87(s,2H) 2.88(q,4H) 1.12(t,6H); <sup>13</sup>C NMR (126 MHz, DMSO) δ 191.13, 189.02, 180.26, 136.15, 128.57, 117.40, 41.39, 11.01.

The three derivatives are synthesized with the same method of TFP.

### **2,4-diformyl 1-naphthol (DFN):**

1.44 g (10 mmol) 1-naphthol and 3.1 g (22 mmol) HMTA was reacted in 10 mL TFA and the yield was 1.7 g (85%).

<sup>1</sup>H NMR (500MHz, DMSO-d<sub>6</sub>) δ 10.31(s,1H) 10.20(s,1H) 9.22(d,1H) 8.48(d,1H) 8.45(s,1H) 7.91(t,1H) 7.73(t,1H); <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ 193.85, 189.63, 170.35, 140.27, 139.11, 124.83, 115.69, 110.09, 34.32, 30.37, 20.97; m/z=201.0545

### **4-bromo diformyl phenol (4BrBFP):**

1.72 g (10 mmol) 4-bromo phenol and 3.1 g (22 mmol) HMTA was reacted in 10 mL TFA and the yield was 1.3 g (57%).

<sup>1</sup>H NMR (500MHz, DMSO-d<sub>6</sub>) δ 11.58(s,1H) 10.20(s,2H) 8.13(s,2H); <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ 190.86, 160.79, 138.48, 125.65, 111.23; m/z=228.9494

### **3-bromo triformyl phenol (3BrTFP):**

1.72 g (10 mmol) 3-bromo phenol and 3.1 g (22 mmol) HMTA was reacted in 10 mL TFA and the yield was 440 mg (yield,17.2%).

$^1\text{H}$  NMR (500MHz, DMSO- $d_6$ )  $\delta$  10.18(s,1H) 10.06(s,2H) 8.30(s,1H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  194.17, 192.37, 164.29, 139.28, 133.56, 132.74, 127.25, 124.69, 124.61, 124.13, 123.63, 115.16;  $m/z=256.9807$

## 2. Performance details

### Figures for detailed sensing performance (S1-S3)

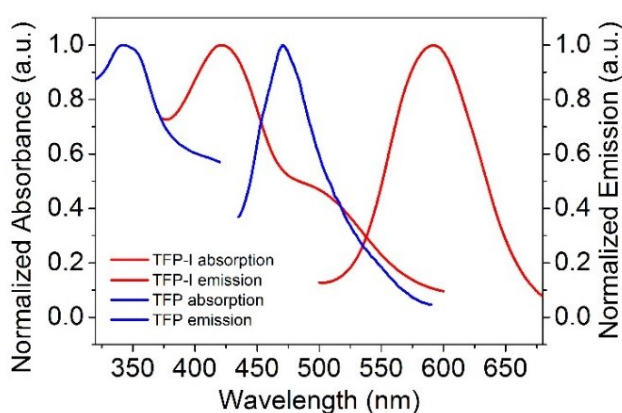


Fig. S1 Absorption and emission spectra of TFP and TFP-I films

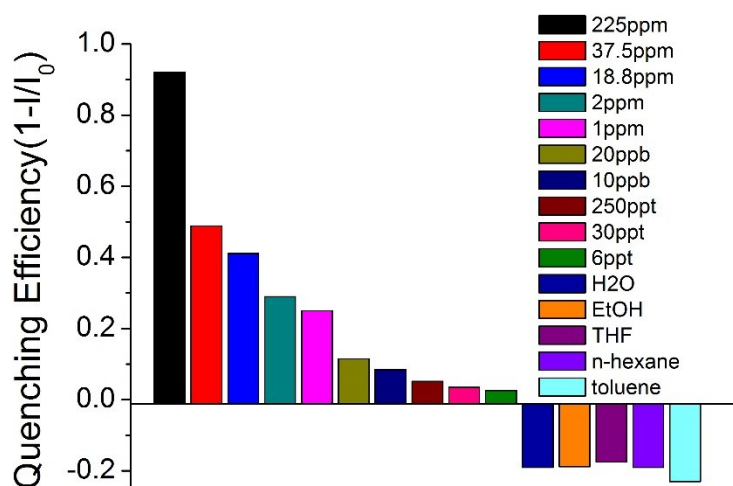
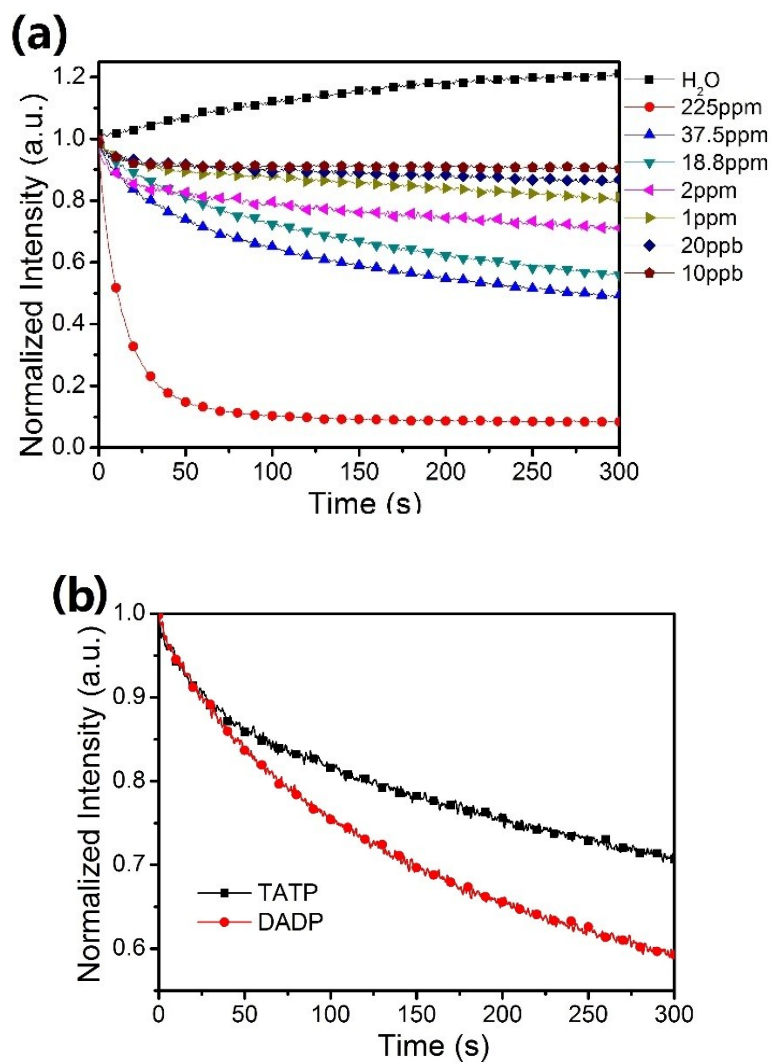


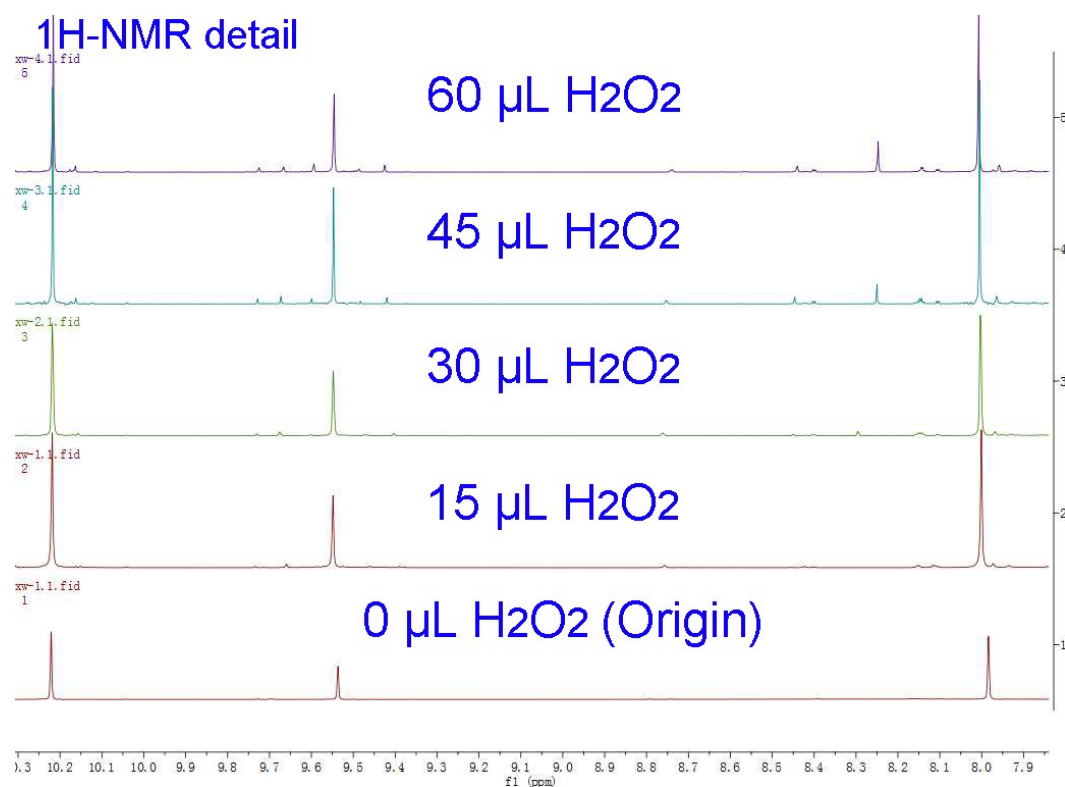
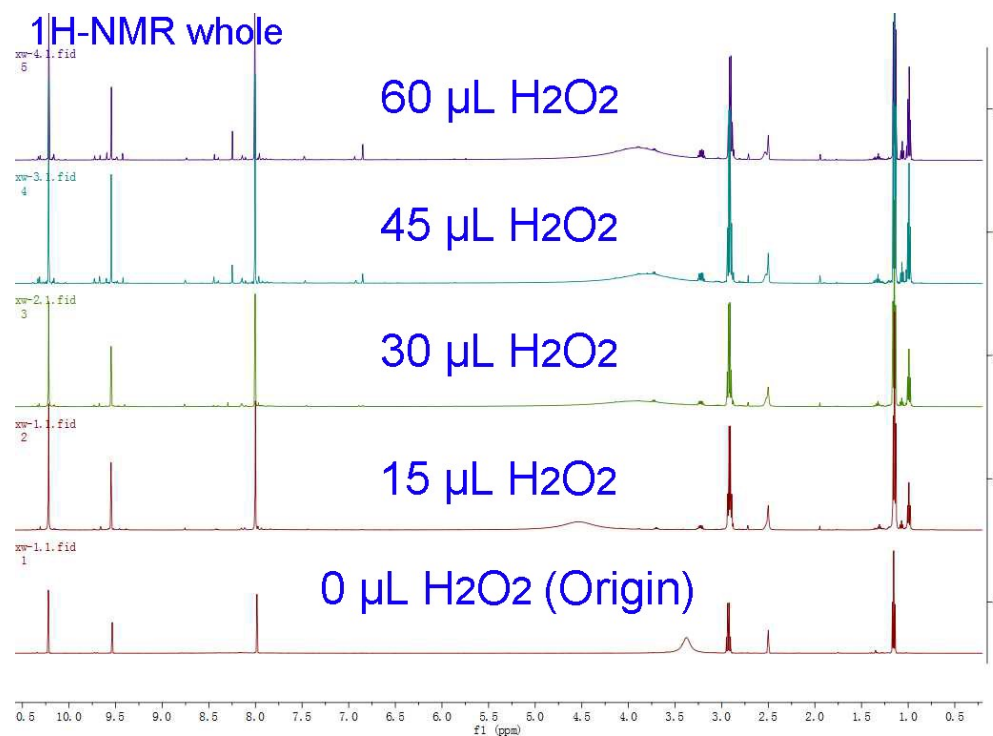
Fig. S2 Quenching rate of TFP-I in vapour of common solvents comparing to different concentration  $\text{H}_2\text{O}_2$  vapour



**Fig. S3** Time course of TFP-I in (a) different concentration of  $H_2O_2$  vapour (b) peroxide explosive vapour

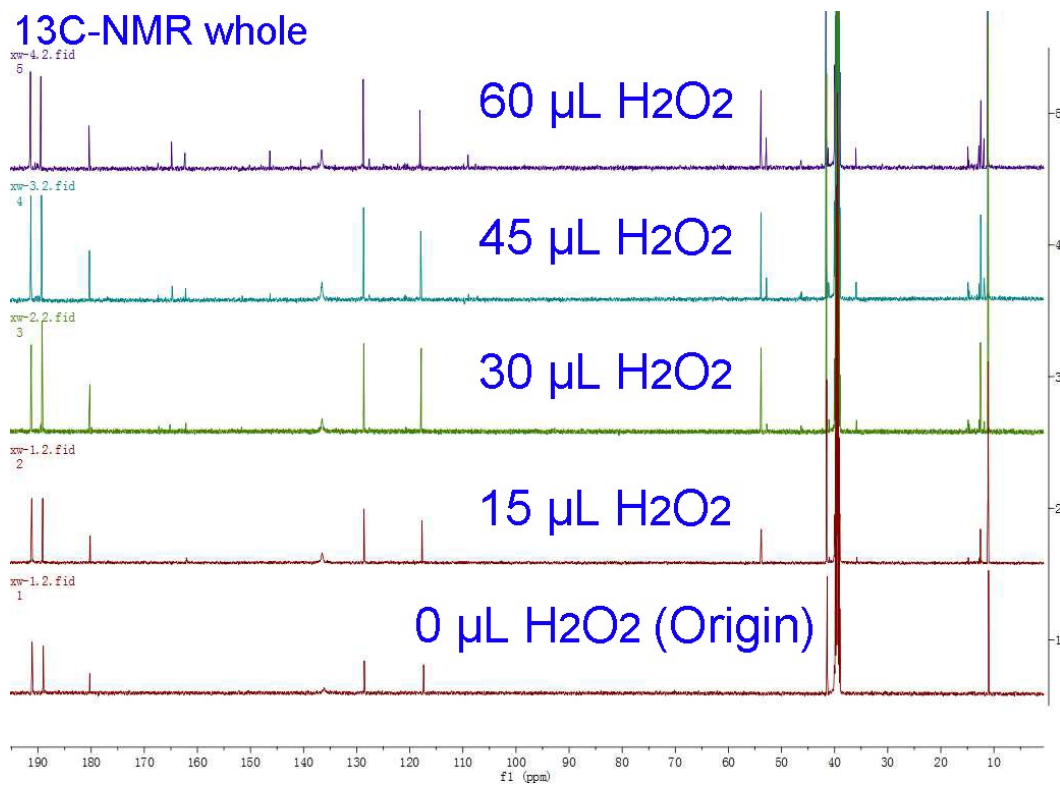
### 3. Experiments about mechanism (S4-S7)

## NMR titration experiment

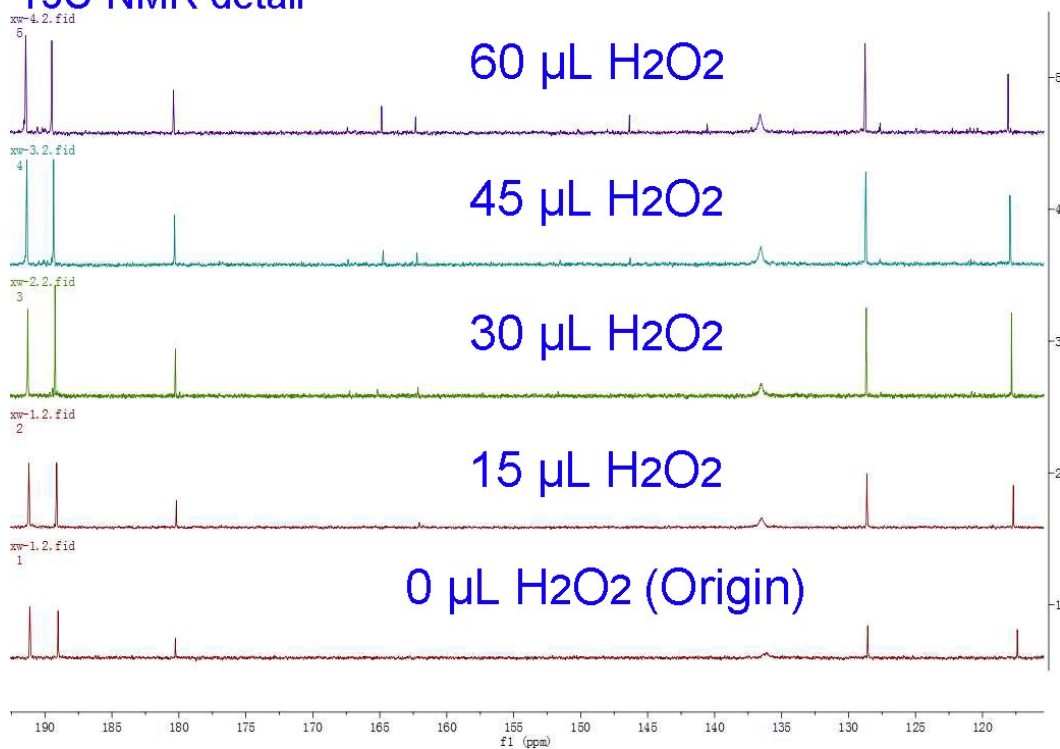


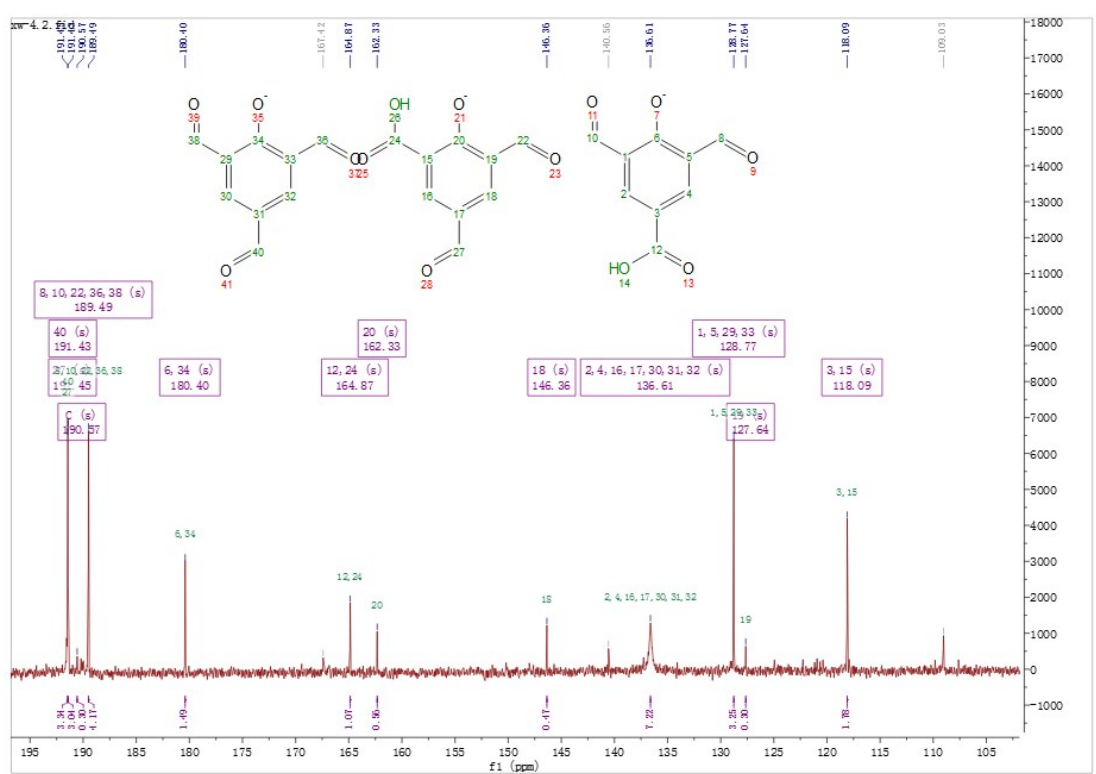


### 13C-NMR whole



### 13C-NMR detail





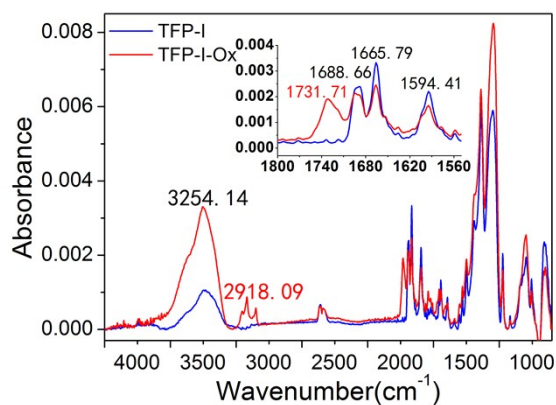
**Fig. S4** The <sup>1</sup>H and <sup>13</sup>C NMR titration experiment. To 1.5 mL TFP-I/d<sub>6</sub>-DMSO (0.15 mmol) was added 30% H<sub>2</sub>O<sub>2</sub> 0 μL (1), 15 μL (2), 30 μL (3), 45 μL (4) and 60 μL (5), corresponding molar ratio of the aldehyde groups and the peroxide ranges from 3:0, 3:1, 3:2, 1:1 to 3:4.

To show the oxidation process from aldehyde group to carboxylic group, NMR titration experiment has been conducted, upon incremental addition of 30% peroxide aqueous solution into four NMR tubes with the same concentration of TFP-I (26.7 mg/0.15 mmol TFP-I solved in 1.5 mL d<sub>6</sub>-DMSO). The addition amount of 30% peroxide aqueous solution is 15 μL (0.15 mmol), 30 μL (0.3 mmol), 45 μL (0.45 mmol) and 60 μL (0.6 mmol) respectively. In Fig. S4, the first and third graph show the whole <sup>1</sup>H and <sup>13</sup>C spectra, while the second and fourth graph are the partial enlarged drawings to show the detail of the spectra. The fifth graph shows the structures and their corresponding chemical shifts in the <sup>13</sup>C-NMR spectra of the most oxidized sample.

New chemical shifts related to the formation of carboxylic groups occur and increase in pace with the increasing addition amount of peroxide solution. The reactivity of the TFP-I in solution decreases a lot compared with the vapour phase

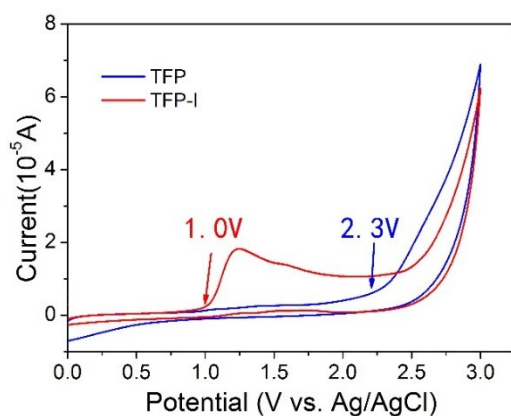
reactivity, so that the oxidation is not complete even enough peroxide solution has been added into the tube. There are many new small peaks in the spectra after the addition of peroxide, but only a few of them is distinct. According to the  $^1\text{H}$  spectra, there are a new peak in the high field area, and the 8.247 ppm peak belongs to the benzene hydrogen of the oxidized product. According to the  $^{13}\text{C}$  spectra, two new peaks has been observed in the area of the carboxylic group. 164.867 ppm peak is related to the carboxylic groups while the 162.326 ppm peak is related to the carbon nearby the phenol anion group.

## IR spectra



**Fig. S5** The infra-red spectra of a TFP-I film before (blue) and after (red) oxidation process

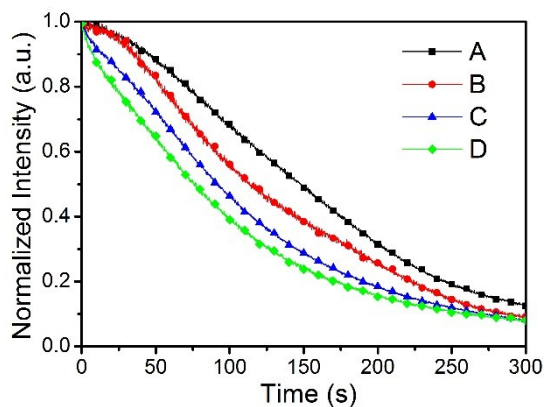
## Cyclic voltammetry curves



**Fig. S6** Cyclic voltammetry curves of TFP and TFP-I

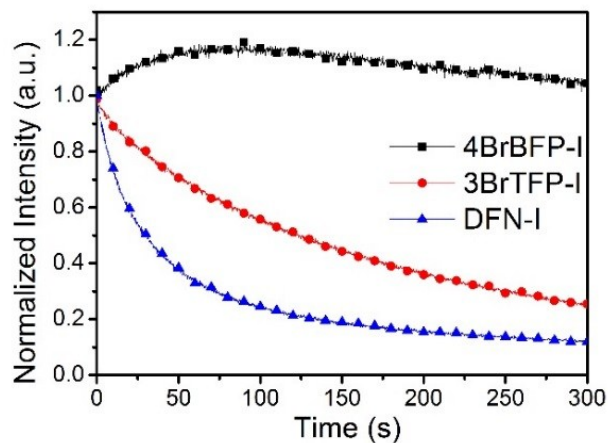
Fig. S6 shows the cyclic voltammetry curves of TFP and TFP-I. Ag/AgCl electrode is used as the reference electrode and the oxidation potentials are separately 1.0V for TFP and 2.3V for TFP-I.

## Carboxylic group doping experiment



**Fig. S7** Quenching curves in saturated H<sub>2</sub>O<sub>2</sub> vapour at 8°C (2 mg/1 mL TFP-I/THF with TFP-O<sub>1</sub>, A:0 mg; B:0.01 mg; C:0.2 mg; D:0.3 mg)

#### 4. Performance of other probes in the system



**Fig. S8** Sensing curve of 4BrBFP-I, 3BrTFP-I and DFN-I in H<sub>2</sub>O<sub>2</sub> vapour

#### 5. Fluorescence properties

**Table S1** H<sub>2</sub>O<sub>2</sub> sensing performance in 300 seconds

Film	Excitation/emission Wavelength(nm)	Vapour	Concentration	Quenching rate (%)
<b>TFP</b>	343/470	air	/	10
		H <sub>2</sub> O <sub>2</sub>	225ppm/saturated	18
<b>TFP-I</b>	420/590	H <sub>2</sub> O <sub>2</sub>	225ppm	92
			225ppm (2 weeks in air)	90
			37.5ppm	48.8
			18.8ppm	41.1

			2ppm	29
			1ppm	25
			20ppb	11.5
			10ppb	8.45
			250ppt	5.15
			30ppt	3.45
			6ppt	2.55
		Air	/	-3
		H <sub>2</sub> O	saturated	-19
		THF	saturated	-17.5
		n-hexane	saturated	-19
		toluene	saturated	-23
		EtOH	saturated	-18.8
<b>DFN-I</b>	360/568	H <sub>2</sub> O <sub>2</sub>	saturated	86
<b>4BrBFP-I</b>	420/517	H <sub>2</sub> O <sub>2</sub>	saturated	-12.5
<b>3BrTFP-I</b>	390/550	H <sub>2</sub> O <sub>2</sub>	saturated	75

**Table S2** sensing property of TFP-I for peroxide explosives in 100 seconds

Vapour	Concentration/ppb	Quenching rate (%)
<b>TATP</b>	78000/saturated	29.3

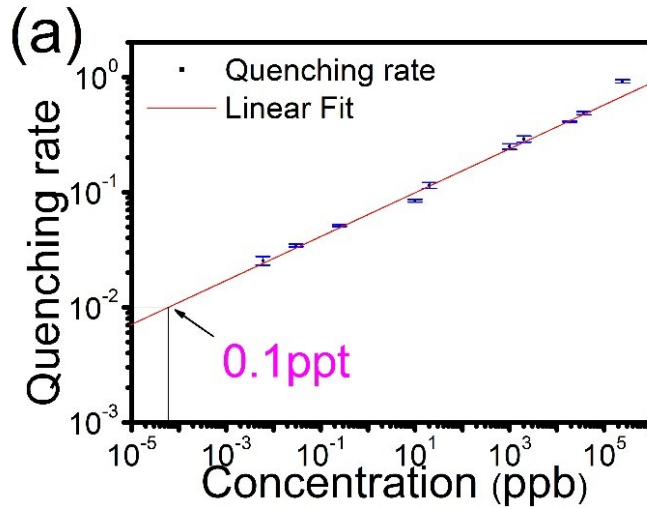
	4875	19.3
	2438	17
	1219	15.1
	610	11.9
	305	8.9
	152	7.8
	78	5
	40	4.7
	20	4
	10	3.3
<b>DADP</b>	saturated	42

## 6. Detail information about linear fit (Figure 2)

To estimate the detection limit, we measured the changes in fluorescence intensity of TFP-I films exposed to H<sub>2</sub>O<sub>2</sub> vapour in a wide range of concentration. Then with the assistance of Origin software, the quenching data of the fluorescence of TFP-I (1- I/I<sub>0</sub>) have been well-fitted in logarithmic coordinates. The linear fit is based on the Langmuir equation with an assumption that the quenching efficiency is proportional to the surface adsorption of vapour. In reference with the state of the test instruments and related articles, the concentration value correspond to 0.01 quenching rate was regarded as the detection limit.

We select one percent fluorescence quenching rate to calculate the detection limit,

with the reference of several published articles. ((a) Y. K. Che, X. M. Yang, S. Loser and L. Zang, Nano Lett., 2008, 8,2219; (b) B. P. Jiang, D. S. Guo and Y. Liu, J. Org. Chem., 2011, 76,6101.)



A(X)	B(Y)	C(Y)	D(Y)	Mean(Y)	SD(yEr-)
Concentration (ppb)	1	2	3	Mean	Standard Deviation
				Statistics	Statistics On Rows
244000	0.92	0.9014	0.96	0.92713	0.02994
37500	0.488	0.469	0.5	0.48567	0.01563
18800	0.411	0.41	0.416	0.41233	0.00321
2000	0.29	0.299	0.325	0.30467	0.01818
1000	0.25	0.245	0.223	0.23933	0.01436
20	0.115	0.115	0.127	0.119	0.00693
10	0.0845	0.083	0.08	0.0825	0.00229
0.25	0.0515	0.05	0.0487	0.05007	0.0014
0.03	0.0345	0.0358	0.034	0.03477	9.29157E-4
0.006	0.0255	0.0287	0.0263	0.02683	0.00167

Linear Fit for Figure2a on linearized scales.

$$y_{scale}(Y) = A + B * x_{scale}(X)$$

Parameter Value Error

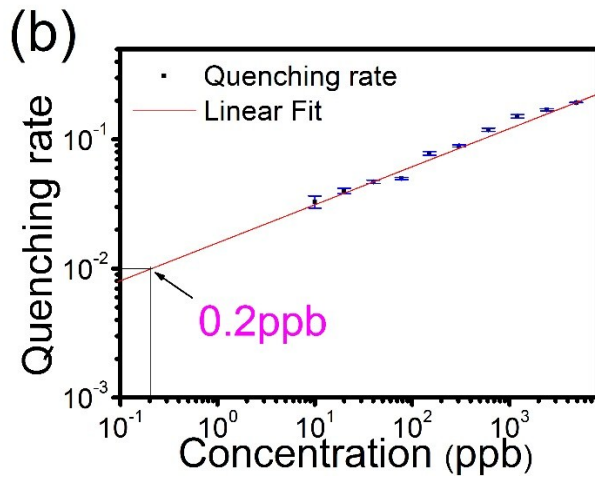
A -1.19377 0.00531

B 0.19079 0.00138

R SD N P

0.99655 4.0653 10 <0.0001





A(X)	B(Y)	C(Y)	D(Y)	Mean(Y)	SD(yEr-)
	Quenching rate			Mean	Standard Deviation
				Statistics	Statistics On Ro
4875	0.193	0.192	0.193	0.19267	5.7735E-4
2438	0.17	0.174	0.176	0.17333	0.00306
1219	0.151	0.156	0.1606	0.15587	0.0048
610	0.119	0.122	0.126	0.12233	0.00351
305	0.089	0.0866	0.0859	0.08717	0.00163
152	0.078	0.0747	0.0797	0.07747	0.00254
78	0.05	0.052	0.0509	0.05097	0.001
40	0.047	0.0497	0.04884	0.04851	0.00138
20	0.04	0.043	0.0394	0.0408	0.00193
10	0.033	0.03	0.037	0.03333	0.00351

Linear Fit for Figure2b on linearized scales.

$$yscale(Y) = A + B * xscale(X)$$

Parameter Value      Error

A    -1.79842    0.01067

B    0.29455    0.00301

R    SD    N    P

0.99375    3.88861    10    <0.0001

## 7. Parameter settings of Materials Studio 7.0

### The frontier molecular orbitals:

#### Step1. Forcite Anneal:

Annealing cycles: 10;  
Initial temperature: 300K  
Mid-cycle temperature: 1000K  
Heating ramps per cycle: 7  
Dynamics steps per ramp: 1000  
Ensemble: NVT  
Optimize after each cycle  
Quality: Ultra-fine  
Forcefield: Dreiding  
Charges: Use current  
Quality: Ultra-fine  
Summation method: Electrostatic: atom based;  
Van der waals: atom based

#### Step2. DMol3 Geometry Optimization

Quality Fine  
Energy 1.0e-5  
Max. force 0.002 Ha/Å  
Max. displacement 0.05 Å  
Max. iterations: 50  
Max. step size: 0.3 Å  
Functional: GGA-BLYP  
Use symmetry  
Intergration accuracy: Fine  
SCF tolerance Fine  
Core treatment All Electron  
Basis set DNP+ 4.4  
Orbital cutoff quality Fine  
Properties: Optics; Orbitals

### Dynamics simulation:

#### Step 1.Forcite Geometry Optimization

Ensemble: NVE  
Quality: Ultra-fine  
Forcefield: COMPASS II  
Charges: Forcefield assigned

#### Step 2.Forcite Dynamics

Ensemble: NVE  
Total simulation time: 500ps  
Quality: Ultra-fine  
Forcefield: COMPASS II

Quality: Ultra-fine

Charges: Forcefield assigned

Summation method: Electrostatic: atom based;

Quality: Ultra-fine

Van der waals: atom based

Summation method: Electrostatic: atom

based; Van der waals: atom based