A Rationally Designed Fluorescence Chemosensor for On-Site Monitoring of Carbon Monoxide in Air

Tengfei Yan,[†] Jin Chen,[†] Song Wu,*[,†] Zhiqiang Mao,[‡] and Zhihong Liu*[,‡]

[†]School of Pharmaceutical Sciences and [‡]Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

S *Supporting Information*

ABSTRACT: A fluorescence chemsensor for carbon monoxide (CO), based on transformation of weakly fluorescent iodide to strong fluorescent amino product upon reacting with CO, shows abilities of quantitative measurement of CO in air at a level of 50−1000 ppm and real-time and on-site monitoring for CO flammation/explosion.
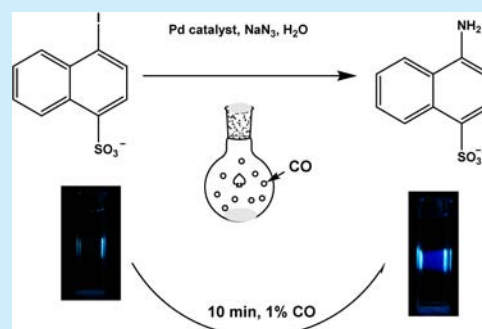
Carbon monoxide is called a silent killer because it is colorless, odorless, and tasteless but toxic, and particularly, it is hard to sense. CO commonly originates from incomplete combustion of carbon-based fuels. Exposure to high concentrations of CO even for a short time may result in acute CO poisoning that severely harms heart and central nervous system and even leads to death. It is reported that more than 40,000 people seek medical attention and approximately 5000 people have died from carbon monoxide poisoning each year in the United States.[1] It is also recognized that a high concentration of CO (over 1%) in afterdamp formed in a gas explosion causes major casualties in mining accidents that affect developing countries.[2] Therefore, CO sensing is of great importance to public health and safety and to social welfare.

Currently the most widely used sensing techniques for CO are based on electrochemistry (EC)[3] and metal oxide semiconductors (MOSs).[4] The EC technology uses metal wire electrodes to react with diffused CO in an electrolyte accompanied by the change of potential, which is proportional to the concentration of CO. Most MOS methods utilize the oxidation of CO to carbon dioxide (CO_2) at high temperature (200−400 °C) on surfaces of metal oxides with preadsorbed oxygen species, thereby donating electrons and leading to a conductance change detectable via resistrometric means. Despite the achievements made in this field in the past years, however, these sensing methods are energy costly and unsuitable for use in extreme surroundings with potential flammation and explosion. Some other methods, such as colorimetric methods based on coordination chemistry exhibit fast response, low limit of detection, and good color contrast, but their poor color modulation toward different CO concentrations still remains a problem.[5]

As a highly sensitive and potential on-site detection method, a fluorescence-based sensor could be a competent alternative for CO sensing. So far there has been only one report, recently contributed by Chang's group, on a palladium-mediated fluorescent chemosensor for CO imaging in live cells.[6] Herein, we report a substitution-based chemosensor with much easier synthesis and greater turn-on response as compared to the existing one, which is the first fluorescence sensing system suitable for CO detection in ambient conditions and can be applicable in on-site warning of CO poisoning or explosion.
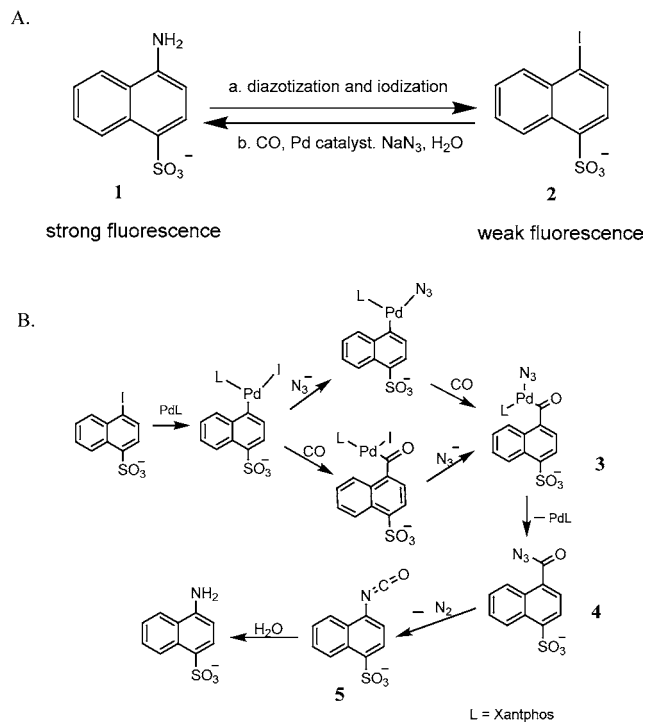
The design of sensors for a certain target depends on the nature of the target. Apart from its reliable metal-coordianation reactivity, typical reactions of CO such as carbonylation and hydrocarboxylation always need strong reaction conditions such as high temperature and/or high pressure.[7] This may explain why development of a CO fluorescence probe working under ambient conditions still remains a great challenge. Recently, Grushin et al. reported their elegant work on the azidocarbonylation of aryl iodides by CO with sodium azide in the presence of a palladium catalyst under very mild conditions.[8] The product, aroyl azide, may further undergo a Curtius rearrangement and hydrolysis to form an amino product in water. This gives us a hint of the possibility to design a fluorometric CO sensing system by simple modification of the iodide substrate. Since an iodine atom attached to an aryl ring tends to quench fluorescence due to the heavy atom effect, replacement of the iodide by an amino group in the reaction may result in an enhancement of fluorescence. On the basis of this speculation, we designed a naphthalene iodide with a sulfonic group appended peripherally (compound **2** in Scheme

1). The introduction of the sulfonic group involves two aspects of consideration. One is to enhance the solubility of the

molecule in water so as to facilitate its practical application, and the other is to improve the photoluminescence property because the electron-withdrawing sulfonic group together with the electron-donating amino group will form a pull−push electronic structure, which increases the polarity of the fluorophore and thus favors its photophysical properties such as the fluorescence quantum yield.

Compound **2** was readily synthesized by diazotization of the sodium 4-aminonaphthalene-1-sulfonate **1** followed by iodization with total yield of 29.8% and was characterized by ^{1}H NMR and ^{13}C NMR, high-resolution MS, and HPLC (Figures S1−S3 in Supporting Information). As expected, compound **2** showed very weak fluorescence with a quantum yield of 0.0063 at λ_{ex} = 320 nm in water (see the Supporting Information for the details of determination). In a preliminary test, a sensing system was constructed by dissolving compound **2**, sodium azide, and palladium acetate/xantphos (2% equiv) in water with 10% DMSO. In this system, all components give very low or zero intrinsic fluorescence, producing an extremely low background. The fluorescence of the mixture dramatically increased within several minutes after exposure to CO gas. The fluorescent product was isolated and identified as compound **1** by means of ^{1}H NMR (Figure S4 in Supporting Information), MS (Figure S5 in Supporting Information), and HPLC (Figure S3 in Supporting Information), confirming the occurrence of the amination of **2** in the reaction. The mechanism of the transformation of the iodine atom into an amino group is demonstrated in Scheme 1B, which is proposed according to Grushin's reaction.[8] In this system, the catalyst complex PdL (L = xantphos) is formed in situ first. After the insertion of Ar−I

bond into Pd[0] oxidatively, two possible pathways, namely, N_3^-/I^{−} exchange followed by insertion of CO or the reverse sequence, both lead to the formation of the intermediate **3**. Removal of the PdL gives the azidocarbonylation product **4**. Subsequent Curtius rearrangement of **4** by releasing N_2 to form isocyanate **5** and hydrolysis offers the final product **1** with strong fluorescence. Notably, the quantum yield of the product in water was as high as 0.767. The more than 100-fold enhancement of the quantum yield is an outstanding level among all the fluorescence turn-on chemosensors, which indicates the rationality of our substitution-based design. Also notable is that the design is straightforward, allowing a very easy synthesis.

To seek an ideal catalyst for the substitution-based CO sensing, we then compared the effect of the ligand of palladium on the reaction. Commercially available $Pd(PPh_3)_4$ and $Pd(dba)_2$ as well as palladium/xantphos were tested under the same CO concentration and identical reaction conditions. The reactivity of the catalysts was compared by measuring the fluorescence intensities of the systems at a fixed reaction time. It was found that Pd/xantphos possesses the highest catalytic activity, while $Pd(dba)_2$ exhibits about two-thirds that of Pd/xantphos, and $Pd(PPh_3)_4$ even lower (Figure S6 in Supporting Information). The exact reason for the reactivity order of Pd/xantphos > $Pd(dba)_2$ > $Pd(PPh_3)_4$ is yet unclear but quite consistent with those findings that prove xantphos a superior ligand for a variety of palladium-catalyzed carbonylation reactions.[9] The amount of the catalyst was also found to profoundly affect the reaction rate. Using 1000 ppm of CO as a model gas, as shown in Figure S7 in Supporting Information, the reaction rate was accelerated upon the increase of Pd/xantphos and reached the maximum with 0.4 equiv of the catalyst when NaN_3 was largely excessive (250 equiv) We then studied impact of environmental factors such as temperature and pH values on fluorescence response to our system that a real-world CO sensing may encounter. As shown in Figure S8 in Supporting Information, compared to that at ambient temperature of 10 °C after reaction with 1000 ppm of CO with the sensing system for 2 h, the fluorescence intensities at 30, 40, and 50 °C increased by 1.61-, 2.24-, and 2.5-fold, respectively. From a practical consideration, we tested the fluorescence response of pH values in a range of 4 to 10. A moderate influence could be observed by the increasing ratio of 0.5 compared the highest fluorescence intensity at pH = 8 with the lowest intensity at pH = 4 (Figure S9 in Supporting Information). The above observations suggest that our CO sensing system is environment-related.

We then investigated the response of this chemosensor toward varying concentrations of CO as a function of time. It is known that the adverse physiological effects of CO to human are associated with both its concentration and the exposure time. It is generally accepted that 50 ppm is the critical concentration for CO at which the gas becomes toxic to a healthy adult with continuous exposure over an 8 h period, while an exposure to 1600 ppm of CO causes serious discomforts such as tachycardia and nausea within 20 min and death in less than 2 h.[10] We tested a wide range of CO concentration, i.e., from 50 ppm to 1% (10,000 ppm), to check the effective coverage of the sensing system. To simulate the on-site CO sensing, we simply purged the gas into a 1 L flask containing the sensing system and gently stirred it at ambient conditions. It should be noted that the concentration of CO denotes the in-air content. The concentrations of CO in the

reaction solution, in consideration of the vapor−liquid equilibrium, were actually much lower than the denoted values. The signals of the reactions are presented with fluorescence enhancement times, $(F - F_0)/F_0$, in which F_0 and F are the fluorescence intensities of the chemosensor before and after reacting with CO. As shown in Figure 1A, the fluorescence of

Figure 2. Photographs of sensing solutions containing 50 μM **2** after exposure to CO in air for 10 min: (A) 0 ppm, (B) 1000 ppm;, (C) 5000 ppm, (D) 1%. All photographs were taken under 320 nm irradiation. Ambient temperature: 10 °C.
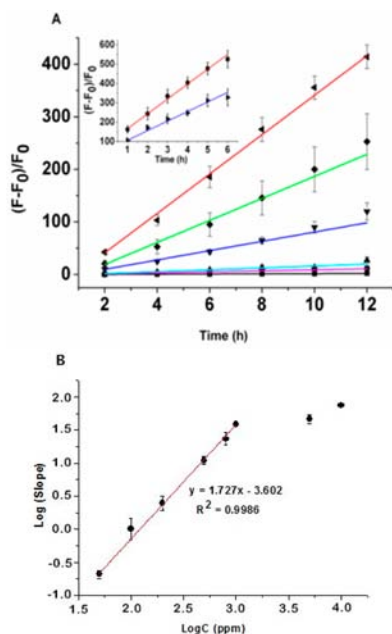

Figure 1. (A) Relationship between fluorescence enhancement and reaction time (CO concentration from upper to lower: 1000, 800, 500, 200, 100, and 50 ppm). Inset: with CO concentration 1% (red) and 5000 ppm (blue). Data are presented as average ± SD from three independent measurements. (B) The double logarithmic relationship between the reaction rate (the slope in panel A) and the concentration of CO (ppm). Ambient temperature: 10 °C.

the systems linearly increased with reaction time at all concentrations studied, implying steady rates (r) of the reactions that can be expressed by the slopes of the curves. Further, we also looked into the dependence of the reaction rate on CO concentration. The kinetic equation of the reaction at a fixed concentration of the iodide **2** can be written as $r = k[CO]^a[azide]^b$ (eq 1), where k is the apparent rate constant. Since the concentration of azide in the reaction was largely excessive to CO, it can be merged to the rate constant and the equation is thus derived as $r = k'[CO]^a$ (eq 2). The bilogarithmic diagram of the reaction rate versus CO concentration showed a linear curve in the range of 50−1000 ppm (Figure 1B), which fit well to eq 2, and the slope of the curve (ca. 1.73) suggested an approximate second-order reaction for CO. The existence of a linear fitting also makes quantitative measurement of CO concentration from 50 to 1000 ppm possible.

To demonstrate the practical applicability of the CO sensor for on-site warning of CO acute poisoning and explosion, we further explored the possibility of visual detection. For safety concerns in the experiments, we tested three CO concentrations, i.e., 1000 ppm, 5000 ppm and 1%, which were below the lower flammation and explosion limit of CO (12.5%). After several minutes, all of the reaction solutions emitted bright blue fluorescence that was easily observable with the naked eye under 320 nm excitation (Figure 2). The corresponding
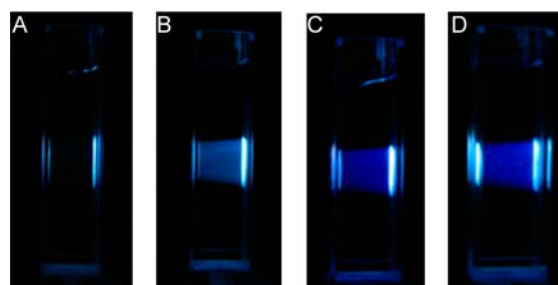
fluorescence spectra are given in Figure S10 in Supporting Information. The brightness of the emission was concentration-dependent and distinguishable by eye between the different concentrations. The fast and unambiguous response of the sensor toward 1000 ppm of CO suggests the potential application for CO acute poisoning warning. As for the concentration of 1%, although it is still far less than the explosion limit of 12.5%, a ca. 25-fold enhancement of fluorescence intensity arose in 10 min (Figure S10 in Supporting Information). Considering the concentration-dependence of the reaction rate, it is safe to deduce that this sensor would give even faster and more distinct response to higher concentrations of CO, suggesting that the system can be particularly useful to CO flammation/explosion monitoring. From a perspective of realistic context application, we also tried to use our sensing system on a solid support. By comparison we found that paper is a good material. We also optimized the sensing conditions in a 10% CO environment that is close to the flamamtion/explosion lower limit (for detail of paper-based sensing see the Supporting Information). As shown in Figure S11 in Supporting Information, even after only 2 min of reaction, the enhancement of fluorescence could be discerned with the naked eye under irradiation of 254 nm wavelength. What is more, with the extension of reaction time, the fluorescence enhanced accordingly. Our preliminary investigation results clearly demonstrate our sensing system is suitable not only for CO flammation/explosion monitoring in solution but also for solid-support-based sensing.

The selectivity of the chemosensor was also investigated. Since CO_2 is often produced accompanying CO in combustion, we first studied the interference of CO_2. As shown in Figure 3, no significant fluorescence variation was observed after long-term exposure (6 h). Other industrial gases such as SO_2, NO, and NO_2 also gave the similar results. This is superior to the sensors employing the coordinating property of CO, because NO and NO_2 at high concentration in some cases may take the place of the coordination center and interfere with the sensing.[5a,b] Also, some commonly used volatile organic compounds (VOC) including chloroform, dichloromethane, hexane, methanol, ethanol, acetone, toluene, xylene, and formaldehyde were tested by separately adding these compounds to the system directly at a very large excessive amount over CO (10^4 equiv), and no significant fluorescence changes were observed. These results indicated pronounced selectivity of the substitution-based sensor toward CO.

In summary, we propose a CO fluorescence chemsensor working in aqueous solution based on the transformation of a weakly fluorescent iodide to a strongly fluorescent amino
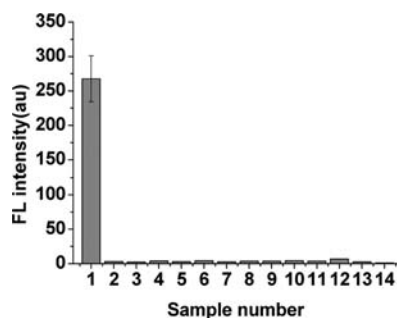
Figure 3. Fluorescence response of 50 μM compound **2** to 1% CO after 0.5 h, VOCs (10^4 equiv), and some other gases (100%) after 6 h: (1) CO, (2) formaldehyde, (3) methanol, (4) ethanol, (5) dichloromethane, (6) chloroform, (7) acetone, (8) toluene, (9) xylene, (10) hexane, (11) carbon dioxide, (12) nitric oxide, (13) nitric dioxide, (14) sulfur dioxide. Ambient temperature: 10 °C.

product. The straightforward substitution-based design allowed a simple synthesis and mild conditions for the target reaction. The pronounced fluorescence enhancement and specificity of the sensor toward CO enabled quantitative CO detection. In addition, the bright emission arising from a short-time reaction also made visual detection of CO possible, suggesting the potential application for on-site CO monitoring. The additional merit is that the amino product **1** can be recoverable. Considering the vast availability of iodide compounds and a variety of fluorophores, our method can be extended to CO sensing with different purposes, i.e., different emissions for specific needs. Further investigations persuing CO fluorescence chemsensors with faster response and higher sensitivity are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information including experimental details, characterization data, and fluorescence measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: songwu@whu.edu.cn.
*E-mail: zhhliu@whu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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