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COMMUNICATION

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

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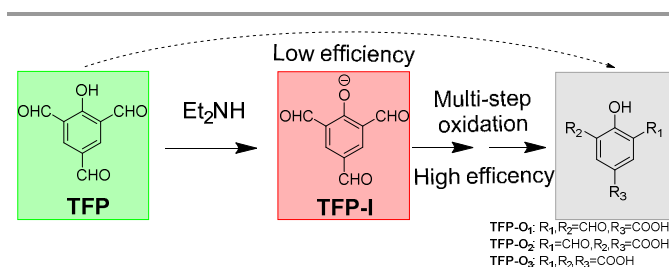
A simple, highly stable, sensitive and selective fluorescent system for peroxide explosives was developed via an aromatic aldehyde oxidation reaction. The high efficiency arises from its higher HOMO level and multiple H-bonding. The sensitivity is obtained to be 0.1 ppt for H₂O₂ and 0.2 ppb for TATP.

In recent decades, peroxide compounds, from hydrogen peroxide (H₂O₂) to organic peroxides, are becoming more and more noticeable for the threat in domestic security¹ and individual health^{2,3}. Organic peroxides, such as triacetone triperoxide (TATP), diacetone diperoxide (DADP) and hexamethylene triperoxide diamine (HMTD), are highly unstable and can be manufactured by a simple reaction using commercially available H₂O₂ and acetone.⁴ These compounds are as destructive as nitro explosives and variety methods have been attempted to detect them. Traditional detection methods, such as electrochemistry analysis⁵, chromatography analysis⁶, mass spectrometry analysis⁷ and biochemistry analysis⁸, have been developed. But these methods are all conducted in solution while some of them require bulky instruments.

Fluorescence method are known in excellent sensitivity, quick response and nice maneuverability⁹, but for peroxide explosives (PEs) detection, the problem is that PEs are not typical fluorescence quencher and they have no nitro group and aromatic rings, which make it difficult to interact with the aromatic fluorophores to afford high sensitivity.^{9,10} Therefore, almost all fluorescence probes are designed based on oxidation reactions, such as deboration reaction¹¹ and the oxidation of sulfoxide (from sulfoxide to sulfone)¹². Especially, much progress has been made on the fluorescent borate probes, for example, He et al successfully introduced ZnO nanorod array as a catalyst substrate to accelerate the deboration rate and realized a quick detection of TATP. Zang et al reported a fluorescence turn-on probe for H₂O₂ with a detection limit of

7.7 ppb. However, the sensitivity and the rate of oxidation is still limited¹³⁻¹⁵, and the synthesis of the borate probes were involved in a complicated column chromatographic separation and low-temperature reaction. Therefore, a much efficient reaction and amplification mechanism for this detection will be highly favoured.

To obtain such a probe, firstly an aromatic aldehyde oxidation were adopt for peroxide explosive vapour sensing. A hydroxyl group was induced to the aromatic aldehyde to construct a donor- π -acceptor system and make it fluorescent. The most simple molecule of the multi-formyl phenol compounds, 2,4,6-triformyl phenol (TFP), was easily synthesized, but it showed poor sensing performance to peroxide.¹⁶



Scheme 1. Sensing process of TFP-I

To improve the sensing performance, we tried to use one aldehyde group to react with malononitrile using Knoevenagel reaction with diethylamine as catalyst to tune the reactivity of the probe. Unexpectedly, TFP tends to react with the diethylamine to form an orange compound TFP-I with enhanced fluorescence, and this compound can be quickly oxidized by peroxide. As a result, several factors related to sensing performance has been greatly optimized after TFP transforms to TFP-I, including quenching rate, sensitivity, selectivity and photo-stability. The synthetic route of the complex was shown in Scheme 1, and the dashed arrow shows the original designed reaction.

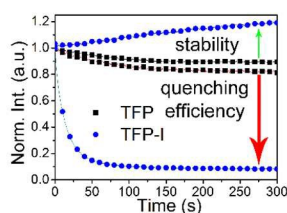


Fig. 1. Stability and quenching curves (in H_2O_2) of **TFP** and **TFP-I** films at room temperature, excited at 420nm and emit at 590nm.

The solubility of **TFP** is poor in many solvents such as THF and ethanol, while **TFP-I** is highly soluble in THF and ethanol. In film state, from **TFP** to **TFP-I**, the maximum absorbance peak red-shifted from 343 to 470 nm (127 nm), and the emission peak showed a bathochromic shift from a green light emission at 420 nm to an orange emission at 590 nm as shown in Fig. S1. Such a large spectral shift means that with the introduction of Et_2NH , the band gap is decreased. And with the absorption band change from ultra-violet to visible wavelength, for sensing application, a noticeable cost saving for the excitation power source and a decreased photo-bleaching for the sensory material could be realized.

Fig. 1 illustrated the photo-stability and the quenching efficiency for 30% H_2O_2 aqueous vapour of **TFP** and **TFP-I**. For **TFP** film, the photo-bleaching is 10% while the quenching rate in H_2O_2 vapour is only 18% within 300 s. As compared, **TFP-I** showed a much better photo-stability and quenching efficiency. In air, the fluorescence showed no decrease, but a slight increase by 3%. The quenching rate sharply increased to 92% in H_2O_2 vapour, and 85% fluorescence quenching took place during the first 50 s. The excellent quenching efficiency and photo-stability suggest **TFP-I** is a nice probe for H_2O_2 vapor detection.

Fig. S2 shows that **TFP-I** has good selectivity towards H_2O_2 vapour with a different extent of fluorescence quenching under different H_2O_2 concentration. Even in a 6 ppt H_2O_2 vapour, a 2.5% quenching could be detected. And in the interference vapour, only fluorescence enhancement was observed. It witnessed a 20% fluorescent enhancement in H_2O vapour, avoided a headache interference for the real detection of fluorescence probe. Fig. S3a presented the quenching efficiency in H_2O_2 vapour with different concentration and H_2O vapour with time. Fig. S3b indicates a 42% quenching in DADP and a 29.3% quenching in TATP vapour within 300 s. The quenching rate went down with the decreased concentration of H_2O_2 vapour. While in H_2O vapour, the fluorescence intensity slightly went up in the first 200 s, opposite the one in H_2O_2 vapour. The detection limit of the **TFP-I** films have been obtained based on the relationship of the quenching efficiency *versus* the concentration of H_2O_2 vapour with a standard deviation below 5%.¹⁸ According to the well-fit linear relation in Fig. 2, the detection limit can be projected to be 0.1 ppt for H_2O_2 vapour within 300 s, which is far lower than the 7.7 ppb limit reported in a recent frontier work¹⁴. Furthermore, the detection limit for TATP is 0.2 ppb within 100 s, which proves that such system

could be directly used for organic peroxide explosives vapour detection at sub-ppb level.

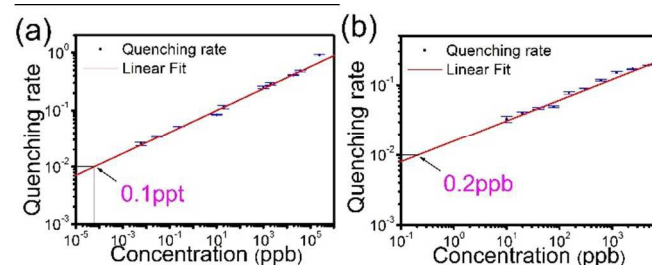


Fig. 2. Linear fit of (a) H_2O_2 and (b) TATP concentration-quenching rate plot. The data for H_2O_2 and TATP quenching are collected at 300 s and 100 s, respectively.

Inspired by the excellent sensory performance, we are interested in the sensing mechanism of **TFP-I**. The sensing mechanism of the sensory process was proposed as shown in Scheme 1. The sensing process starts with an oxidation reaction, the aldehyde units are gradually oxidized to partly oxidized intermediates and the final product tri-carboxylic phenol (**TFP-O₃**). Experimentally, **TFP-I** was converted to an insoluble white solid in common solvents after oxidation. Luckily, it is soluble in NaOH aqueous solution. ^1H NMR in $\text{D}_2\text{O}/\text{NaOD}$ gives a singlet peak at 8.41 ppm. The NMR titration (^1H and ^{13}C) of **TFP-I** with peroxide (Fig. S4), together with the infra-red spectra (Fig. S5), confirmed the conversion from aldehyde to carboxylic group. New absorbance bands at 2918.09 cm^{-1} (hydroxyl of $-\text{COOH}$) and 1731.71 cm^{-1} (carbonyl of $-\text{COOH}$) occurs while the peak at 3254.14 cm^{-1} (phenolic hydroxyl) triples its original intensity. Also Mass spectra exhibit two peaks at 193.1 and 207.0, respectively, suggesting one or two more oxygen atoms was introduced to **TFP**.

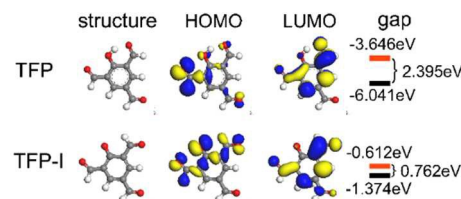


Fig. 3 Frontier molecular orbitals of **TFP** and **TFP-I** simulated with Materials Studio 7

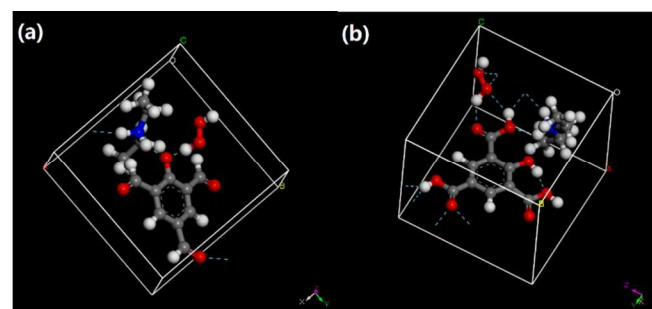
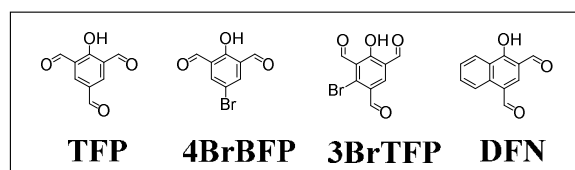


Fig. 4 Intermolecular interactions (a) before and (b) after the oxidation reaction simulated with Materials Studio 7

Since the sensing is an oxidation process, the reactivity of **TFP-I** should be related to the electron cloud distribution especially for its HOMO level. Materials Studio was used for dynamics (Forcite plus) and orbitals (DMol3) calculation, using GGA-BLYP as the DFT-method and COMPASS II (dynamics)/Dreiling (orbitals) as the force field. As shown in Fig. 3. The HOMO level of ionized molecule **TFP-I** is -1.37 eV while the neuter molecule **TFP** is -6.04 eV. Therefore, the HOMO level is elevated significantly, which makes it easier to be oxidized. With the cyclic voltammetry data, the oxidizing potential of **TFP** is 2.3 V (HOMO -5.72 eV) while the oxidizing potential of **TFP-I** is 1.0 V (HOMO -4.42 eV), so that **TFP-I** actually shows a better response to oxidants. And also based on the results, the band gap is decreased from **TFP** to **TFP-I** resulting in a red shifted absorption and emission.

Actually, the high sensing efficiency is more than a simple oxidation reaction. The formation of carboxylic products could increase the adsorption capacity of the sensing film to H_2O_2 vapour and hence enhance the quenching efficiency. To interpret it with calculation, crystal cells with periodic boundary conditions are used to place **TFP-I** (Fig. 4a) or **TFP-O₃** (Fig. 4b) and H_2O_2 molecules. A large difference of the stabilized states was found after a same dynamics simulation. Three more H_2O_2 -related hydrogen bonds formed in the **TFP-O₃** box, demonstrating an enhanced intermolecular interactions after the reaction. It could be observed experimentally¹⁹ via the sensing experiment at low temperature (for a slower quenching speed). Fig. S7 indicates, by doping a small amount of **TFP-O₁** into the sensory film (0 ~ 0.15:1, **TFP-O₁**/**TFP-I** (w/w)), the quenching efficiency to saturated H_2O_2 vapour at 8°C increases from 32% (0:1) to 61% (0.15:1) upon the doping, even a 0.005:1 ratio can result in an increase of the quenching efficiency to 44% in 100 s.



Scheme 3. Structure of multi-formyl phenols **TFP**, **4BrBFP**, **3BrTFP** and **DFN**

A further structural modification is also applicable to tune the sensing performance and to afford a much efficient peroxide vapour probe. A series of molecules and their each multi-formyl phenol/amine system were synthesized. Firstly, introducing one bromo to **TFP** to afford **3BrTFP**, the quenching efficiency reaches 75%. Secondly, the aldehyde on the *para* position of phenol was substituted with bromo resulted in the complete loss of the sensing performance to H_2O_2 , suggesting the *para*-aldehyde is also important in the sensing performance. The phenyl ring was further replaced by naphthyl unit (**DFN-I**), a decent 86% quenching efficiency was obtained.

Conclusions

This simple multi-formyl phenol/amine system is highly efficient, sensitive, photo-stable and selective, leading to new fluorescent probes for peroxide explosive vapour. The sensitivity of **TFP-I** is obtained to be 0.1 ppt for H_2O_2 and 0.2 ppb for TATP, with excellent selectivity towards interference vapour including H_2O . The substitution group and aromatic unit will significantly influence the sensing process suggesting a further structure modification could afford a more efficient peroxide vapour sensor for on-site, quick and sensitive safety check. Furthermore, the idea of utilizing a reaction product to strengthen the interaction between the probe and the analytes opened a new way for the fluorescent probe design.

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Notes and references

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