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A TCF-based colorimetric and fluorescent probe for highly selective detection of oxalyl chloride

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ABSTRACT

We herein reported a new fluorescent probe **TCF-EA** for detection of oxalyl chloride in dichloromethane. Probe **TCF-EA** exhibits high selectivity and sensitivity to oxalyl chloride with a low detection limit (2.9 nM) and fast response (<5min). The probe displays dual channel responses to oxalyl chloride, the color is changed from pink to light yellow, and the fluorescence is quenched at 614 nm. The detection mechanism was proved to undergo amidation and esterification tandem reactions between **TCF-EA** and oxalyl chloride. Moreover, the probe can be applied to prepare test strips to detect oxalyl chloride in the gas phase.

Introduction

Oxalyl chloride is an important chemical that was widely used in organic synthesis such as for synthesis of insecticide [1,2], it is a very effective acylating agent in industry and has a wide range of applications [3,4]. For example, it is an intermediate for synthetic insecticide [5]. However, oxalyl chloride is highly toxic and corrosive, it is extremely volatile and irritating to human skin and eyes [6]. Inhalation of a small amount of oxalyl chloride can causes breathing difficulties and vision loss [7,8], which endangers people's health. In order to prevent accidental leakage in industrial production [9,10], it is badly needed to develop a portable, highly selective and simple operation method should be designed to detect oxalyl chloride gas to ensure public safety [11,12].

To this end, various methods including gas chromatography [13,14], potentiometric titration [15,16], and step titration [17,18] have been developed for the detection of oxalyl chloride. Whereas, due to the drawbacks of poor portability [19], time-consuming analysis, and complex sample processing, these methods still have inconveniences in terms of sensitivity and on-site detection. Fluorescence technique has attracted wide attention due to its high sensitivity [20,21], high specificity [22,23], fast response [24,25], and simple quantitative analysis [26,27]. To date, only very few fluorescent probe for oxalyl chloride detection has been documented [28,29]. Recently, Li and Wang et al reported a benzothiadiazole-based fluorescence 'turn on' probe (**BTA**) for simultaneously detecting oxalyl chloride and phosgene. The main design strategy for the probe is to use *o*-phenylenediamine as the reactive recognition site and benzothiadiazole the fluorophore moiet [30,31]. The probe **BTA** can differentiate these two species through the formation of six- and five-membered rings between OPD moiety with oxalyl chloride and phosgene, respectively. Nevertheless, the recognition processes resulted in very close emission wavelengths of the recognition products, and lack of obvious naked eye observable color changes, which make it difficult to achieve effective resolution by visual inspection. Therefore, development of oxalyl chloride specific fluorescent probe is still badly required.

2-Dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dih-ydrofuran (**TCF**) [32], as a strong-attractive electron acceptor, has been widely used to construct long wavelength emissive fluorescent probes due to the effective ICT [33] effect of the conjugate system [34,35]. Based on this idea, we herein designed and synthesized a new TCF-based fluorescent probe **TCF-EA** (Scheme 1). We link ethanolamine to the styryl para position of the TCF form a donor-π conjugation-acceptor (D-π-A) structure, which will cause a large red shift in the UV-visible absorption and fluorescence spectra. The NH and OH groups in **TCF-EA** provide two reaction sites for condensation with oxalyl chloride, the anticipated amide formation will inhibit intramolecular charge transfer by changing

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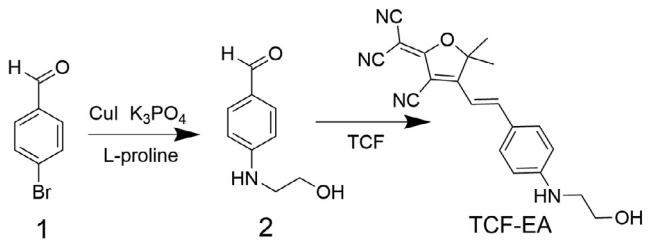


Scheme 1. Synthetic pathway of probe **TCF-EA.**

amine to amide group, thus resulting in a blue-shifted emission wavelength. The probe possesses specificity toward oxalyl chloride with strong anti-interference ability, high sensitivity, rapid response, low detection limit (2.9 nM), in addition, **TCF-EA** was made into a portable test strip to measure oxalyl chloride vapor with obvious color and fluorescence changes.

Results and discussion

The synthesis of probe **TCF-EA** is shown in Scheme 1. Then, compound 2 [36] and TCF were heated under reflux in ethanol to obtain **TCF-EA** with a yield of 78%. The structure of **TCF-EA** was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS analysis (see Supplementary Data).

With the probe in hand, we first investigated the optical response of **TCF-EA** to oxalyl chloride in dry dichloromethane. As shown in Fig. 1, probe **TCF-EA** (10 μM) exhibits a strong absorption band centered at 545 nm. On stepwise addition of oxalyl chloride (0 to 10 equiv.) to the probe solution, the absorption band at 545 nm gradually decreases accompanied with the increase of absorption band at 434 nm. Meanwhile, a noticeable color change from pink to light yellow can be observed. The fluorescence response of **TCF-EA** to oxalyl chloride was also examined. As shown in Fig. 2, when oxalyl chloride was added at different concentrations (0–100 μM), the initial strong emission band at 614 nm gradually decreased and reached complete fluorescence quenching when 100 μM oxalyl chloride was added. It was confirmed that the ICT characteristics of **TEA-EA** decreased after coupling NH and OH groups with oxalyl chloride. It shows that the probe **TCF-EA** has good optical response to oxalyl chloride.

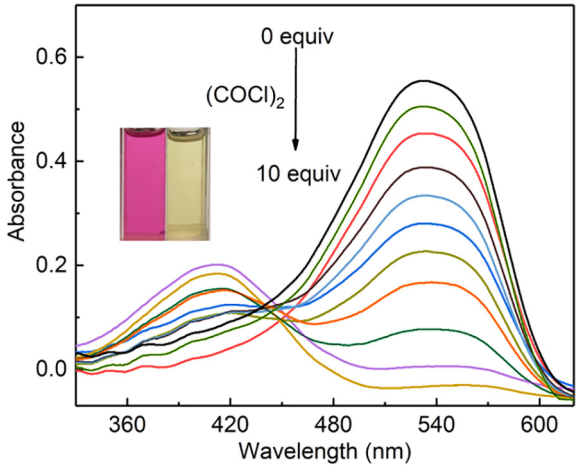


Fig. 1. Changes in absorption spectrum of **TCF-EA** (10 μM) in dry dichloromethane upon incremental addition of oxalyl chloride (0–10 equiv.). Inset: Color changes of **TCF-EA** solution before and after addition of oxalyl chloride under day light.

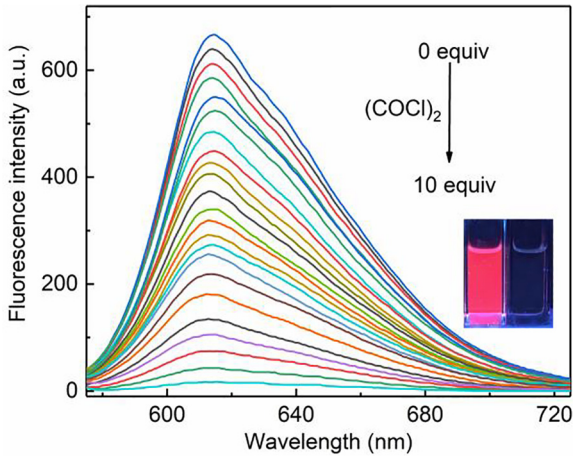


Fig. 2. Change of fluorescence spectrum of probe **TCF-EA** with addition oxalyl chloride (0–10 equiv.) in dry DCM. Inset: Fluorescence image of probe **TCF-EA** before and after addition of oxalyl chloride. λ_{ex} = 545 nm.

Based on the fluorescence titration results, the fluorescence intensity (614 nm) against the oxalyl chloride concentration (0–100 μM) displays a good linear relationship (R^2 > 0.99). The detection limit of the probe for oxalyl chloride was calculated to be 2.9 nM using a method of LOD = $3\sigma/\rho$. The detection limit is either comparable or better than that of some reported probes (Table S1), manifesting its high sensitivity to oxalyl chloride. We also measured the response time of **TCF-EA** (10 μM) to oxalyl chloride (Fig. 3). As shown in (Fig. S1), with the addition of 100 μM oxalyl chloride, the emission intensity at 614 nm gradually decreased and reached constant after 5 min. Therefore, the probe **TCF-EA** can quickly detect oxalyl chloride in real time.

To explore the selectivity of **TCF-EA** for oxalyl chloride, we examined the changes of emission spectrum of **TCF-EA** (10 μM) in the individual presence of oxalyl chloride and other analytes in dry dichloromethane (Fig. 4). After addition of these analytes, only oxalyl chloride induced a dramatic fluorescence spectrum variation, other chlorides including toluenesulfonyl chloride (TsCl), $POCl_3$, acetyl chloride (AC), dichlorosulfoxide, sulfonyl chloride, and triphosgene (0.01% TEA), caused no or slight emission spectrum changes. The selectivity of **TCF-EA** to oxalyl chloride was also confirmed by UV–vis spectrum. As shown in Fig. 5, probe **TCF-EA** in dichloromethane showed an absorption band centered at 545 nm. When 10 equiv. of oxalyl chloride were added, a new absorption

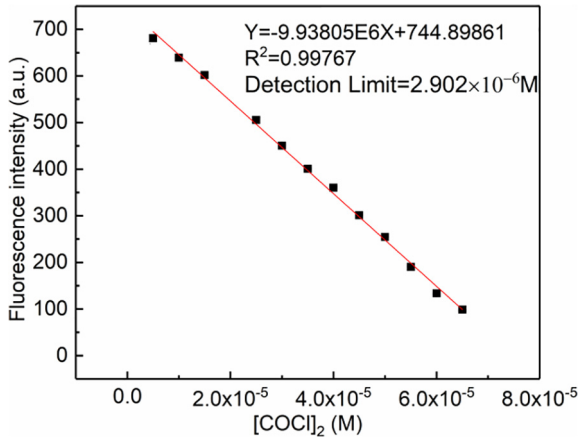


Fig. 3. Linear relationship between fluorescence emission intensity (614 nm) and oxalyl chloride concentration.

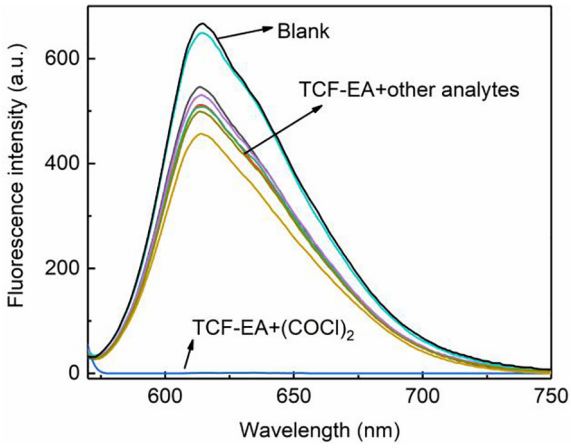


Fig. 4. Changes in fluorescence spectrum of **TCF-EA** (10 μM) in dry dichloromethane on addition of oxalyl chloride (100 μM) and other analytes (100 μM). λ_{ex} = 545 nm.

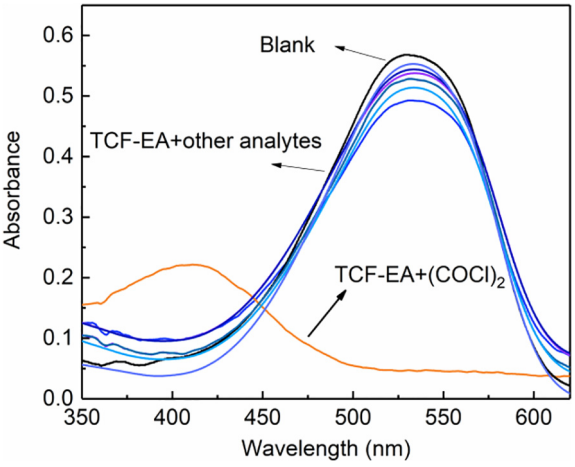


Fig. 5. Changes in UV–vis absorption spectrum of **TCF-EA** (10 μM) in dry DCM on addition of oxalyl chloride (100 μM) and other analytes (toluenesulfonyl chloride (TsCl), $POCl_3$, acetyl chloride (AC), dichlorosulfoxide, sulfonyl chloride, and triphosgene (0.01% TEA), 100 μM of each).

band appeared at 410 nm was observed. However, addition of other analytes to the solution did not cause a significant change in the absorption spectrum. These results indicate that **TCF-EA** has an excellent selectivity to oxalyl chloride.

Subsequently, the anti-interference ability of **TCF-EA** for recognizing oxalyl chloride was investigated in order to gain deeper insight into the practicability of the probe. In the presence of other chlorides (100 μM), the emission intensity of the probe **TCF-EA** did not change, we continued to add an equivalent amount of oxalyl chloride, it was found that the emission intensity at 614 nm significantly decreased (red column in Fig. 6). Similarly, the corresponding UV–Vis spectrum shows a significant decrease in the absorption intensity at 545 nm in the presence of oxalyl chloride (red column in Fig. 7). Both **TCF-EA** fluorescence emission spectrum (Fig. 6) and UV–visible light absorption spectrum (Fig. 7) show that **TCF-EA** has good selectivity and anti-interference to oxalyl chloride.

Recognition mechanism of TCF-EA to oxalyl chloride

According to relevant literature reports [37], we speculate that the sensing mechanism of **TCF-EA** toward oxalyl chloride is based

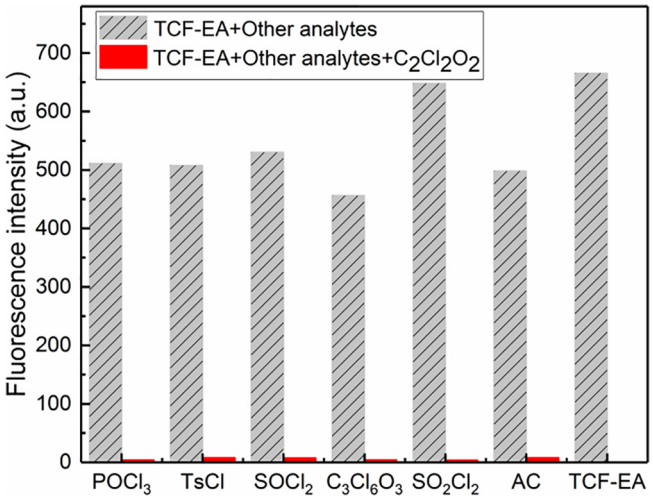


Fig. 6. Fluorescence intensity (at 614 nm) changes of probe **TCF-EA** (10 μM) in the presence of other chlorides (100 μM) and followed by addition of oxalyl chloride (100 μM) for 5 min. λ_{ex} = 545 nm.

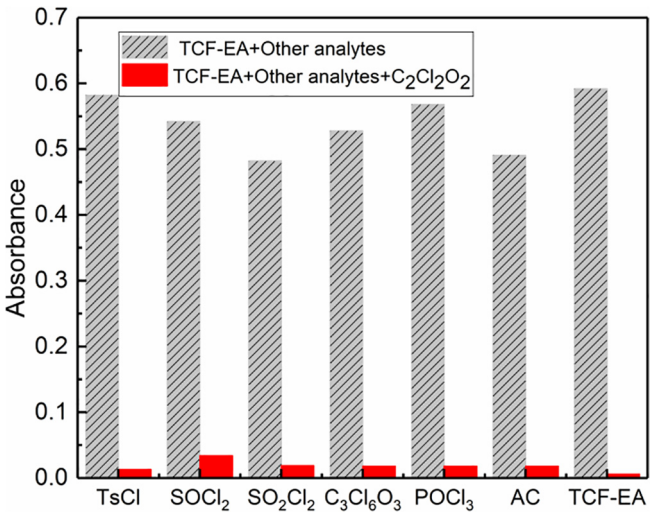


Fig. 7. Absorbance (at 545 nm) change of probe **TCF-EA** (10 μM) in the presence of other chlorides (100 μM) and followed by addition of oxalyl chloride (100 μM).

on the reaction between **TCF-EA** and oxalyl chloride. In order to ascertain the mechanism, we separately conducted a reaction of **TCF-EA** with oxalyl chloride, and the main product was separated and subjected to ^{1}H NMR and HRMS analysis. In the ^{1}H NMR spectrum of of the probe, the signal of NH appeared at 7.477 ppm (Ha) (Fig. 8a). This signal disappeared in the isolated product (Fig. 8b). Concomitantly, the proton signals of $-CH_2$ (Hb and Hc) in **TCF-EA** appeared at 3.358 ppm (Hb) and 3.574 ppm (Hc) are significantly downfield-shifted to 4.166 ppm (Hb′) and 4.683 ppm (Hc′), we speculate that the –NH in **TCF-EA** has undergone an intermolecular amidation reaction. In addition, The HRMS spectrum of the product revealed a peak at m/z = 401.1244, which is assignable to the species of **TCF-B** $[M+H]^+$ (m/z = 401.1211). We thus speculate that the –NH and –OH in **TCF-EA** have undergone two consecutive steps of intermolecular amidation and intramolecular esterification, respectively. Therefore, we speculated that –NH and –OH in **TCF-EA** underwent two consecutive steps of intermolecular amidation and intramolecular esterification reactions, which greatly restricts the charge transfer process from aniline N atom to TCF moiety, resulting in a significant fluorescence quenching. The detection

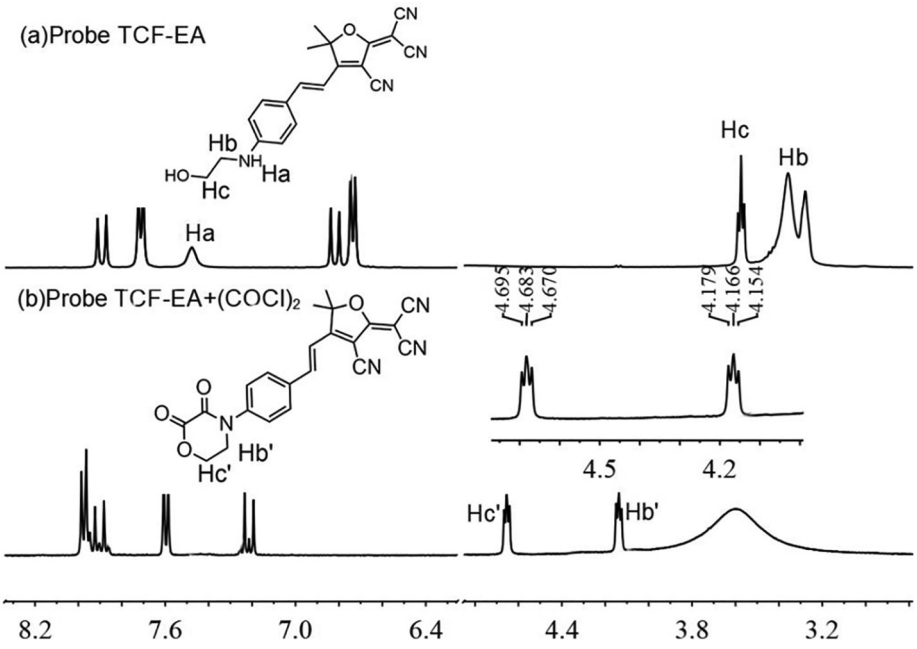
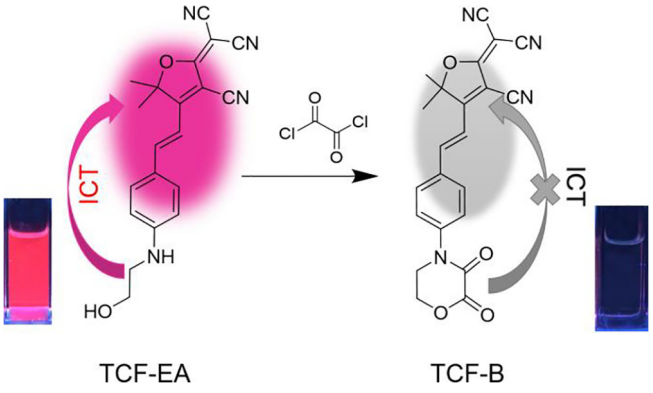


Fig. 8. Partial ^{1}H NMR spectrum of probe **TCF-EA** (a), **TCF-B** (b).



Scheme 2. Design strategy of probe **TCF-EA** for identify oxalyl chloride.

mechanism of probe **TCF-EA** to oxalyl chloride was shown in Scheme 2.

Application of probe TCF-EA in detection

In order to put the prominent features of the probe into practical application, a test strip was made to conveniently and quickly detect oxalyl chloride in the gas phase (Fig. S2). The test strip emits bright pink fluorescence when illuminated by a handheld UV lamp (365 nm) (Fig. 9a). Under natural light, the color of the **TCF-EA** test strip gradually changed from pink to light yellow (Fig. 9b). Thus the probe **TCF-EA** behaves dual signal channel to detect oxalyl chloride. After exposing the test paper to different concentrations of oxalyl chloride (0–20 ppm) for 5 min, the bright fluorescence was gradually quenched. It is worth noting that even with the

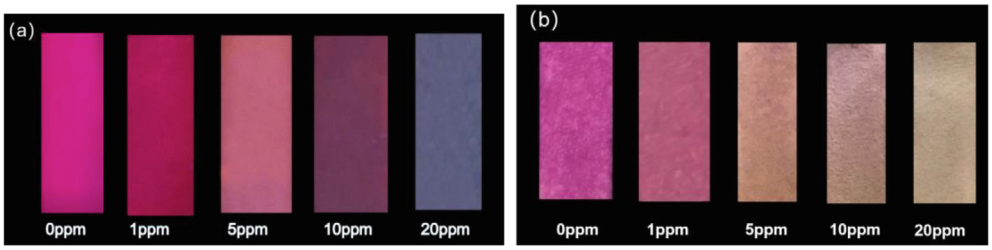


Fig. 9. Photographs of **TCF-EA**-based test papers upon exposure to various oxalyl chloride (0–20 ppm) vapor for 5 min. The picture was taken under a 365 nm handheld UV lamp (a), and the photo was taken in natural light (b).

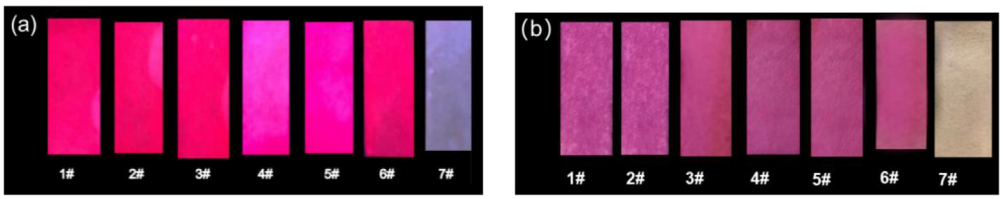


Fig. 10. Photographs of **TCF-EA**-based test strips when exposed to oxalyl chloride (20 ppm) vapor and various other analyte (60 ppm) vapors: 1. toluenesulfonyl chloride (TsCl), 2. $POCl_3$, 3. acetyl chloride (AC), 4. dichlorosulfoxide, 5. sulfonyl chloride, 6. triphosgene, 7. oxalyl chloride. The picture was taken under a 365 nm handheld UV lamp (Fig. 10a) and natural light (Fig. 10b).

concentration of oxalyl chloride as low as 1 ppm, the test strips using **TCF-EA** still represent a response (Fig. S3).

The selectivity of **TCF-EA** test strips to oxalyl chloride and other analytes was also studied. As shown in Fig. 10, the **TCF-EA** test paper was exposed to oxalyl chloride (20 ppm) vapor and various other analyte vapors (60 ppm), and the fluorescence of these test papers was captured under 365 nm light (Fig. 10a) and natural light (Fig. 10b) after 5 min. No changes in other analyte vapors toluenesulfonyl chloride (TsCl), $POCl_3$, acetyl chloride (AC), dichlorosulfoxide, sulfonyl chloride, and triphosgene) were observed, only changes were made to oxalyl chloride, which is in line with the aforementioned results. Therefore, these observations and results indicate that **TCF-EA** can use a test strip as a simple and safe method for specifically identifying oxalyl chloride (Fig. S4).

Conclusion

In summary, we have developed a new TCF-derived fluorescent probe **TCF-EA** for visual detection of oxalyl chloride in dry dichloromethane, which can react with oxalyl chloride to generate a significant color change from pink to light yellow and a distinct fluorescence quenching at 614 nm. The probe behaves high selectivity to oxalyl chloride over other analytes with a good anti-interference ability and a low detection limit (2.9 nM) and fast response (<5 min). The sensing mechanism was investigated by ^{1}H NMR and HRMS analysis and was proved to undergo tandem reactions between **TCF-EA** and oxalyl chloride. Furthermore, a portable test strips with **TCF-EA** was also made for visual inspection of oxalyl chloride in the gas phase, demonstrating the practicability of the probe.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2020.152470.

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