



Selective turn-on fluorescence detection of formaldehyde in the gas phase

Chenglong Liao^a, Miao Zhang^a, Qingyun Tian^a, Xiaomei Yang^b, Jiangfan Shi^{b,c}, Shuai Chen^{d,*}, Yanke Che^e, Chuanyi Wang^a, Ling Zang^{b,c,**}

^a School of Environmental Science and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, Shaanxi, China

^b Nano Institute of Utah, University of Utah, Salt Lake City 84112, UT, USA

^c Department of Materials Science and Engineering, University of Utah, Salt Lake City 84112, UT, USA

^d Jiangxi Engineering Laboratory of Waterborne Coatings, Nanchang 330013, Jiangxi, China

^e University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Keywords:

Fluorescence sensor
Formaldehyde
Hydroxylamine
Aldimine condensation
Perylene diimide

ABSTRACT

Reliable detection of formaldehyde in gas phase still remains a challenge regarding either sensitivity or selectivity or both. In this study we report on a simple, unique sensor composite, which enables efficient detection of gaseous formaldehyde with both low limit of detection (LOD) and extremely high selectivity. The primary components of the sensor composite include a hydroxylamine sulfuric acid salt $((\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4)$ and a fluorescence turn-on probe, which both are coated within the porous matrix of a cellulose plate. The fluorescence probe is based on a perylene diimide (PDI) molecule modified with an aniline group, which is non-fluorescent in its pristine state due to the photoinduced intramolecular electron transfer. Upon interaction with formaldehyde, the hydroxylamine salt will be converted to the corresponding Schiff base through aldimine condensation, releasing the sulfuric acid. The acid released will protonate the aniline group on PDI, resulting in a quick fluorescence turn-on. By measuring the fluorescence increase we can detect formaldehyde both quantitatively and specifically. Under the optimized condition, the sensor demonstrated a LOD of 3.7 ppb, which is much lower than the air quality threshold set by WHO. The sensor was also proven highly selective towards formaldehyde, with negligible response towards other common chemicals. The work reported will not only provide a new sensor for formaldehyde, but moreover open a unique design pathway for sensor composite that combines reactive components with various fluorescence indicators so as to enable highly efficient detection of many other air pollutants and toxic chemicals.

1. Introduction

Formaldehyde, a common airborne environmental pollutant [1,2], can cause various adverse health effects, such as skin irritation, asthma, cancer, etc. [3] A lot of household materials contain formaldehyde within the adhesives that are used to bind veneers, particle board, and pressed wood products. The World Health Organization (WHO) has guideline determining that a maximum permissible indoor formaldehyde concentration must not exceed 80 ppb over 30 min [4]. Various methods have been developed for gaseous phase detection of formaldehyde, including those based on chromatography [5], IR and cavity ring-down spectroscopy [6], surface acoustic wave [7], electrochemistry [8,9], and among others. However, many of the methods (particularly those involving bench-top instrumentations) are bulky and/or

expensive, and require sophisticated operation training, and tedious sampling and processing protocols [6]. These technical drawbacks can potentially be addressed by employing chemical sensors such as those based on colorimetric [10,11], fluorometric [12–14] and chemiresistive [15–17] sensing modes. As evidenced from numerous examples, the chemical sensors often provide simple and quick detection of formaldehyde in gaseous phase. Moreover, many sensors can potentially be developed as portable, handheld or even wearable devices taking advantages of the small and flexible form factor of the sensor materials. Depending on the materials used the whole sensor system could also be made in significantly low cost.

Among all the chemosensors developed thus far, fluorescence sensors are superior in its simplicity, high sensitivity, low cost, adaptation to automation and real-time analysis, as well as diverse signal output

* Corresponding author.

** Corresponding author at. Nano Institute of Utah, University of Utah, Salt Lake City 84112, UT, USA.

E-mail addresses: shuaichen@jxstnu.edu.cn (S. Chen), lzang@eng.utah.edu (L. Zang).

<https://doi.org/10.1016/j.snb.2022.132861>

Received 30 July 2022; Received in revised form 12 October 2022; Accepted 15 October 2022

Available online 17 October 2022

0925-4005/© 2022 Elsevier B.V. All rights reserved.

modes [18]. Particularly in comparison to the colorimetric sensors, for which the sensitivity is primarily relied on measurement of light absorption, the fluorescence measurement generally provides significantly higher sensitivity. Moreover, fluorescence sensors provide wide range of options for molecular design and structural engineering to improve the detection selectivity [12,19]. This is in contrast to the chemiresistive sensors, for which the detection is mostly based on metal oxide semiconductors as sensor materials, and improvement of selectivity is generally limited by the minimal option of surface modification of metal oxides. Indeed, metal oxide sensors often demonstrate serious competitive response from the environment interferents such as moisture alcohols and other common chemicals. While many nanostructures and composite materials (e.g., those based on metal-organic frameworks, namely MOFs) have been explored in order to improve the selectivity of chemiresistive sensors, the detection sensitivity for gaseous formaldehyde still remains low, in the range of ppm [17]. Clearly, there exists large potential for fluorescence sensors to be improved to reach both high sensitivity and selectivity.

Many types of fluorescence sensors (or more generally, fluorescence probes, covering both the reversible and irreversible sensing responses), such as those based on small organic molecules [20–22], organic-inorganic hybrid materials [23], MOFs [24,25], have been developed for detection of formaldehyde. The sensing mechanisms are generally relied on the aza-Cope reaction or the condensation of amine with the carbonyl group of formaldehyde. However, most of the sensor or probe systems reported are for liquid phase detection (see summary in Table S1, S2). The challenge of adapting the detection system from liquid to gas phase lies in maintaining the sensor reactivity at the gas-solid interface, for which the same molecular reaction (e.g., aza-Cope reaction) may become significantly slow and less efficient in gas phase compared to liquid phase. Indeed, most of the fluorescence sensors based on aza-Cope reaction take extended time (over one hour) to reach sufficiently low limit of detection (LOD) in ppb range when employed for gas phase detection of formaldehyde [12,26–29]. Therefore, it remains highly imperative to develop a novel sensor composite material that can not only afford the intrinsic specificity, but also high efficiency for the sensing reaction at the gas-solid interface.

Ideally, molecular dispersion of the fluorescence sensors or probes on the solid surface is deemed critical for maximizing the reactivity with the gaseous analytes, and thus the detection sensitivity. Moreover, in order to reach low LOD the solid substrate used for supporting the fluorophores must be in porous structure with large open surface area in order to afford maximal absorption of gas species. Especially for the gaseous analytes in very trace level that is undetectable by normal chemical sensors, such porous substrate may help pre-concentrate the species in the matrix (depending on the exposure time) so as to reach the detectable level for the fluorescence sensors deposited therein. To the regard of practical application, a sensor based on solid state materials is usually conducive to fabrication as a portable or even wearable device that is easy to be used by itself or integrated into the current air monitoring system for quick detection of airborne pollutants [12–16,18].

The concept of combining chemical sensing with pre-concentration in a single material system as mentioned above has recently been proven with a paper-based colorimetric sensor for formaldehyde recently developed from our lab [30]. The sensing mechanism is based on the specific aldimine condensation reaction between amine and formaldehyde forming the corresponding Schiff base. The amine used is hydroxylamine in the format of sulfuric acid salt, for which the protonated amine provides much faster reaction with aldehyde than the free base amine. As a result of the condensation reaction, sulfuric acids (protons) are released and this can be easily detected with pH indicators as revealed by the color change. By incorporating the hydroxylamine salt and pH indicators into the matrix of paper towel (a low cost substrate possessing open porosity), an effective sensor was developed for gaseous detection of formaldehyde. To further improve the detection sensitivity, glycerin was also used as an additive to enhance the

hydrophilicity of the coating, which in turn facilitates the surface adsorption of formaldehyde that is highly hydrophilic. Taking all these features, the paper-based sensor was proven capable of detecting formaldehyde in gas phase with LOD of 10 ppb under an exposure time of 10 min.

Inspired by the initial success with colorimetric sensor, we aim herein to further improve the sensor performance regarding sensitivity by adapting the sensing mode from colorimetric to fluorescent response. In general, fluorescence measurement is significantly more sensitive than the color or absorption measurement. As illustrated in Scheme 1, the fluorescent sensor relies on a perylene diimide (PDI) fluorophore modified with an aniline group, which is non-fluorescent in the free base state due to the intramolecular photoinduced electron transfer (PET) from the amine moiety to PDI backbone, but becomes strongly fluorescent when the amine gets protonated as the protonation lowers the energy level of amine, thus blocking the PET process [31]. Such a fluorescence turn-on response can be used to signal the presence of acids, which in turn is produced from the aldimine condensation reaction between hydroxylamine sulfuric acid salt and formaldehyde as evidenced in the colorimetric sensor [30]. By blending the PDI fluorophore with hydroxylamine sulfuric acid salt it is expected to produce a unique sensor composite that can potentially detect formaldehyde with both high specificity and sensitivity, as enabled by the specific aldimine condensation reaction and fluorescence turn-on sensing, respectively. To assure homogeneous molecular dispersion of the fluorophore, a cellulose acetate plate is used as supporting matrix for the sensor composite. The highly porous structure of cellulose material is not only conducive to the dispersion of sensor molecules, but also helps facilitate the diffusion and adsorption of gas analyte. Moreover, the mechanical rigidity of the plate allows for repeatable fluorescence measurement. Combination of these features makes the supported sensor composite shown in Scheme 1 an ideal platform for effective detection of formaldehyde in gas phase.

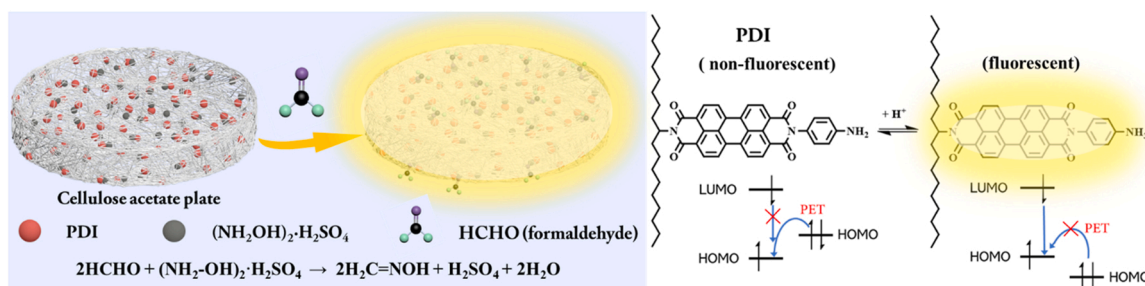
2. Experimental section

2.1. Reagents and material

All commercially obtained solvents and reagents are of analytical grade or above, and used without further purification. The aniline modified PDI fluorophore was synthesized following the protocol previously developed from our and others' labs [31–33]. Ultrapure deionized water (18 MW) was produced by an ultrapure water treatment system (EPED-S2–90DF, Nanjing EPED Technology Ltd.). Porous cellulose acetate plates were purchased from Dongguan Chengyao Technology Ltd.

2.2. Preparation of sensor plates

A porous cellulose acetate plate (Diameter: 8 mm, thickness: 3 mm) was immersed in a 1 mL solution of PDI in DMF for 5 min, for which varying concentrations of PDI were used for comparative experiments in order to find the optimal amount of PDI to be coated that can afford the maximal fluorescence turn-on response. The impregnated plate was then dried under vacuum at 35 °C for 10 min, followed by 1 min immersion in a 0.5 mL water solution containing 0.05 g (0.61 M) hydroxylamine sulfuric salt ((NH₂OH)₂·H₂SO₄) or 0.02 g (0.59 M) hydroxylamine hydrochloride salt (NH₂OH·HCl) and appropriate amount of glycerin. After the immersion, the plate was dried under vacuum at 25 °C for 8 min, and the plate thus obtained was ready for the sensor testing upon exposure to gaseous formaldehyde. The hydroxylamine salt was coated to the maximal extent of adsorption capacity of the plate, aiming to assure maximal reaction efficiency with formaldehyde, especially at low concentrations. Certain amount of glycerin was also used as part of the sensor composite in order to enhance the hydrophilicity and thus the absorption affinity towards formaldehyde. The concentration of glycerin



Scheme 1. Schematic illustration of the PDI-based fluorescence turn-on sensor for gaseous detection of formaldehyde based on the specific aldimine condensation reaction between hydroxylamine sulfuric salt and formaldehyde, which in turn releases stoichiometric amount of acids that can turn on the fluorescence of PDI through protonation of the aniline group as shown in the right panel. All the sensor components are impregnated in a porous cellulose acetate plate affording efficient diffusion and adsorption of gas analytes. HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital.

used in the immersion solution was varied (at 0 %, 5 % and 10 % volume ratio), and the effect on the sensing response in terms of the fluorescence increase was investigated. The comparative results would help determine the optimal condition for the coating of glycerin as described below.

2.3. Generation of gaseous formaldehyde and testing for the sensor plate

Gaseous formaldehyde was generated from a homemade environmental chamber as shown in Fig. S1, which can produce formaldehyde in varying concentrations under precisely controlled temperature and humidity. Details of the chamber can be found in the Supporting Information. The gaseous concentration of formaldehyde generated was calibrated by a PPM-400ST formaldehyde Meter (PPM Technology Ltd., England). The exposure to formaldehyde was realized by flowing the air containing formaldehyde over the sensor plate enclosed in a glass tube connected in the flow cycling loop, which helps maintain constant concentration of formaldehyde, as well as the humidity. All tests were performed at 28 °C and 45 % RH. The fluorescence spectra or intensity of the sensor plate were measured in situ during the test using an Ocean Optics USB 2000 spectrometer (Ocean Insight, USA) equipped with a fluorescence optical fiber probe (FPB-405-1.5-SS, Shanghai Oceanhood Opto-electronics Technology Co., China), which allows for both excitation and emission collection at high efficiency. For each series of testing, the fluorescence measurement was performed at the same point and angle on the sensor plate to minimize the measurement fluctuation. The wavelength of the excitation light used was 405 nm.

3. Results and discussion

3.1. Verification of the fluorescence turn-on sensing mechanism

As illustrated in Scheme 1, the working mechanism of the sensor relies on two subsequent reactions, aldimine condensation between hydroxylamine salt and formaldehyde producing an acid, followed by protonation of the aniline group of PDI by the acid, thus turning on the fluorescence of PDI. Yet there exists another possibility that the primary amine moiety of aniline may react directly with formaldehyde following the same type of aldimine condensation forming the Schiff base. Such a direct reaction can also significantly lower the energy level of the aniline group, resulting in fluorescence turn-on of PDI [31]. However, the condensation reaction between aniline and formaldehyde was proven to be a very slow process, and no fluorescence increase could even be observed within the testing period as evidenced in Fig. S2. First of all, no fluorescence was measured for a 20 μM solution of the PDI in DMF, which is consistent with the complete quenching mediated by the photoinduced intramolecular electron transfer as illustrated in Scheme 1. Upon mixing with excessive formaldehyde (10 mM), there was still no fluorescence measurable even after 40 min of mixing. The slow reaction observed for aniline is a common phenomenon for aldimine

condensation process, for which the reaction can normally be facilitated by acid catalysis. In comparison, the condensation reaction of hydroxylamine (especially in the format of acidic salt) with formaldehyde is significantly faster, thereby becoming kinetically competitive over aniline for reacting with formaldehyde.

As shown in Fig. 1, a sensor plate fabricated with PDI and hydroxylamine sulfuric salt ((NH₂OH)₂·H₂SO₄) demonstrated sensitive fluorescence response towards gaseous formaldehyde by ca. 27 times increase in fluorescence intensity upon exposure to 9 ppm of formaldehyde for 20 min. Before exposed to formaldehyde there was some slight level of fluorescence measured, which was likely due to the partial protonation of the aniline group by the sulfuric acid bound to hydroxylamine. The pK_a of hydroxylamine, 6.0, is larger than that of aniline, 4.6, meaning that the acidic salt of the former would be much more stable than the latter. When aniline is mixed with the acidic salt of hydroxylamine (e.g., (NH₂OH)₂·H₂SO₄) reaching an equilibrium state, the aniline group may get partially protonated upon interaction with the acid, while the hydroxylamine salt would mostly remain as is. As the protonation forms an ammonium salt that is relatively stable (non-volatile), the sensor response is not reversible regarding the temporality needed for onsite detection. But on the other hand, since the free amine can be recovered by treating the ammonium salt with some strong base like sodium hydroxide, the sensor material can still be considered reversible. Nonetheless, in the real practice the whole sensor disk can be simply used as a disposable part without bothering the recovery taking

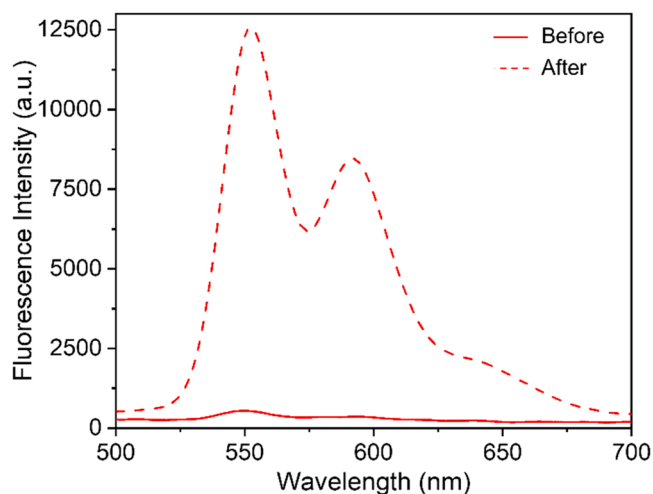


Fig. 1. Fluorescence spectra of the sensor plate measured before and after exposed to 9 ppm gaseous formaldehyde for 20 min. The plate was fabricated by subsequent impregnation in 1 mL of 100 μM solution of PDI in DMF and 0.5 mL of aqueous solution containing 0.05 g (NH₂OH)₂·H₂SO₄ and 0.025 mL glycerin.

advantage of the low-cost.

In addition to the sulfuric salt, the hydrochloride salt of hydroxylamine ($\text{NH}_2\text{OH}\cdot\text{HCl}$) was also examined following the same testing protocol as shown in Fig. 1. Surprisingly, the sensor plate fabricated with $\text{NH}_2\text{OH}\cdot\text{HCl}$ did not demonstrate significant fluorescence turn-on response towards formaldehyde as shown in Fig. S3, wherein the sensor plate fabricated with $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ demonstrated drastic increase in fluorescence when tested under the same condition. The different observation is likely due to the relatively high volatility of HCl , which may quickly evaporate from the surface once produced from the aldimine condensation, thus leaving no chance to react with aniline. Especially, the sensor testing was performed under continuous air flowing (Fig. S1), which would help facilitate the evaporation of HCl . To this regard, in the following experiments we kept using $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ as the primary reactive component of the sensor composite, taking advantage of its low volatility.

3.2. Optimization of sensor composition

As described above (Scheme 1), the sensor composite impregnated within the cellulose plate contains two major reactive components, PDI and $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$. While the hydroxylamine salt was coated to the maximal loading capacity of the plate, the coating of PDI still has large room to be adjusted and optimized. On one hand, less PDI coated would help ensure molecular dispersion of the fluorophore on the surface, but may result in low fluorescence intensity to be measured, which will likely affect the signal-to-noise ratio of detection. Molecular dispersion of PDI on the surface allows for maximal protonation by the acid produced in proximity, thus turning on the fluorescence. As the fluorescence response is dependent on the stoichiometric protonation process, the molecular dispersion of fluorophores (in comparison to the aggregation state) would enhance the sensing efficiency under the same conditions. On the other hand, increasing the coating amount of PDI will produce high fluorescence intensity and thus improve the measurement accuracy, though after passing certain amount of coating, the surface dispersion of PDI molecules may become saturated, leading to formation of aggregates, which otherwise would result in quenching of the molecular fluorescence of PDI [34,35]. To address such a tradeoff, we fabricated a series of sensor plates by immersion in varying concentrations of PDI solutions (20, 50, 100, 200 μM) and tested the sensing response under the same condition with results shown in Fig. S4 and S5. Similar to what observed in Fig. 1, when exposed to 9 ppm of formaldehyde, all the four plates demonstrated fluorescence turn-on, and the fluorescence intensity increased with the concentration of PDI solution up to about 100 μM . Further increasing the concentration to 200 μM results in a significant decrease in fluorescence intensity, even below the level obtained for the solution of 50 μM . The significant decrease in fluorescence overserved for the higher concentration coating is mostly due to the aggregation induced quenching of PDI. To further understand this, the fluorescence spectra obtained for the plates fabricated with 20 and 200 μM PDI solutions are normalized at the emission maximum (corresponding to 0–0 transition) as shown in Fig. S4b. It is clear to see that the emission at the longer wavelength (corresponding to 0–1 and 0–2 transition) gets relatively enhanced, which is indicative of the aggregation state as previously overserved for other PDI molecules [36]. Consistent with the relatively enhanced emission at longer wavelength from the aggregate of PDI (despite the overall low quantum yield), the fluorescence image of the plate fabricated with 200 μM PDI solution showed more of red color, which is characteristic of the emission of PDI aggregates [32,33,36,37]. Taking all the observations into account, it was determined that the concentration of 100 μM would be optimal for the PDI solution to be used for coating the sensor plate. Under this concentration, the plate fabricated would provide the maximal fluorescence intensity, while maintaining mostly the molecular dispersion state of the fluorophore. For the rest of experiments in this study, all the sensor plates will be fabricated with 100 μM solution of PDI.

The other additive of the sensor composite is glycerin, which helps enhance the hydrophilicity and binding affinity towards formaldehyde. However, too much glycerin added may diminish the porosity of the plate, leading to a decrease in gas diffusion and adsorption within the plate matrix. Therefore, it is essential to determine the optimal amount of glycerin to be coated in terms of the sensor response. As shown in Fig. S6, significant turn-on fluorescence was observed even when glycerin was absent, indicating that glycerin is not an essential component as directly involved in the sensor reactions. Nonetheless, when 5 % volume concentration of glycerin was added in the impregnation solution, significant enhancement of the fluorescence intensity was obtained under the same testing condition. This is consistent with the hypothesis made above that the presence of glycerin would enhance the binding interaction with formaldehyde. Further increasing the concentration of glycerin up to 10 % vol resulted in a decrease in the fluorescence intensity, implying that excess of glycerin would likely block the porous structure of the plate, thus reducing the surface adsorption of formaldehyde. Consistently, the fluorescence images taken over the plates also show the same comparative result, with the plate fabricated from 5 % vol glycerin providing the brightest and most uniform emission. The uniform emission indicates the homogeneous distribution of sensor composites within the cellulose matrix of the plate. In this study, the concentration of glycerin used for the impregnation of plate was kept at 5 % vol.

3.3. Kinetics of fluorescence sensing

With the sensor plate fabricated under the optimal conditions, we aimed at investigating the fluorescence turn-on kinetics by measuring the fluorescence spectra of plate at different time intervals after exposed to formaldehyde. As shown in Fig. 2a, upon exposure to 850 ppb formaldehyde the fluorescence gradually increased with time. By plotting the intensity measured at 550 nm as a function of the exposure time (Fig. 2b), one can clearly see that the fluorescence intensity increases quickly at the beginning, then slows down gradually, and eventually gets saturated after about 20 min of exposure under the testing condition. The data shown in Fig. 2b can be fitted well with the first order reaction kinetics, for which the only reactant with concentration varying is the PDI fluorophore. Details of the kinetics analysis can be found in the Supporting Information. The same first order kinetics has also been observed for other fluorescence turn-on and colorimetric sensors [38, 39]. From the kinetics fitting, we can estimate the sensor response time to be ca. 1.9 s by assuming the lowest detectable signal (here the fluorescence increase) to be three times of the standard derivation of measurement. Quick response in seconds is critical for a chemical sensor to be used in realtime detection of air pollutants like formaldehyde [12,40, 41].

Despite the quick sensing response, the sensor plate still took as long as 20 min to get saturated in terms of the increase in fluorescence, which was mainly a result of the slow diffusion of formaldehyde into the porous structure of cellulose plate. In this study the exposure to formaldehyde was carried out by flowing the gas sample parallel over the surface of sensor plate. Under this condition, the capture and adsorption of formaldehyde are mainly through the natural diffusion. In comparison, if the gas sample were introduced by enforced flow perpendicular through the sensor plate, the time needed to reach the saturation state would be much reduced. Indeed, as observed in our pervious study on the colorimetric sensor for gaseous formaldehyde based on the same hydroxylamine sulfuric salt [30], the time needed to reach the color saturation was only about 5 min when the gas sample was introduced by passing right through the sensor substrate (a paper strip). Nonetheless, the cellulose plate used in this study was too thick (3 mm) to allow gas to flow through. In future we may consider fabricating thinner plate or disk that still remain the same level porosity and surface area as the current cellulose plate so as to enable direct gas flowing through, thus speeding up the diffusion to reach the saturation (equilibrium) state.

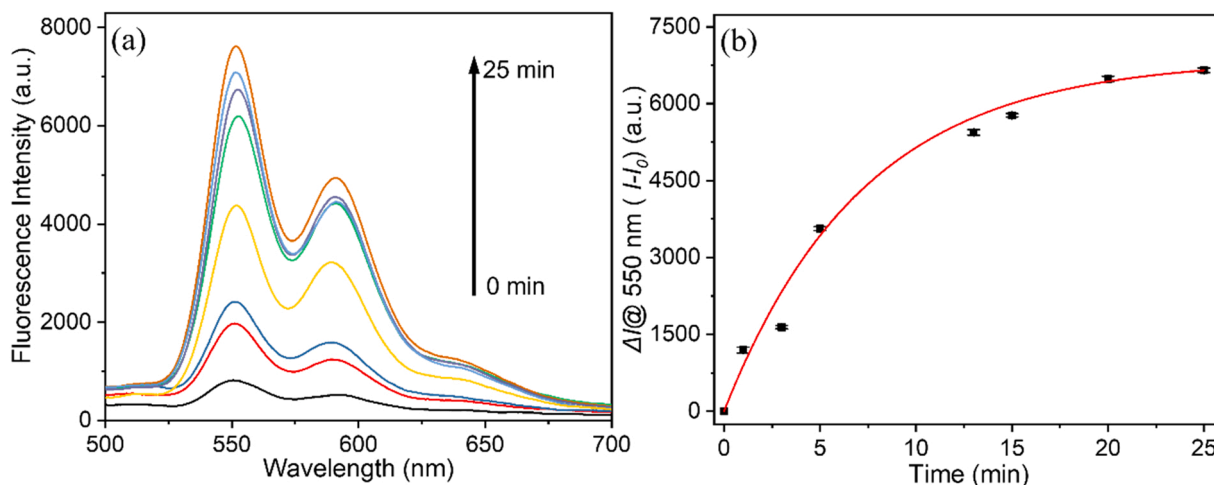


Fig. 2. (a) Fluorescence spectra of the sensor plate recorded at various time intervals after exposure to 850 ppb formaldehyde. (b) The increase in fluorescence intensity (ΔI) measured at 550 nm as a function of the exposure time.

3.4. Limit of detection and sensing selectivity

To explore the limit of detection (LOD), the sensor plate was examined by exposure to various concentration of formaldehyde (0–900 ppb) for 20 min. For each concentration, the increase in fluorescence intensity at 550 nm was measured, and plotted as a function of the concentration. Assuming that a quasi-equilibrium was reached within 20 min of exposure (as implied from the result shown in Fig. 2), the data shown in Fig. 3 should follow the Langmuir adsorption model (See the Supporting Information). After fitting the data with the Langmuir equation, the LOD of this sensor plate was projected to be 3.7 ppb by defining an intensity increase of 3 times the standard deviation of measurement as the detectable signal. It is worth to note that the LOD obtained is more than twenty times lower than the air quality threshold (80 ppb) set for formaldehyde by the WHO.

In addition to the high sensitivity, the sensor plate also demonstrated excellent selectivity towards formaldehyde against other common gases and chemicals as shown in Fig. 4. While significant fluorescence increase was obtained upon exposure to 9 ppm formaldehyde, almost no response was observed for all the ten references tested under the same condition despite that the concentrations of the references were 10–70 times higher than that of formaldehyde. Such a drastic difference

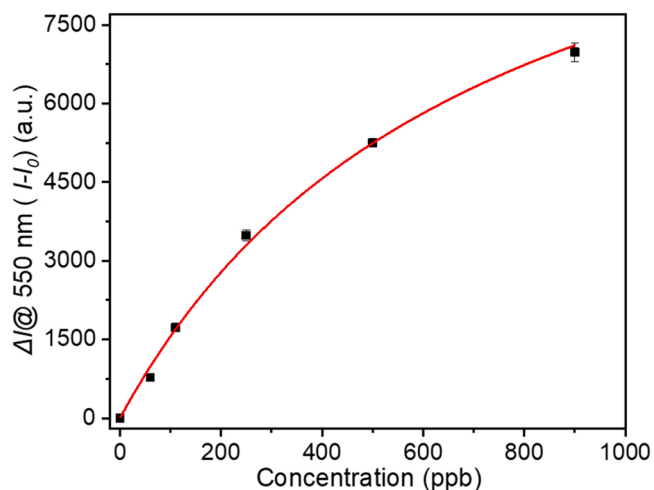


Fig. 3. Increase in fluorescence intensity (ΔI) as a function of the concentration of formaldehyde, for which the data points are fitted following the Langmuir adsorption model (see the Supporting Information).

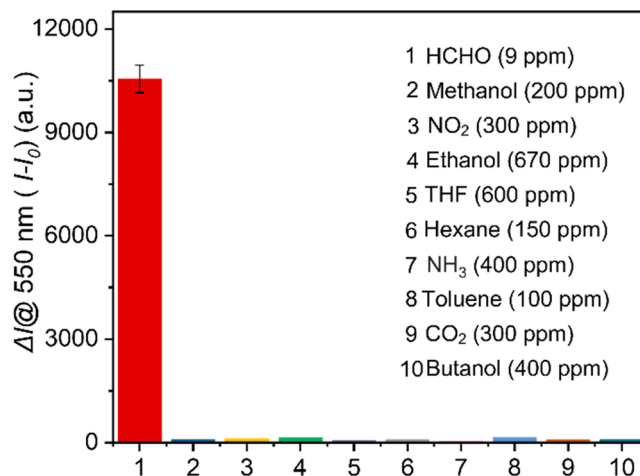


Fig. 4. Increase in fluorescence intensity (ΔI) as tested for the sensor plate upon exposure to 9 ppm formaldehyde, in comparison to other common gases and chemicals under much higher concentrations.

in response provides the sensor with sufficient selectivity towards formaldehyde. The excellent selectivity thus obtained is apparently due to the specific aldime condensation reaction between hydroxylamine and formaldehyde as discussed above. Especially for the two acidic gases tested, NO_2 and CO_2 , which may form the corresponding acids (nitric and carbonic acid, respectively) upon reaction with water under certain level of humidity (e.g., 45 % RH in this study), there was no fluorescence response observed, although there exists the possibility that the formed acid may turn on the fluorescence by direct protonation of the aniline group of the fluorophore. Such a drastic observation is likely due to the high volatility of the nitric and carbonic acids, which may escape quickly from the surface once formed, similar to the case observed above for HCl (Fig. S3). Moreover, the carbonic acid is too weak (with pKa of 6.4) to protonate the aniline group (pKa 3.45) [31] on the PDI fluorophore. For the same reason, acetic acid, another common acid that may exist in the environment, is also a weak acid (pKa 4.8), and can hardly cause significant protonation of the aniline group. The weak acidity, together with the high volatility of acetic acid, would mitigate its potential influence on the sensor response. Clearly, the main reason why the sulfuric salt of hydroxylamine works effectively for the sensor composite lies in the low volatility of sulfuric acid, which also helps mitigate the potential interference from other volatile acids that may be

present in gas phase.

4. Conclusions

We have developed a simple, but efficient fluorescence turn-on sensor for highly selective detection of formaldehyde in gas phase. The sensing mechanism is based on the specific aldimine condensation reaction between formaldehyde and hydroxylamine sulfuric salt, which in turn releases the acid. The released acid then protonates the aniline group modified on a PDI molecule, and turns on the characteristic fluorescence of PDI. All the sensor components are incorporated in the porous matrix of a cellulose plate, which provides large open surface for capture and adsorption of gas analytes. Quantitative detection of formaldehyde can be realized simply by measuring the increase in fluorescence intensity of PDI. The sensing response towards formaldehyde was found in the time range of secs. Fast response paves the way for a sensor to be applied in realtime detection, especially in the scenarios like monitoring of air pollution or public safety. The LOD of the sensor is projected as 3.7 ppb, which is significantly lower than the safety threshold of formaldehyde (80 ppb) set by the WHO, meaning that the sensor developed will be capable of reliable monitoring of airborne formaldehyde. More strikingly, the sensor demonstrated highly specific response towards formaldehyde with almost no interference from other common gases or chemicals (e.g., organic solvents). Combination of the high sensitivity and selectivity provides the sensor great potential for future application, not only in air quality monitoring, but also in many other areas such as medical diagnostics where formaldehyde may be produced as a biomarker. The main innovation of this work derives from the integration of the reaction specificity of aldimine condensation reaction, the high sensitivity of fluorescence response, and the porous structure of cellulose matrix, so as to enable high sensor performance as expected. The design and optimization strategy developed for the sensor composite is extensible to other materials and fluorophores to enable detection of broad range of other air pollutants or chemicals of interest.

CRedit authorship contribution statement

Chenglong Liao: Conceptualization, carrying out experiments, data processing and analysis, Writing – original draft. **Miao Zhang, Qingyun Tian and Jiangfan Shi:** data analysis and discussion. **Xiaomei Yang:** Conceptualization, mechanism discussion, and editing manuscript. **Shuai Chen:** Conceptualization, Visualization, Project administration. **Yanke Che:** Conceptualization, Data analysis, Discussion. **Chuanyi Wang:** Conceptualization, Data analysis, Discussion. **Ling Zang:** original research ideas and plans, overall supervision, revision of manuscript.

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.

Data Availability

Data will be made available on request.

Acknowledgements

This work was supported by the Scientific Research Fund of Shaanxi University of Science and Technology and the China Scholarship Council (No. 201808360327).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.snb.2022.132861](https://doi.org/10.1016/j.snb.2022.132861).

References

- [1] T. Salthammer, S. Mentese, R. Marutzky, Formaldehyde in the indoor environment, *Chem. Rev.* 110 (2010) 2536–2572.
- [2] T. Salthammer, Formaldehyde in the ambient atmosphere: from an indoor pollutant to an outdoor pollutant? *Angew. Chem. Int. Ed.* 52 (2013) 3320–3327.
- [3] Y. Zhang, Y. Yang, X. He, P. Yang, T. Zong, P. Sun, et al., The cellular function and molecular mechanism of formaldehyde in cardiovascular disease and heart development, *J. Cell. Mol. Med.* 25 (2021) 5358–5371.
- [4] J. Hu, X. Chen, Y. Zhang, Batch fabrication of formaldehyde sensors based on LaFeO₃ thin film with ppb-level detection limit, *Sens. Actuators B* 349 (2021), 130738.
- [5] H. Zhu, J. She, M. Zhou, X. Fan, Rapid and sensitive detection of formaldehyde using portable 2-dimensional gas chromatography equipped with photoionization detectors, *Sens. Actuators B* 283 (2019) 182–187.
- [6] S. Dugheri, D. Massi, N. Mucci, G. Marrubini, G. Cappelli, A. Speltini, et al., Exposure to airborne formaldehyde: sampling and analytical methods-a review, *Trends Environ. Anal. Chem.* 29 (2021), e00116.
- [7] J. Wang, Y. Guo, G. Long, Y.L. Tang, Q. Tang, X.T. Zu, et al., Integrated sensing layer of bacterial cellulose and polyethyleneimine to achieve high sensitivity of ST-cut quartz surface acoustic wave formaldehyde gas sensor, *J. Hazard. Mater.* 388 (2020), 121743.
- [8] H. Xi, X. Chen, Y. Cao, J. Xu, C. Ye, D. Deng, et al., Electrochemical determination of formaldehyde via reduced AuNPs@ PPy composites modified electrode, *Microchem. J.* 156 (2020), 104846.
- [9] S. Ishihara, J. Labuta, T. Nakanishi, T. Tanaka, H. Kataura, Amperometric detection of sub-ppm formaldehyde using single-walled carbon nanotubes and hydroxylamines: a referenced chemiresistive system, *ACS Sens* 2 (2017) 1405–1409.
- [10] C. Martínez-Aquino, A.M. Costero, S. Gil, P. Gaviña, Resorcinol functionalized gold nanoparticles for formaldehyde colorimetric detection, *Nanomater* 9 (2019) 302.
- [11] Q. Meng, T. Han, G. Wang, N. Zheng, C. Cao, S. Xie, Preparation of a natural dye doped Ormosil coating for the detection of formaldehyde in the optical gas sensor, *Sens. Actuators B* 196 (2014) 238–244.
- [12] C. Liao, J. Shi, M. Zhang, R. Dalapati, Q. Tian, S. Chen, et al., Optical chemosensors for the gas phase detection of aldehydes: mechanism, material design, and application, *Mater. Adv.* 2 (2021) 6213–6245.
- [13] S. Pan, S. Roy, N. Choudhury, P.P. Behera, K. Sivaprakasam, L. Ramakrishnan, et al., From small molecules to polymeric probes: recent advancements of formaldehyde sensors, *Sci. Technol. Adv. Mater.* 23 (2022) 49–63.
- [14] A. Bi, S. Yang, M. Liu, X. Wang, W. Liao, W. Zeng, Fluorescent probes and materials for detecting formaldehyde: from laboratory to indoor for environmental and health monitoring, *RSC Adv.* 7 (2017) 36421–36432.
- [15] C. Lou, G. Lei, X. Liu, J. Xie, Z. Li, W. Zheng, et al., Design and optimization strategies of metal oxide semiconductor nanostructures for advanced formaldehyde sensors, *Coord. Chem. Rev.* 452 (2022), 214280.
- [16] Z. Yuan, C. Yang, F. Meng, Strategies for improving the sensing performance of semiconductor gas sensors for high-performance formaldehyde detection: a review, *Chemosensors* 9 (2021) 179.
- [17] N. Jafari, S. Zeinali, Highly rapid and sensitive formaldehyde detection at room temperature using a zif-8/mwcnt nanocomposite, *ACS Omega* 5 (2020) 4395–4402.
- [18] P.R. Chung, C.T. Tzeng, M.T. Ke, C.Y. Lee, Formaldehyde gas sensors: a review, *Sensors* 13 (2013) 4468–4484.
- [19] J.A. Kaczmarek, J.A. Mitchell, M.A. Spence, V. Vongsouthi, C.J. Jackson, Structural and evolutionary approaches to the design and optimization of fluorescence-based small molecule biosensors, *Curr. Opin. Struct. Biol.* 57 (2019) 31–38.
- [20] Y. Tang, X. Kong, A. Xu, B. Dong, W. Lin, Development of a two-photon fluorescent probe for imaging of endogenous formaldehyde in living tissues, *Angew. Chem., Int. Ed.* 55 (2016) 3356–3359.
- [21] Y. Tang, X. Kong, A. Xu, B. Dong, W. Lin, A biotin-guided formaldehyde sensor selectively detecting endogenous concentrations in cancerous cells and tissues, *Chem. Commun.* 52 (75) (2016) 11247–11250.
- [22] B. Zhai, Y. Zhang, Z. Hu, J. He, J. Liu, C. Gao, et al., A ratiometric fluorescent probe for the detection of formaldehyde in aqueous solution and air via aza-Cope reaction, *Dyes Pigm* 171 (2019), 107743.
- [23] S. Xue, X.F. Jiang, G. Zhang, H. Wang, Z. Li, X. Hu, et al., Surface plasmon-enhanced optical formaldehyde sensor based on CdSe@ ZnS quantum dots, *ACS Sens* 5 (2020) 1002–1009.
- [24] S. Nandi, E. Sharma, V. Trivedi, S. Biswas, Metal-organic framework showing selective and sensitive detection of exogenous and endogenous formaldehyde, *Inorg. Chem.* 57 (2018) 15149–15157.
- [25] S. Bej, S. Mandal, A. Mondal, T.K. Pal, P. Banerjee, Solvothermal synthesis of high-performance d¹⁰-mofs with hydrogel membranes @ “Turn-On” monitoring of formaldehyde in solution and vapor phase, *ACS Appl. Mater. Interfaces* 13 (2021) 25153–25163.
- [26] S.K. Manna, T.K. Achar, S. Mondal, Recent advances in selective formaldehyde detection in biological and environmental samples by fluorometric and colorimetric chemodosimeters, *Anal. Methods* 13 (2021) 1084–1105.
- [27] J. Chen, K. Chen, B. Han, Y. Xue, W. Chen, Z. Gao, et al., A novel single-fluorophore-based ratiometric fluorescent probe for detection of formaldehyde in air, *Tetrahedron* 76 (2020), 131681.
- [28] H. Ge, G. Liu, R. Yin, Z. Sun, H. Chen, L. Yu, et al., An aldimine condensation reaction based fluorescence enhancement probe for detection of gaseous formaldehyde, *Microchem. J.* 156 (2020), 104793.

- [29] X. Zhao, C. Ji, L. Ma, Z. Wu, W. Cheng, M. Yin, An aggregation-induced emission-based “turn-on” fluorescent probe for facile detection of gaseous formaldehyde, *ACS Sens* 3 (2018) 2112–2117.
- [30] C. Liao, M. Zhang, N. Gao, Q. Tian, J. Shi, S. Chen, et al., Paper-Based Vapor Detection of Formaldehyde: Colorimetric Sensing with High Sensitivity, *Chemosensors* 9 (2021) 335.
- [31] L. Zang, R. Liu, M.W. Holman, K.T. Nguyen, D.M. Adams, A single-molecule probe based on intramolecular electron transfer, *J. Am. Chem. Soc.* 124 (2002) 10640–10641.
- [32] L. Zang, Y. Che, J.S. Moore, One-dimensional self-assembly of planar π -conjugated molecules: adaptable building blocks for organic nanodevices, *Acc. Chem. Res.* 41 (2008) 1596–1608.
- [33] S. Chen, P. Slattum, C. Wang, L. Zang, Self-assembly of perylene imide molecules into 1d nanostructures: methods, morphologies, and applications, *Chem. Rev.* 115 (2015) 11967–11998.
- [34] M.K. Bera, P. Pal, S. Malik, Solid-state emissive organic chromophores: design, strategy and building blocks, *J. Mater. Chem. C* 8 (2020) 788–802.
- [35] G. Chen, W. Li, T. Zhou, Q. Peng, D. Zhai, H. Li, et al., Conjugation-induced rigidity in twisting molecules: filling the gap between aggregation-caused quenching and aggregation-induced emission, *Adv. Mater.* 27 (2015) 4496–4501.
- [36] K. Balakrishnan, A. Datar, T. Naddo, J. Huang, R. Oitker, M. Yen, et al., Effect of side-chain substituents on self-assembly of perylene diimide molecules: morphology control, *J. Am. Chem. Soc.* 128 (2006) 7390–7398.
- [37] Y. Che, X. Yang, K. Balakrishnan, J. Zuo, L. Zang, Highly polarized and self-waveguided emission from single-crystalline organic nanobelts, *Chem. Mater.* 21 (2009) 2930–2934.
- [38] M. Xu, B.R. Bunes, L. Zang, Paper-based vapor detection of hydrogen peroxide: colorimetric sensing with tunable interface, *ACS Appl. Mater. Interfaces* 3 (2011) 642–647.
- [39] M. Xu, J.M. Han, Y. Zhang, X. Yang, L. Zang, Selective fluorescence turn-on sensor for trace vapor detection of hydrogen peroxide, *Chem. Commun.* 49 (2013) 11779–11781.
- [40] S. Chen, N. Gao, B.R. Bunes, L. Zang, Tunable nanofibril heterojunctions for controlling interfacial charge transfer in chemiresistive gas sensors, *J. Mater. Chem. C* 7 (2019) 13709–13735.
- [41] M. Zhang, J. Shi, C. Liao, Q. Tian, C. Wang, S. Chen, et al., Perylene imide-based optical chemosensors for vapor detection, *Chemosensors* 9 (2021) 1.

Chenglong Liao graduated from Henan University of Urban Construction (China) in 2019 with a major in environmental science. After that he has been studying as a master student at Shaanxi University of Science and Technology (China) under the supervision of Prof. Ling Zang and Prof. Shuai Chen. His research is focused on the real-time detection of formaldehyde in gas phase by optical chemosensor methods.

Miao Zhang graduated with a major in environmental science from Shanxi Agriculture University, China, in 2019, and is now an MS student under the supervision of Prof. Ling Zang and Prof. Shuai Chen at the Shaanxi University of Science and Technology, China. Her research is focused on organic thin film chemosensors for the trace level detection of environmental pollutants in water.

Qingyun Tian graduated from the Soochow University (China) in 2017 with major in chemical engineering and technology. She then finished her master degree in analytical chemistry from Jiangxi Science & Technology Normal University (China) in 2020. She is

now a PhD student at Shaanxi University of Science and Technology (China) under the supervision of Prof. Chuanyi Wang, Prof. Ling Zang and Prof. Shuai Chen. She currently engages in the research of environmental analysis via modern electrochemical and optoelectronic methods.

Xiaomei Yang is a research scientist at Nano Institute of Utah, University of Utah. She received both her B.S. and Ph.D. in chemistry from Tsinghua University. Her current research focuses on computational modeling and design of functional molecules with potential application in chemical sensors and optoelectronic devices.

Jiangfan Shi graduated with a BS degree in materials science and engineering from Hunan University, China, in 2019. He is now a PhD student under the supervision of Prof. Ling Zang at the University of Utah. His current research focuses on functional organic nano-materials, as well as their applications in chemical sensors.

Shuai Chen is an associate professor at Jiangxi Science & Technology Normal University, China. He earned his PhD degree in materials physics and chemistry from the University of Chinese Academy of Sciences in 2015 under the supervision of Prof. Chuanyi Wang, and was a postdoctoral fellow with Prof. Ling Zang at the University of Utah during 2018–2020. His current research emphasizes the design and fabrication of new organic semiconductor composites for electrochemical sensors, chemosensors and clean energy conversion applications, as well as conducting polymers, conductive coatings and their optoelectronic applications.

Yanke Che is currently a professor at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS). He received his B.S. from Xi'an Jiaotong University and obtained his PhD degree from ICCAS. His current research mainly focuses on the development of new emissive materials via novel self-assembly techniques and their applications in fluorescence sensors for various hazardous chemicals.

Chuanyi Wang, Fellow of the Royal Society of Chemistry, has been a Distinguished Professor at the Shaanxi University of Science & Technology (China) since 2017. He obtained his PhD degree from the Institute of Photographic Chemistry of Chinese Academy of Sciences (CAS) in 1998, worked in Germany as an Alexander von Humboldt research fellow with Prof. Detlef Bahnemann and in the U.S. (Tufts University and Missouri University-Kansas City) as a research faculty from 1999 to 2010, and then in the Xinjiang Technical Institute of Physics & Chemistry of CAS as a distinguished professor during 2010–2016. His research covers catalysis and photo/electro-catalysis with nanostructured materials.

Ling Zang is a USTAR professor at University of Utah. He is also an adjunct professor at Shaanxi University of Science and Technology. He received his B.S. in chemistry from Tsinghua University and Ph.D. in chemistry from the Chinese Academy of Sciences. He is a Fellow of the National Academy of Inventors (NAI), and the American Association for the Advancement of Science (AAAS), and was previously an Alexander von Humboldt Fellow, NSF CAREER Award winner, and K. C. Wong Foundation Research Fellow. His current research focuses on nanoscale imaging and molecular probing, organic semiconductor nanostructures, optoelectronic sensors and nanodevices, with the long-term goal to achieve real applications in the areas of public safety, health monitoring, renewable energy, and clean environment.