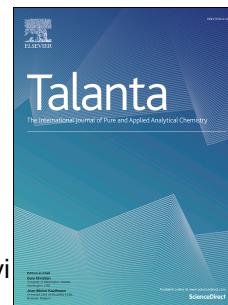


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Employing a fluorescent and colorimetric picolyl-functionalized rhodamine for the detection of glyphosate pesticide

Jianping Guan, Jiao Yang, Yue Zhang, Xiaoxue Zhang, Huajuan Deng, Juan Xu, Jinyi Wang, Mao-Sen Yuan



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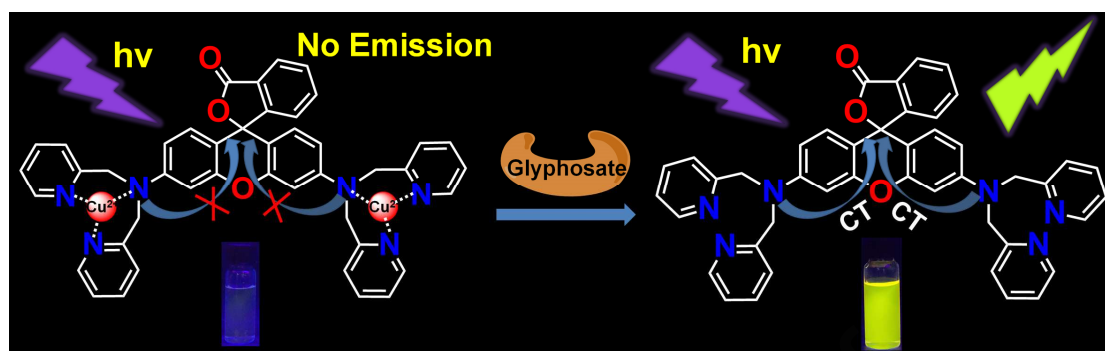
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Credit Author Statement

M.S. Yuan and J. Wang initiated and supervised the research program. J. Guan and J. Yang were responsible for the material preparation and characterizations. J. Guan, J. Yang and Y. Zhang were responsible for the spectroscopic tests. X. Zhang performed the sample preparations of unspiked and spiked soil and cabbage. H. Deng and J. Xu participated the preparation of the test strips. J. Guan and M.S. Yuan wrote the manuscript.

Graphical Abstract



Employing a fluorescent and colorimetric picolyl-functionalized rhodamine for the detection of glyphosate pesticide

Jianping Guan,^{†,‡} Jiao Yang,^{†,‡} Yue Zhang,^{†,‡} Xiaoxue Zhang,[†] Huajuan Deng,[†] Juan Xu,[†] Jinyi Wang^{*,†} and Mao-Sen Yuan^{*,†,§}

[†] College of Chemistry & Pharmacy, Northwest A&F University, Yangling, Shaanxi 712100, P. R. China, and [§] State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, China

Corresponding author:

[†] College of Chemistry & Pharmacy, Northwest A&F University, Yangling, Shaanxi 712100, P. R. China, and [§] State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, China

E-mail: jywang@nwsuaf.edu.cn; yuanms@nwsuaf.edu.cn

[‡] *These authors contributed equally to this work.*

ABSTRACT

The ongoing poisoning of agricultural products has pushed the security problem to become an important issue. Among them, exceeding the standard rate of pesticide residues is the main factor influencing the quality and security of agricultural products. Monitoring pesticide residues and developing simple, yet ultrasensitive detection systems for pesticide residues are urgently needed. In this study, we successfully developed a novel rhodamine derivative as fluorescent and colorimetric chemosensor **R-G** for the rapid, selective and ultrasensitive detection of glyphosate pesticide residue in aqueous solution. Through a Cu^{2+} -indicator displacement strategy, glyphosate can displace an indicator (**R-G**) from a Cu^{2+} -indicator complex due to its strong affinity to bind with Cu^{2+} to give a turn-on of fluorescence and distinct color change. Moreover, a test strip was also fabricated to achieve a facile detection of glyphosate pesticide. To demonstrate the possibility of practical applications, glyphosate was detected on the surface of cabbage and in a spiked soil sample. The detection limit of 4.1 nM and the response time of 2 min. indicate that the method is enough sensitive and rapid to detect the glyphosate residue at or below levels that pose a health risk.

KEYWORDS

Glyphosate; Pesticide residue; Chemosensor; Rhodamine; Ultrasensitive detection

1. Introduction

At present, food safety issues have become a spotlight of public concern and present a significant challenge all over the world.^{1,2} Especially, the ongoing poisoning of agricultural products push the security problem to become an important issue, and have caused widespread social panic.^{3,4} The factors influencing the quality and safety of agricultural products are complicated, and unreasonable application of pesticide is a major threat.^{5,6} Glyphosate (*N*-(phosphonomethyl)glycine), a non-selective and broad-spectrum organophosphorus herbicide, is extensively used worldwide to control weeds because of its high herbicidal performance.⁷⁻⁹ The abuse of glyphosate has introduced a large amount of residues in soil and drinking water, which will enter the food chain to the human body, due to its aquatic use pattern and high environmental stability.¹⁰ Terribly, glyphosate can irreversibly inactivate acetylcholinesterase (AChE) to cause different physiological reactions, such as respiratory, myocardial, and neuromuscular dysfunctions, even death.¹⁰⁻¹³ Furthermore, recent studies have indicated that the glyphosate is potentially carcinogenic to humans and can inhibit steroid hormone secretion in men, which may lead to decreased fertility.^{14,15} The US Environmental Protection Agency (EPA) has set a maximum contaminant level (MCL) of glyphosate of 4.1 μM in drinking water.^{11,16} Therefore, monitoring in agriculture products, soil and drinking water, and developing simple yet effective detection system for glyphosate has become an urgent need.

Arising from the increasingly relevant threat of pesticide residue, many efforts have been devoted to the development of detection techniques for glyphosate over the past few years, including high performance liquid chromatography (HPLC),^{17,18} and gas chromatography-mass spectrometry (GC-MS),¹⁹ ion chromatography (IC),²⁰ capillary electrophoresis (CE)²¹ and enzyme-linked immunosorbent assay (ELISA).²² Although these methods have relatively high sensitivity and accuracy, the disadvantages of these methods are very distinct, and usually require expensive instruments, professional operators, time-consuming sample pretreatment, and the high detection costs, which greatly limits their application in actual sample detection. In comparison with these instrumental analysis

systems, methods based on colorimetry or fluorometry are much simpler to operate, cost-effective, and rapid. However, due to glyphosate lacking a chromophore or fluorophore in its molecular structure, also the absence of any traditional molecular recognition sites,⁷ the design and development of ideal chromogenic and fluorogenic detection systems are quite challenging. To date, there are only a few elegant optical sensors for successful detection of this pesticide residue. For example, Jiang and Wang et al. reported a gold nanoparticle assay with dual readouts to detect organophosphorus pesticides based on the inhibition of these pesticides for the activity of AChE.²³ He et al. designed a colorimetric method for in situ detection of glyphosate on plant tissues by using cysteamine-modified gold nanoparticles.²⁴ Ding et al. reported a carbon dot-based fluorescent probe, and the Cu²⁺-quenched fluorescence of the carbon dots could recover with the addition of glyphosate.²⁵ In spite of the convenience, these innovative chemosensors still have one or more limitations, such as long response times, high limit of detections and complex synthetic procedures. The development of new fluorescent and colorimetric detection systems that meet the criteria of rapidity, simplicity, sensitivity and on-site analysis of glyphosate is still highly desired.

Rhodamine derivatives have been widely used in chemosensors due to the lactam “closed-open” spirocycle structural characteristic, where the “closed” nonfluorescent spirocycle form can turn into the “open” fluorescent quinoid form upon an appropriate external stimulus.²⁶⁻³¹ To detect different analytes, regulating the specific spiral structure to generate the respective stimuli-response is the main strategy for the design of rhodamine-based fluorescence probes.³²⁻³⁹ During the process of the formation of quinoid form, the amidogen (phenylamine) of rhodamine is critical due to its induced intramolecular charge transfer (ICT) based on the lone pair of electrons. However, few of the reported rhodamine-based probes identified the analyte through the functionalization of the amidogen. Here, we rationally designed a chemosensor, **R-G**, by modifying the amidogen of rhodamine using a picolyl group to produce Cu²⁺ ion traps (Scheme 1). After adding Cu²⁺, the **R-G** sensor captured the Cu²⁺ by the chelation of two pyridines and one nitrogen center. As a result, the transformation of rhodamine from spirocycle to quinoid was blocked due to the attraction of the electron pair of the amidogen for Cu²⁺, ultimately leading to

fluorescence quenching. The presence of glyphosate could rapidly increase the fluorescence because of the quick displacement of glyphosate for Cu^{2+} from rhodamine, originating from the strong competition in coordination with Cu^{2+} , which is due to the strong chelation of two oxygen atoms (from phosphonyl ($-\text{PO}(\text{OH})_2$) and carboxyl ($-\text{COOH}$)) and one nitrogen atom (from amidogen) of glyphosate with Cu^{2+} . And the inhibited ICT process was restored and finally results in an enhancement of green emission and color change from colorless to red. Thus, this Cu^{2+} -indicator based chemosensor can easily achieve rapid, sensitive and selective detection of glyphosate in environmental samples in solution or test strip with a low detection limit of 4.1 nM.

2. Experimental section

2.1. Chemicals and materials.

2-Chloromethylpyridine hydrochloride, 3-aminophenol, *o*-phthalic anhydride and glyphosate were purchased from Energy Chemical or Aladdin Reagent Company, and used without any further purification. The liquid solvents used for synthesis and analysis were analytical grade. Glufosinate, chlorpyrifos, dichlorvos, clopissulfuron, paraquat, imidacloprid, chlorantraniliprole, chlorothalonil aqueous solution, methamidophos, were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Column chromatography purification generally used silica gel (200–300 mesh) for the separations. The metal salt solutions were all formulated using Milli-Q system purified water (purified to $18.2 \text{ M}\Omega \cdot \text{cm}$).

2.2. Spectroscopic Characterization.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C) in CDCl_3 . Element analyses (C, H) were performed using a German Vario EL III elemental analyzer. Mass analyses were performed by an Agilent 5973N MSD Spectrometer. UV-visible absorption spectra for solutions were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301PC fluorescence spectrometer. The fluorescence quantum yield (Φ) of solutions was determined by using rhodamine B in ethanol as the

reference. Steady state fluorescence spectra and decay curves were obtained on an Edinburgh FLS920 fluorescence spectrometer equipped with a 450 W Xe lamp and a time-correlated single photon counting (TCSPC) card.

2.3. Synthesis and characterization of 3',6'-bis(bis(pyridin-2-ylmethyl)amino)-3H-spiro[isobenzofuran-1,9'-xanthen]-3-one (R-G).

To a suspended solution of 3-(bis(pyridin-2-ylmethyl)amino)phenol (291 mg, 1.0 mmol) in concentrated sulfuric acid (10 mL) an excess of phthalic anhydride (75 mg, 0.5 mmol) was added. Next, the solution was heated at 150 °C under nitrogen for 24 h with stirring. The reaction mixture was cooled to room temperature, and then poured into 150 mL of ice-water mixture. The precipitate was filtered and washed with brine three times. After drying, the resulting residue was finally purified by silica gel chromatography (CH₂Cl₂: EtOAc = 3:1, *v/v*) to afford compound **R-G** as a red purple solid (258 mg, 74.4% yield). M.p. 195–197 °C. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 4H), 7.94 (s, 1H), 7.57–7.68 (m, 6H), 7.20–7.31 (m, 9H), 6.51–6.54 (m, 4H), 6.39–6.40 (d, 2H), 4.84 (s, 8H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 169.50, 157.94, 153.03, 150.20, 137.00, 134.59, 129.39, 129.06, 127.62, 124.80, 124.14, 122.27, 120.77, 108.90, 107.97, 99.20, 57.11. TOF-MS-EI: *m/z* 694.29 [M]⁺. Anal. Calcd for C₄₄H₃₄N₆O₃: C, 76.06; H, 4.93; N, 12.10. Found: C, 75.99; H, 4.89; N, 12.24.

2.4. General solution preparation of metal ions and pesticides.

The parent stock solution of the fluorescence probe, **R-G** (10 μM), was prepared in absolute CH₃OH, which was then diluted with CH₃OH/H₂O (2:8 *v/v*) to prepare an analytical solution. The metal salts used included NaCl, CaCl₂, AlCl₃·6H₂O, CuCl₂·2H₂O, AgClO₄·6H₂O, ZnCl₂, FeCl₃·6H₂O, CoCl₂, KCl, HgCl₂, FeCl₂·4H₂O, MgCl₂, BaCl₂, MnCl₂, CrCl₃, CdCl₂·H₂O and PbCl₂. These metal salts were dissolved in ultrapure water to make a stock solution having a concentration of 100 μM for analysis. Various commercially available pesticides including glyphosate, glufosinate, chlorpyrifos, dichlorvos, clopissulfuron, paraquat, imidacloprid, chlorantraniliprole, and chlorothalonil are formulated as 0.5 mmol/L aqueous solutions.

2.5. Preparation of the test strip with R-G and R-G-Cu²⁺.

The 100 μM CH_3OH solution of **R-G** was prepared, and then poured into a culture dish. A semi-quantitative Whatman 1 paper filter (4×4 cm, 20 pieces) was immersed in the solution for 3 min and then the solvent was evaporated to dryness by heating to 35 $^\circ\text{C}$ in a vacuum drying oven. Finally, the paper with **R-G** was cut into a strip (1.0 cm \times 1.0 cm) to serve as the test paper for detection of Cu^{2+} . The test strip for glyphosate was prepared according to the same method above using the $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (2:8 v/v) solution containing both **R-G** and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1:2 equivalent).

2.6. Detection of glyphosate in real samples.

Spiked water samples were taken and collected from washed cabbages using $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (2:8 v/v). One group was pretreated with glyphosate as the experiment group (spiked) and the other group, without any pretreatment, was the control (unspiked). The method of processing samples follows a previously established protocol.⁴⁰ As for the soil samples, soil was spiked using a solution of glyphosate in CH_3OH . The solvent was evaporated by heating to 35 $^\circ\text{C}$ in a vacuum drying oven to obtain dry soil, spiked with glyphosate. The unspiked soil sample was directly used without further treatment.

3. Results and discussion

3.1. Synthesis and characterization of R-G

The target probe **R-G** was synthesized according to the synthetic approach shown in Scheme S1 in the Supporting Information (SI). Intermediate **1** was prepared according to literature procedures, and 3-aminophenol was used as the starting material and reacted with 2-chloromethylpyridine hydrochloride to yield the product. The reaction of compound **1** with phthalic anhydride in concentrated sulfuric acid yielded the crude product **R-G**. After purifying by column chromatography on silica gel, the target probe was produced as a red-purple powder in a 74.4% yield. Details of the synthesis and purification processes of the relevant compounds, along with ^1H and ^{13}C NMR data, mass spectrometry results are given in SI.

3.2. Fluorescence response toward Cu²⁺

Designing a chemosensor to directly recognize glyphosate is challenging because of the complex molecular structure of glyphosate and the absence of a chromophore or fluorophore. In our design strategy, based on the strong chelation of glyphosate for Cu²⁺, a Cu²⁺-indicator displacement method was utilized. So, a trap for Cu²⁺ was constructed in the rhodamine molecule, which can grasp the Cu²⁺ through the coordination interaction of three nitrogen atoms for Cu²⁺ (Scheme 1). First, the photoresponse of the **R-G** chemosensor for Cu²⁺ was evaluated. As expected, the solution of **R-G** displayed an obvious color change from red-purple to colorless, as well as green fluorescence quenching for Cu²⁺. Further a titration experiment was carried out to determine the quantitative relationship between **R-G** and Cu²⁺. The fluorescent spectral change of **R-G** in the H₂O/CH₃OH (8:2 vol.) solutions (0.2 μM) upon the addition of CuCl₂ is shown in Fig. 1a. The incremental addition of Cu²⁺ caused a gradual degradation of the fluorescence of **R-G** at 539 nm ($\lambda_{\text{ex}} = 350$ nm), and until completely quenching upon with the addition of 2.0 equivalents of Cu²⁺ to **R-G**, which indicated Cu²⁺ was an efficient quencher for **R-G**. Correspondingly, the absorption spectrum of **R-G** also changed dramatically with the vanishing of the absorption band at both 354 and 530 nm upon addition of Cu²⁺. In addition, what was most surprising was that **R-G** exhibited specific selectivity to Cu²⁺. As shown in Fig. 1b, when various metal ions (100 μM), including Na⁺, K⁺, Ca²⁺, Ba²⁺, Ag⁺, Mg²⁺, Pb²⁺, Mn²⁺, Zn²⁺, Ni²⁺, Cd²⁺, Co²⁺, Fe³⁺, Al³⁺, Cr³⁺ and Hg²⁺, were added, the fluorescence spectra of the **R-G** probe were barely changed. Only Cu²⁺ caused the largest change of fluorescence of **R-G**, which demonstrated that **R-G** was capable of detecting Cu²⁺ in aqueous solution. Furthermore, this also indicated that, as the exchanger and indicator of Cu²⁺ in the processor of sensing glyphosate, the **R-G** probe was scarcely influenced by the other metal ions.

3.3. Detection of glyphosate in aqueous solution

After confirming the required equivalents of Cu²⁺, we went on to explore the detection of glyphosate. A solution of H₂O/CH₃OH (8:2 vol.) with 0.2 μM **R-G** and 0.4 μM Cu²⁺ was prepared. Next, the fluorescence titration experiment was carried out by adding a glyphosate aqueous solution (0-0.6 μM) to

the **R-G**/Cu²⁺ system, and then the fluorescence spectra were subsequently recorded. As shown in Fig. 2a, with the increase of the concentration of glyphosate, the fluorescence intensity of the probing system shows a significant increase at 539 nm ($\lambda_{\text{ex}} = 350$ nm). The solutions containing 2.5 equivalents of glyphosate (0.5 μM) reached maximum fluorescence intensity, which was approximately 20-fold higher than that of the solution without glyphosate. In addition, the fluorescence intensity showed good linearity with the concentration of glyphosate ($R^2 = 0.99501$). The detection limit of the **R-G**/Cu²⁺ system for glyphosate is about 4.1 nM based on signal-to-noise ratio (S/N) of 3:1, which is sufficiently low to detect the residue glyphosate in aqueous solutions and agricultural products. Under the same test conditions, the quantification limit reaches 13.8 nM. These values are much lower than most fluorescent chemosensors (see Table 1). In addition, the dramatic fluorescent boost of the **R-G**/Cu²⁺ solution from colorless to yellow green provides it with the capacity for convenient “naked-eye” detection of glyphosate. Moreover, the response time of **R-G** for glyphosate reaches 2 min., to the best of our knowledge, which is the fastest response among the reported chemosensors for glyphosate.

Next, we investigated the selectivity of **R-G** for glyphosate by testing potential interfering compounds under the optimum conditions. Eight other pesticides (glufosinate, parathion, atrazine, malathion, carbendazim, paraquat, chlorpyrifos and dimethoate) were measured using the **R-G**/Cu²⁺ system. The probing system barely had a response towards these interfering pesticides with high concentration (0.5 mM), and no evident fluorescence enhancement was observed (Fig. 2b). When glyphosate was added to the probing solution containing all the above potential interfering pesticides, fluorescence enhancement and color change occurred, indicating that these species do not interfere with the detection of glyphosate. The results of the competitive experiments indicate that other interfering pesticides can not affect the detection of glyphosate by **R-G**/Cu²⁺ system (Fig. S4). In addition, the results also display the good repeatability and reproducibility of the detection.

3.4. Detection of glyphosate in soil and vegetable

It is known that glyphosate behaves with high environmental stability and can remain active in soil and on the surface of vegetables for a long period following deployment. To investigate the reliability

and practicality of **R-G** in practical analysis, we chose soil and cabbage as analysis objects. The soil and the surface of cabbage were respectively spiked using a methanol solution of glyphosate. After the solvent was evaporated in a vacuum drying oven, the samples were treated with **R-G** in H₂O/CH₃OH (8:2 vol.) containing two equivalents of Cu²⁺ at room temperature. The unspiked samples were treated as a control. As shown in Fig. 3a, the solutions of the unspiked soil and cabbage samples exhibited almost no emission. Obvious fluorescent enhancement was observed for the spiked soil and cabbage samples based on the content glyphosate in the respective samples. Correspondingly, their absorption spectra also exhibited similar changes, with the increase of absorption peaks at 350 and 530 nm (Fig. 3b). Moreover, the measured concentration of glyphosate in the spiked soil and cabbage samples were consistent with the calibration curve, the satisfactory recoveries obtained were 93.57% and 102.28% with respectively 7% and 3% errors, which indicates that this method can be applied to practical samples.

3.5. Detection of glyphosate using test strips

For more convenient and simple detection of glyphosate as well as Cu²⁺, the test strips for Cu²⁺ and glyphosate were respectively fabricated using filter paper. The test strip treated with **R-G** solution showed fuchsia (Fig. 4), and when the test strips were dipped in different concentration solutions of Cu²⁺, the color of the strips gradually faded until pale yellow. However, the test strip treated with **R-G**/Cu²⁺ solution showed pale yellow, and they can be used as the indicator of glyphosate in the concentration range from 0 - 5 μM due to the distinct and detectable color change of the test strips with the concentration change of glyphosate. The detection limit concentration of the test strip for glyphosate reaches 0.1 μM, which demonstrated the potential application in the quantitative detection of glyphosate in actual environmental samples.

4. Conclusion

In summary, we have successfully developed a novel chemosensor, **R-G**, based on a rhodamine derivative for the rapid, selective and ultrasensitive detection of glyphosate pesticide residue, in aqueous solution. In our approach, we take advantage of the Cu²⁺-indicator displacement strategy. The picolyl group was used to functionalize the amidogen of rhodamine, producing traps of the Cu²⁺ ion. The

captured Cu^{2+} can effectively quench the emission of the **R-G** indicator due to the restriction of the transformation of rhodamine from spirocycle to quinoid configuration. The presence of glyphosate could rapidly increase fluorescence because of its quick displacement of Cu^{2+} from **R-G**. To demonstrate the possibility of practical applications, glyphosate on the surface of cabbage and in a spiked soil sample was detected. The detection limit and response time for glyphosate respectively reach 4.1 nM and 2 min., indicating that the method is sensitive enough to detect the glyphosate residue at or below levels that pose a health risk. Furthermore, the fabricated test strips using **R-G**/ Cu^{2+} solution indeed simplify the detection of glyphosate in actual environmental samples.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2020>.

References

- [1] M. Valcke, M. H. Bourgault, L. Rochette, L. Normandin, O. Samuel, D. Belleville, C. Blanchet, D. Phaneuf, Human health risk assessment on the consumption of fruits and vegetables containing residual pesticides: A cancer and non-cancer risk/benefit perspective, *Environ. Int.* 108 (2017) 63–74.
- [2] S. Farooq, J. Nie, Y. Cheng, Z. Yan, J. Li, S. A. S. Bacha, A. Mushtaq, H. Zhang, Molecularly imprinted polymers' application in pesticide residue detection, *Analyst* 143 (2018) 3971–3989.
- [3] M. Chiari, C. Cortinovis, N. Vitale, M. Zanoni, E. Faggionato, A. Biancardi, F. Caloni, Pesticide incidence in poisoned baits: A 10-year report, *Sci. Total Environ.* 601–602 (2017) 285–292.
- [4] F. P. Carvalho, Agriculture, pesticides, food security and food safety, *Environ. Sci. Policy* 9 (2006) 685–692.

- [5] W-H. Leong, S-Y. Teh, M. M. Hossain, T. Nadarajaw, Z. Zabidi-Hussin, S-Y. Chin, K-S. Lai, S-H. E. Lim, Application, monitoring and adverse effects in pesticide use: The importance of reinforcement of Good Agricultural Practices (GAPs), *J. Hazard. Mater.* 260 (2020) 109987.
- [6] X. Wang, Z. Mu, F. Shangguan, R. Liu, Y. Pua, L. Yin, Rapid and sensitive suspension array for multiplex detection of organophosphorus pesticides and carbamate pesticides based on silica-hydrogel hybrid microbeads, *J. Hazard. Mater.* 273 (2014) 287–292.
- [7] J. Guo, Y. Zhang, Y. Luo, F. Shen, C. Sun, Efficient fluorescence resonance energy transfer between oppositely charged CdTe quantum dots and gold nanoparticles for turn-on fluorescence detection of glyphosate, *Talanta* 125 (2014) 385–392.
- [8] J. J-L ó pez, E.J. L-Mart í nez, P. O-Barrales, A. R-Medina, Graphene quantum dots-silver nanoparticles as a novel sensitive and selective luminescence probe for the detection of glyphosate in food samples, *Talanta* 207 (2020) 120344
- [9] K. A. Rawat, R. P. Majithiya, J. V. Rohit, H. Basu, R. K. Singhal, S. K. Kailasa, Mg²⁺ ion as a tuner for colorimetric sensing of glyphosate with improved sensitivity via the aggregation of 2-mercapto-5-nitrobenzimidazole capped silver nanoparticles, *RSC Adv.* 6 (2016) 47741–47752.
- [10] Y-C. Chang, Y-S. Lin, G-T. Xiao, T-C. Chiu, C-C. Hu, A highly selective and sensitive nanosensor for the detection of glyphosate, *Talanta* 161 (2016) 94–98.
- [11] X. Wang, M. Sakinati, Y. Yang, Y. Ma, M. Yang, H. Luo, C. Hou, D. Huo, The construction of a CND/Cu²⁺ fluorescence sensing system for the ultrasensitive detection of glyphosate, *Anal. Methods* 12 (2020) 520–527.
- [12] M. Gui, J. Jiang, X. Wang, Y. Yan, S. Li, X. Xiao, T. Liu, T. Liu, Y. Feng, Copper ion-mediated glyphosate detection with N-heterocycle based polyacetylene as a sensing platform, *Sens. Actuators B: Chem.* 243 (2017) 696–703.
- [13] H. Liu, P. Chen, Z. Liu, J. Liu, J. Yi, F. Xia, C. Zhou, Electrochemical luminescence sensor based on double suppression for highly sensitive detection of glyphosate, *Sens. Actuators B: Chem.* 304 (2020) 127364
- [14] F. Qu, H. Wang, J. You, Dual lanthanide-probe based on coordination polymer networks for ratiometric detection of glyphosate in food samples, *Food Chem.* 323 (2020) 126815.
- [15] J. Zheng, H. Zhang, J. Qu, Q. Zhu, X. Chen, Visual detection of glyphosate in environmental water samples using cysteamine-stabilized gold nanoparticles as colorimetric probe, *Anal. Methods* 5 (2013) 917–924.
- [16] X. Ding, K-L. Yang, Development of an oligopeptide functionalized surface plasmon resonance biosensor for online detection of glyphosate, *Anal. Chem.* 85 (2013) 5727–5733
- [17] M. V. Khrolenko, P. P. Wiczorek, Determination of glyphosate and its metabolite aminomethylphosphonic acid in fruit juices using supported-liquid membrane preconcentration method with high-performance liquid chromatography and UV detection after derivatization with p-toluenesulphonyl chloride, *J. Chromatogr. A* 1093 (2005) 111–117.
- [18] Y. Sun, C. Wang, Q. Wen, G. Wang, H. Wang, Q. Qu, X. Hu, Determination of glyphosate and aminomethylphosphonic acid in water by LC using a new labeling reagent, 4-methoxybenzenesulfonyl fluoride, *Chromatographia* 72 (2010) 679 – 686.

- [19] T. Saito, H. Aoki, A. Namera, H. Oikawa, S. Miyazaki, A. Nakamoto, S. Inokuchi, Mix-mode TiO₂-C18 monolith spin column extraction and GC-MS for the simultaneous assay of organophosphorus compounds and glufosinate, and glyphosate in human serum and urine, *Anal. Sci.* 27 (2011) 999–1005.
- [20] Y. Zhu, F. F. Zhang, C. L. Tong, W. P. Liu, Determination of glyphosate by ion chromatography *J. Chromatogr. A* 850 (1999) 297–301.
- [21] E. Orejuela, M. Silva, Rapid and sensitive determination of phosphorus- containing amino acid herbicides in soil samples by capillary zone electrophoresis with diode laser- induced fluorescence detection, *Electrophoresis* 26 (2005) 4478–4485.
- [22] D. Wang, B. Lin, Y. Cao, M. Guo, Y. Yu, A highly selective and sensitive fluorescence detection method of glyphosate based on an immune reaction strategy of carbon dot labeled antibody and antigen magnetic beads, *J. Agric. Food Chem.* 64 (2016) 6042–6050.
- [23] D. Liu, W. Chen, J. Wei, X. Li, Z. Wang, X. Jiang, A highly sensitive, dual-readout assay based on gold nanoparticles for organophosphorus and carbamate pesticides, *Anal. Chem.* 84 (2012) 4185–4191.
- [24] Q. Tu, T. Yang, Y. Qu, S. Gao, Z. Zhang, Q. Zhang, Y. Wang, J. Wang, L. He, In situ colorimetric detection of glyphosate on plant tissues using cysteamine-modified gold nanoparticles, *Analyst* 144 (2019) 2017–2025.
- [25] L. Wang, Y. Bi, J. Gao, Y. Li, H. Ding, L. Ding, Carbon dots based turn-on fluorescent probes for the sensitive determination of glyphosate in environmental water samples, *RSC Adv.* 6 (2016) 85820–85828.
- [26] M. Beija, C. A. M. Afonso, J. M. G. Martinho, Synthesis and applications of Rhodamine derivatives as fluorescent probes, *Chem. Soc. Rev.* 38 (2009) 2410–2433.
- [27] P-Y. Wang, X. Luo, L-L. Yang, Y-C. Zhao, R. Dong, Z. Li, S. Yang, A rhodamine-based highly specific fluorescent probe for the in situ and in vivo imaging of the biological signalling molecule salicylic acid, *Chem. Commun.* 55 (2019) 7691–7694.
- [28] K. Li, Y. Xiang, X. Wang, J. Li, R. Hu, A. Tong, B. Z. Tang, Reversible photochromic system based on rhodamine B salicylaldehyde hydrazone metal complex, *J. Am. Chem. Soc.* 136 (2014) 1643–1649.
- [29] W-L. Jiang, Y. Lia, H-W. Liu, D-Y. Zhou, J. Ou-Yang, L. Yi, C-Y. Li, A rhodamine-deoxylactam based fluorescent probe for fast and selective detection of nitric oxide in living, *Talanta* 197 (2019) 436–443.
- [30] G. Bartwal, K. Aggarwal, J. M. Khurana, A highly selective pH switchable colorimetric fluorescent rhodamine functionalized azo-phenol derivative for thorium recognition up to nano molar level in semi-aqueous media: Implication towards multiple logic gates, *J. Hazard. Mater.* 360 (2018) 51–61.
- [31] H. Zheng, X-Q. Zhan, Q-N. Biana, X-J. Zhang, Advances in modifying fluorescein and rhodamine fluorophores as fluorescent chemosensors, *Chem. Commun.* 49 (2013) 429–447.
- [32] H. N. Kim, M. H. Lee, H. J. Kim, J. S. Kim, J. Yoon, A new trend in rhodamine-based chemosensors: application of spirolactam ring-opening to sensing ions, *Chem. Soc. Rev.* 37 (2008) 1465–1472.
- [33] M. E. Jun, B. Roy, K. H. Ahn, “Turn-on” fluorescent sensing with “reactive” probes, *Chem. Commun.* 47 (2011) 7583–7601.

- [34] Y. M. Yang, Q. Zhao, W. Feng, F. Y. Li, Fluorescent chemosensors based on spiroring-opening of xanthenes and related derivatives, *Chem. Rev.* 112 (2012) 1910–1956.
- [35] Y. Huo, J. Miao, L. Han, Y. Li, Z. Li, Y. Shi, W. Guo, Selective and sensitive visualization of endogenous nitric oxide in living cells and animals by a Sirhodamine deoxylactam-based near-infrared fluorescent probe, *Chem. Sci.* 8 (2017) 6857–6864.
- [36] J. Gong, M-K. Lv, M-L. Zhang, Z- Z. Kong, G-J. Mao, A novel two-photon fluorescent probe with long-wavelength emission for monitoring HClO in living cells and tissues, *Talanta* 192 (2019) 128–134.
- [37] C. Zhang, H. Xie, T. Zhan, J. Zhang, B. Chen, Z. Qian, G. Zhang, W. Zhang, J. Zhou, A new mitochondrion targetable fluorescent probe for carbon monoxide-specific detection and live cell imaging, *Chem. Commun.* 55 (2019) 9444–9447
- [38] W. Chen, T. Matsunaga, D. L. Neill, C. Yang, T. Akaike, M. Xian, Rational design of a dual-reactivity-based fluorescent probe for visualizing intracellular HSNO, *Angew. Chem. Int. Ed.* 58 (2019) 16067–16070
- [39] L. Zhou, Q. Wang, X-B. Zhang, W. Tan, Through-bond energy transfer-based ratiometric two-photon probe for fluorescent imaging of Pd²⁺ ions in living cells and tissues, *Anal. Chem.* 87 (2015) 4503–4507.
- [40] L. Lan, Q. Niu, T. Li, A highly selective colorimetric and ratiometric fluorescent probe for instantaneous sensing of Hg²⁺ in water, soil and seafood and its application on test strips, *Anal. Chim. Acta* 1023 (2018) 105–114.

Caption for Table

Table 1. Summary for the reported chemosensors for glyphosate.

Caption for Scheme

Scheme 1. Schematic illustration of glyphosate sensing process.

Captions for Figures

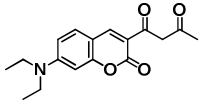
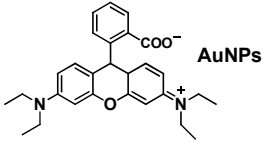
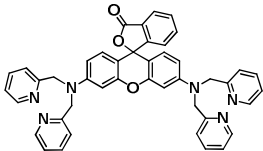
Fig. 1. (a) Fluorescence titration of **R-G** (0.2 μM) in $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (8:2 vol.) upon gradual addition of Cu^{2+} (0-0.4 μM), $\lambda_{\text{ex}}=350$ nm. Inset: Ratiometric changes in fluorescence with increasing concentrations of Cu^{2+} . (b) Fluorescence responses of probe **R-G** (0.2 μM) to Cu^{2+} at 539 nm in the absence and presence of various metal ions, $\lambda_{\text{ex}}=350$ nm.

Fig. 2. (a) Fluorescence titration of **R-G/Cu²⁺** (0.2 μM) in $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (8:2 vol.) upon gradual addition of glyphosate (0-0.5 μM), $\lambda_{\text{ex}}=350$ nm; Inset: Ratiometric changes in fluorescence with increasing concentrations of glyphosate. (b) Fluorescence responses of **R-G/Cu²⁺** (0.2 μM) to various pesticides, $\lambda_{\text{ex}}=350$ nm .

Fig. 3. The fluorescence (a) and absorption (b) responses of **R-G/Cu²⁺** (0.2 μM) with the glyphosate-spiked soil and cabbage samples. Inset: the visual fluorescent (a) and colorimetric color of the glyphosate-spiked soil and cabbage samples.

Fig. 4. Colorimetric responses of the test strips for Cu^{2+} (top) and glyphosate (below) with different concentration.

Table 1

	Structure/Material	Test Condition	Detection limit (for glyphosate)	Response time	Reference
1		Ethanol/Tris-HCl buffer (9:1 vol)	0.11 μM	5 min	<i>Anal. Methods</i> , 2020, 12, 520
2	CDs/Cu ²⁺	PBS buffer solution (pH = 6.0)	0.095 μM	12 min	<i>RSC Adv.</i> , 2016, 6, 85820
3	 AuNPs	NaHCO ₃ /NaOH buffer (pH = 10.0)	5.9×10^{-4} μM	5 min	<i>Anal. Chem.</i> , 2012, 84, 4185
4	AuNPs-Cys	0.01 M HCl solution (pH = 4.56)	5.9 μM	15 min	<i>Analyst</i> , 2019, 144, 2017
5	TGA-CdTe-QDs. CS-AuNPs	purified water (pH = 7.0)	5.8×10^{-5} μM	15 min	<i>Talanta</i> , 2014, 125, 385
6	GMP/Tb@GMP/Eu/DPA	Tris-HCl buffer (pH = 8.4)	41 μM	30 min	<i>Food Chem.</i> , 2020, 323, 126815
7	IgG-CDs	0.1 M PBS 0.2 (pH = 7.4)	0.047 μM	2h	<i>J. Agric. Food Chem.</i> , 2016, 64, 6042
8	AuNPs/Pb ²⁺	purified water (pH = 7.0)	2.4×10^{-3} μM	15 min	<i>Anal. Methods</i> , 2017, 9, 2890
9	CS-AuNPS	HAC-NaAC buffer (pH = 7.0)	0.059 μM	30 min	<i>Anal. Methods</i> , 2013, 5, 917
10	CuO/MWCNTS	Tris borate buffer solution (pH = 7.0)	4.0×10^{-3} μM	2 h	<i>Talanta</i> , 2016, 161, 94
11	Cd-PVA sensors strips	purified water	0.59 μM	50 min	<i>Sens. Actuators B</i> , 2015, 206, 357
12		H ₂ O/CH ₃ OH (8:2 vol.) or purified water	4.1×10^{-3} μM	2 min	This work

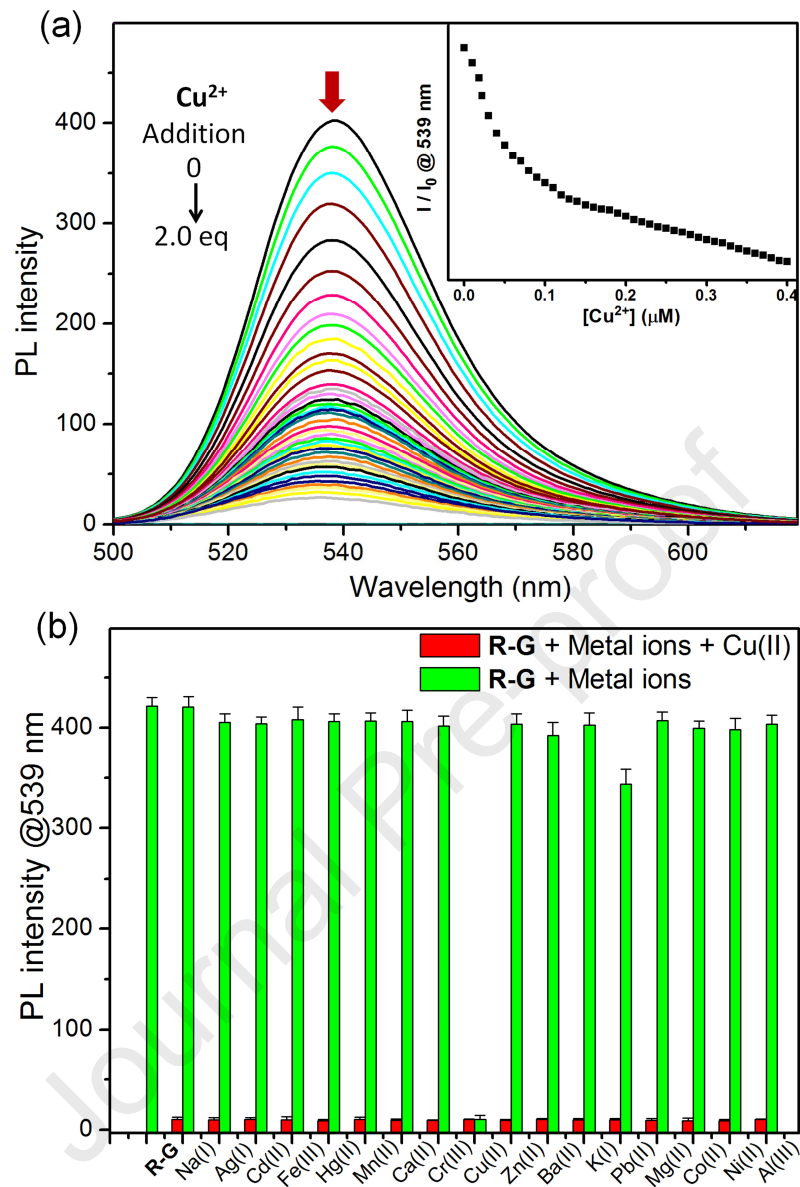


Figure 1

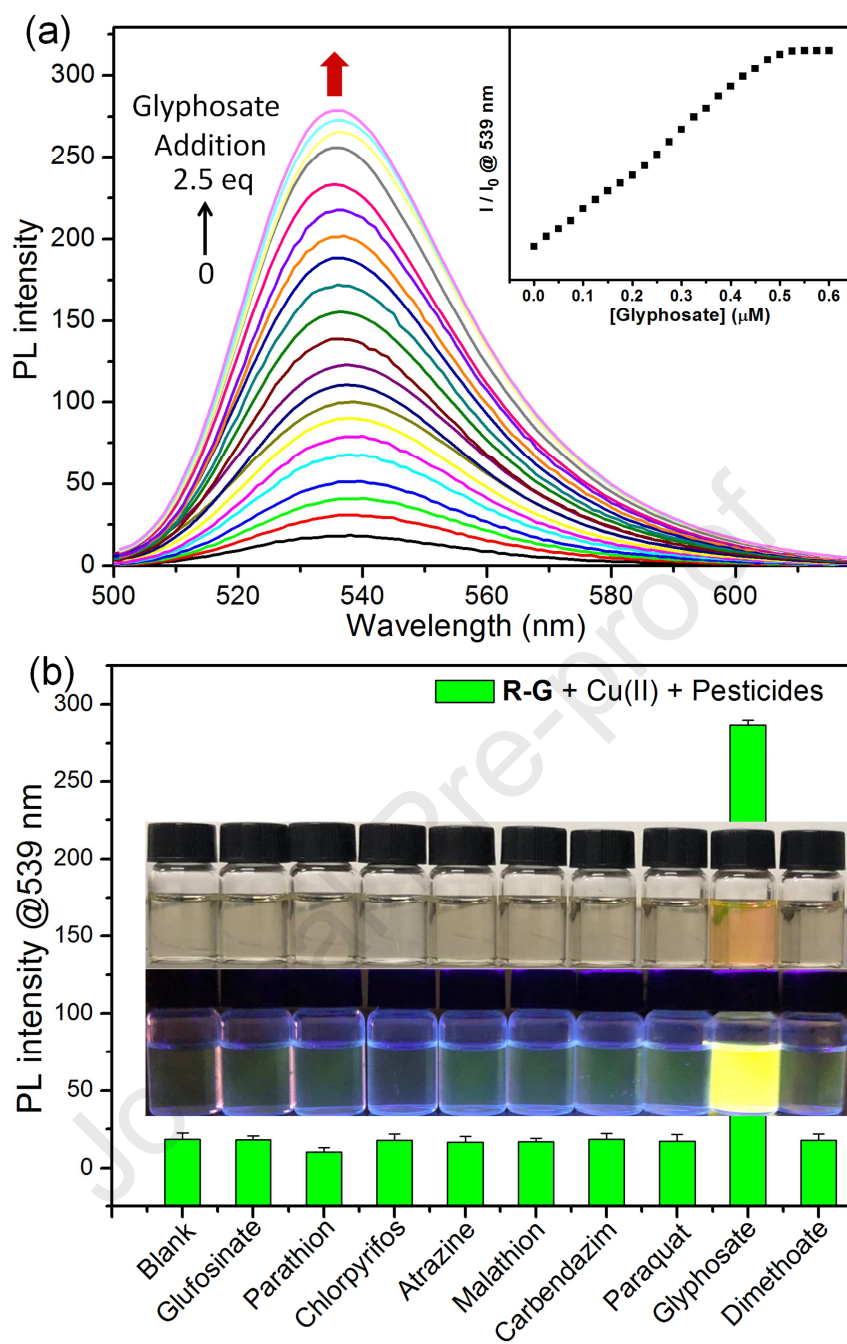


Figure 2

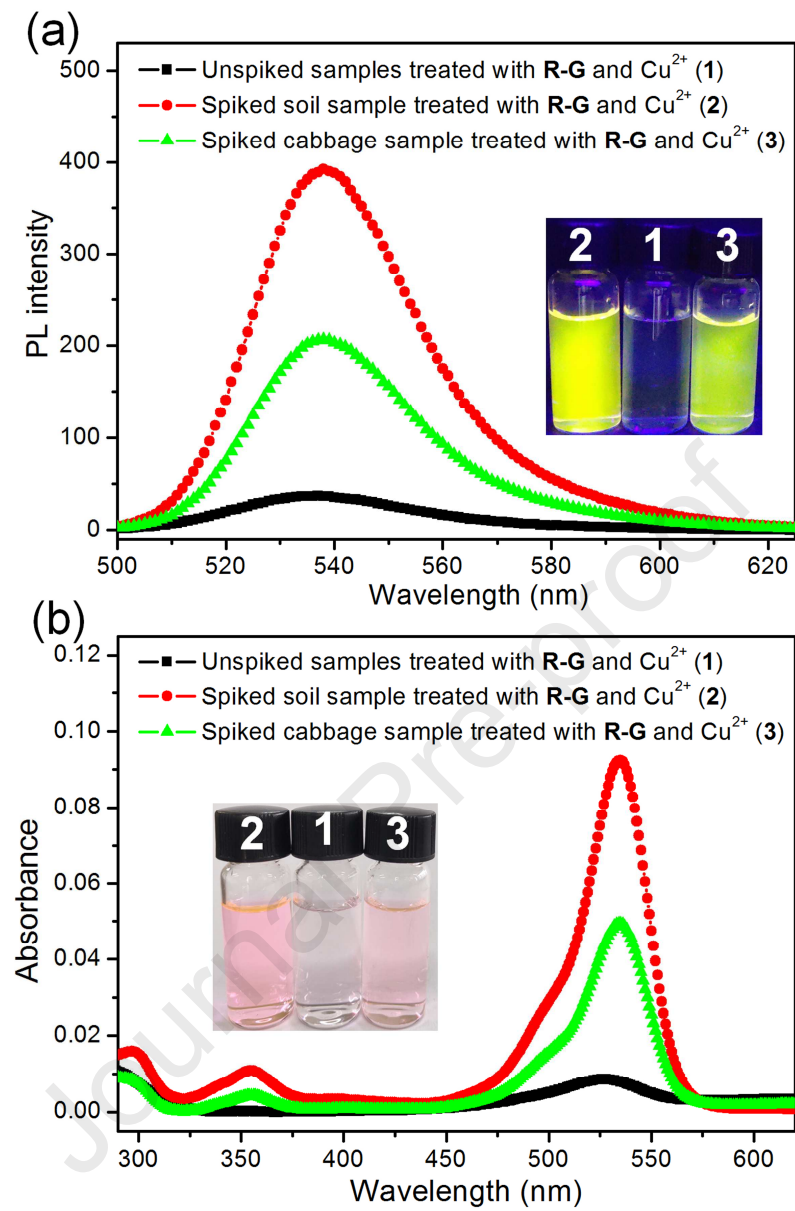
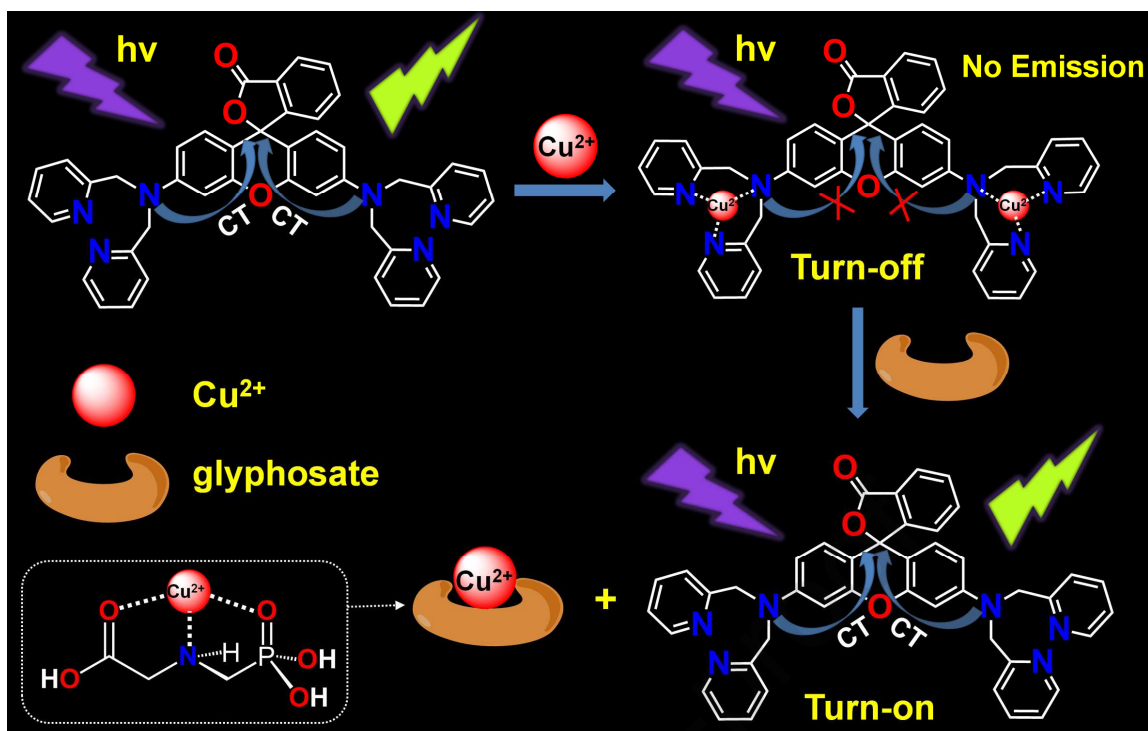
**Figure 3**



Figure 4

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Scheme 1

Highlights:

> A new rhodamine derivative was synthesized as glyphosate sensor. > It exhibited obvious fluorescence enhancement and chromogenic change for glyphosate. > It can rapidly and super-sensitively detect glyphosate residue. > The test strip was fabricated to achieve a facile detection of glyphosate.

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Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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