ARTICLE

An on-off-on fluorescent probe for the detection of glyphosate based on Cu^{2+}-assisted squaraine dye sensor

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Shuhua Zhao[a,b,#], Lei Shi[a,#], Xiufeng Zhang[a], Xiaoran Sun[a], Wenxuan Zhu[b,c], Lijia Yu[b,*]

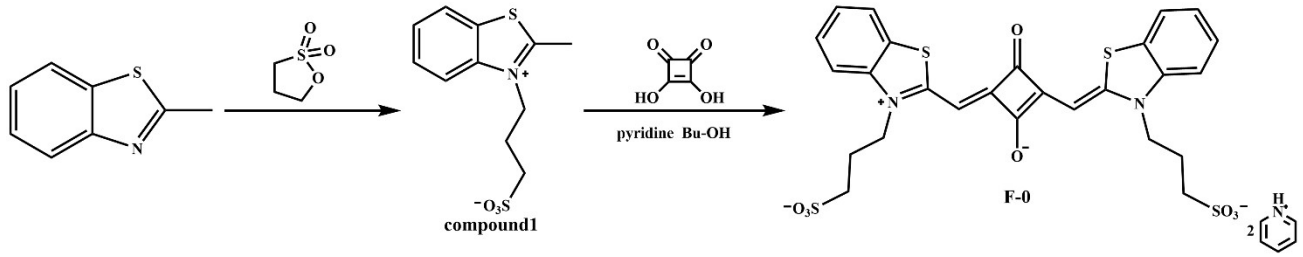
Synthesis and characterization of F-0

3-(2-methylbenzo[d]thiazol-3-ium-3-yl)propane-1-sulfonate (compound 1)

2-methylbenzothiazole (1.49 g, 10 mmol) and 1,3-propanesultone lactone (1.83 g, 15 mmol) were added into a 50 ml flask and reacted at 120℃ for 5 hours. The product was light yellow solid, which was crushed and washed three times with methanol to obtain compound 1.

(Z)-3-oxo-2-((Z)-(3-(3-sulfopropyl)benzo[d]thiazol-2(3H)-ylidene)methyl)-4-((3-(3-sulfopropyl)benzo[d]thiazol-3-ium-2-yl)methylene)cyclobut-1-en-1-olate (F-0)

The squaraine dye (F-0) was synthesized by our previous work. 3-(2-methylbenzo[d]thiazol-3-ium-3-yl)propane-1 sulfonate(0.43 g, 16 mmol) and square acid (0.10 g,0.88 mmol) were added into 50 ml flask, then 4 ml of n-butanol and 2 ml of pyridine were added, refluxed at 115℃ for 12 hours under the argon protection, and the precipitate was washed with ether for three times to obtain bluish-black solid. Silica gel column purification was performed by using DCM/MeOH= 5:1 to obtain F-0. ^{1}H NMR (400 MHz, DMSO) δ 7.84 (d, J = 7.7 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.43 (s, 2H), 7.25 (s, 2H), 5.84 (s, 2H), 4.39 (s, 4H), 2.60 (d, J = 7.0 Hz, 4H), 2.01 (s, 4H).



Scheme S1 The synthesis route for F-0

[a] North China University of Science and Technology, Tangshan, 063210, China.
[b] National Center for Occupational Safety and Healthy, NHC, Beijing, 102308, China.
[c] University of South China, Hengyang, 421001, China.
[d] # Shuhua Zhao and Lei Shi contributed equally.
[e] * Corresponding Author, e-mail: yulijia@iccas.ac.cn.
[f] Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

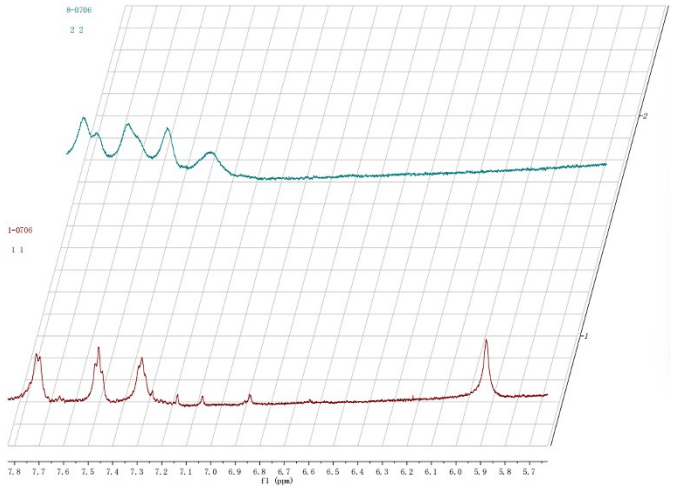


Chart S1 The ^{1}H-NMR spectra of F-0 (deep red line) in Dimethyl sulfoxide-d6, and the ^{1}H-NMR spectra of 23.8 mmol/L F-0 with 1 eq Cu^{2+} in D_2O after 1 h incubation (blue line).

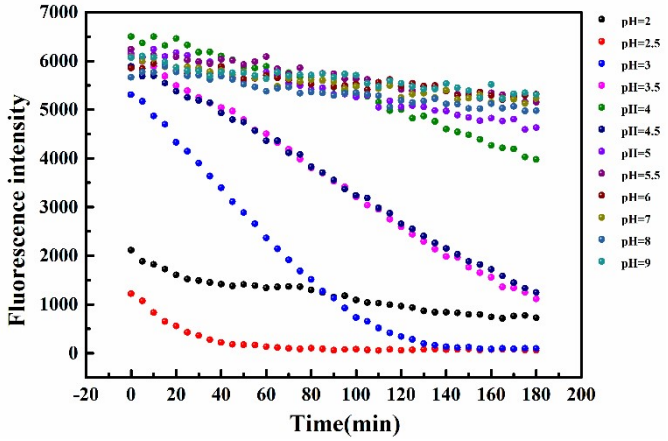


Chart S2 The fluorescence intensity of F-0 at 658 nm changes with time in different pH environments.

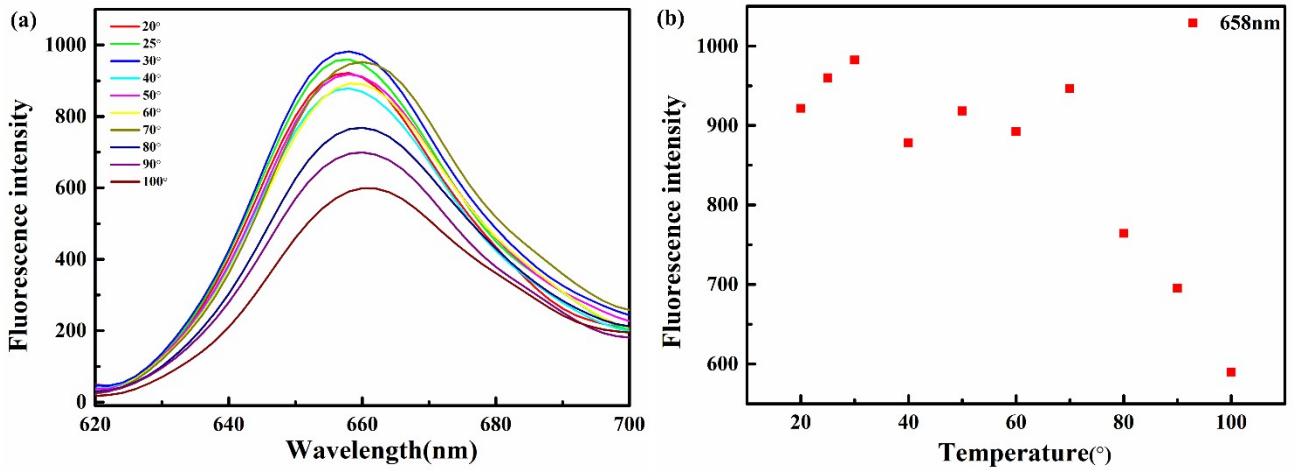


Chart S3 (a) The change of F-0 fluorescence spectrum with temperature (b) The change of F-0 fluorescence intensity at 658 nm with temperature.

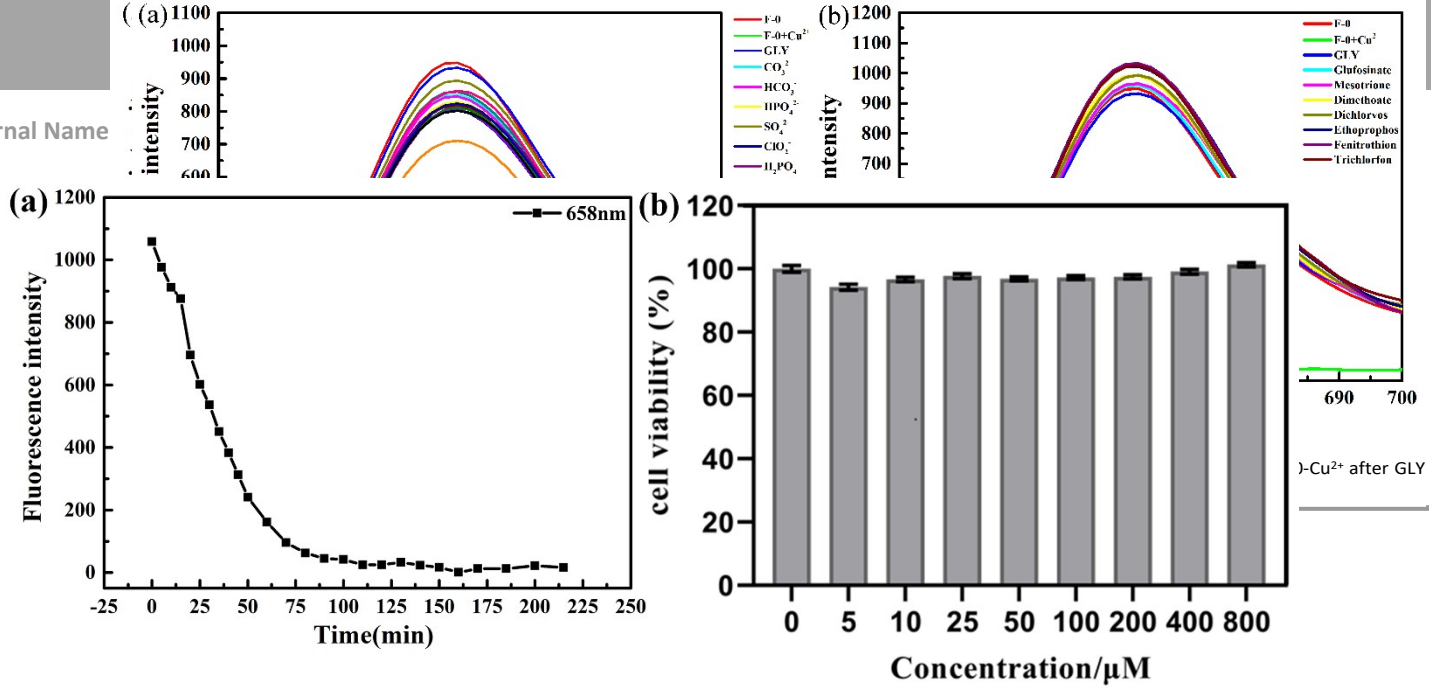


Chart S4 (a) Fluorescence intensity of F-0 at 658 nm after natural light irradiation for different times (b) Cell viability value (%) of A375 cells in different concentrations of F-0.

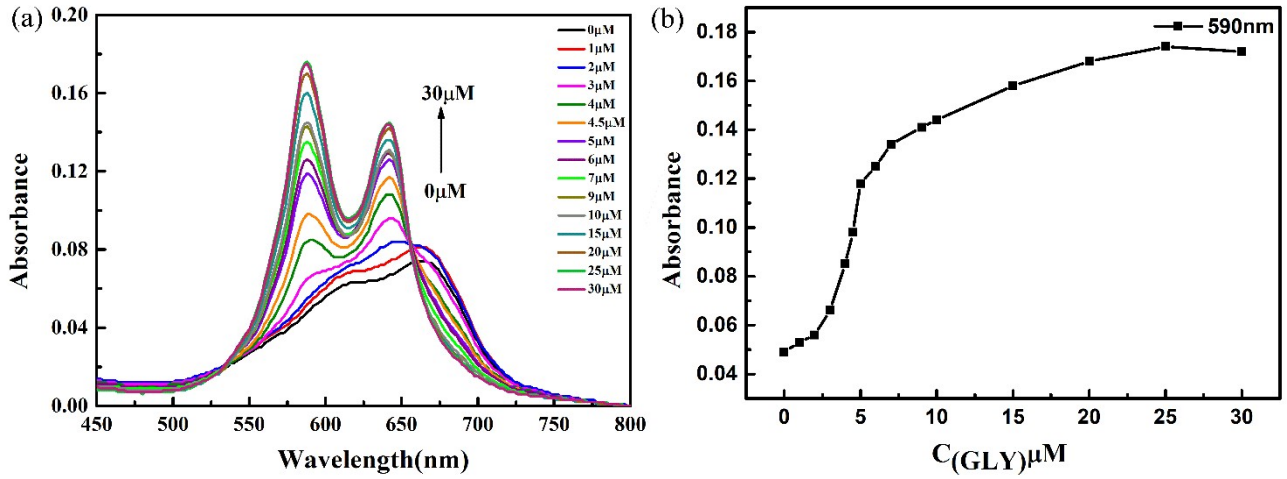


Chart S5 (a) UV-vis absorption spectra of F-0 (15 μmol/L) at different concentrations of GLY (0-30 μmol/L) in the presence of Cu^{2+} (5 μmol/L) (b) With the increase of GLY concentration (0-30 μmol/L), the change curve of F-0 absorption value at 590 nm. All spectral experiments were performed in PBS.

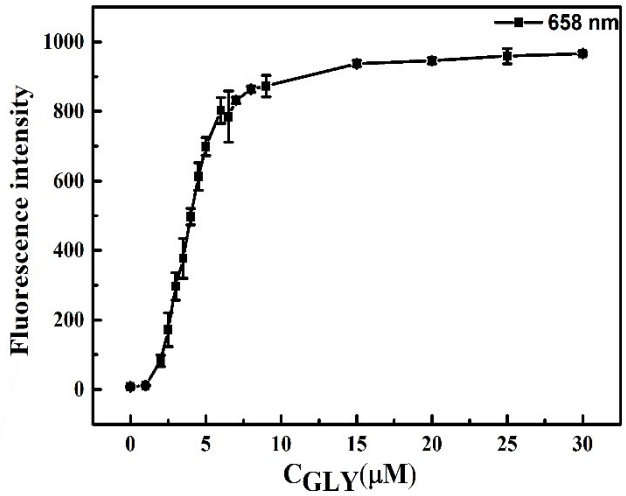


Chart S6 With the increase of GLY concentration (0-30 μmol/L), the change curve of F-0 fluorescence intensity at 658 nm. All spectral experiments were performed in PBS. λ_{ex} = 590 nm. Error bars represent mean values ± SD. (n = 3).