

Supporting Information

Highly-selective Lanthanide-containing Probe for Ratiometric Luminescence

Detection of an Anthrax Biomarker

*Xiao Liu,^a Bin Li,^a Yang Xu,^a Zhiqiang Li,^{*ac} Ying Zhang,^a Zhi-jun Ding,^{*b} Hui Cui,^c*

*Jing Wang,^d Hong-Biao Hou,^e Huanrong Li^{*a}*

^aSchool of Chemical Engineering and Technology, Hebei University of Technology,

GuangRong Dao 8, Hongqiao District, Tianjin 300130, P. R. China.

E-mail: zhiqiangli@hebut.edu.cn, lihuanrong@hebut.edu.cn

^bBeijing Institute of Pharmaceutical Chemistry, Beijing 102205, China.

E-mail: zhijunding01@gmail.com

^cDepartment of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0698, USA.

^dCollege of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310014, P.R. China.

^eNational Center for Nanoscience and Technology, Chinese Academy of Sciences, Beijing 100190, China

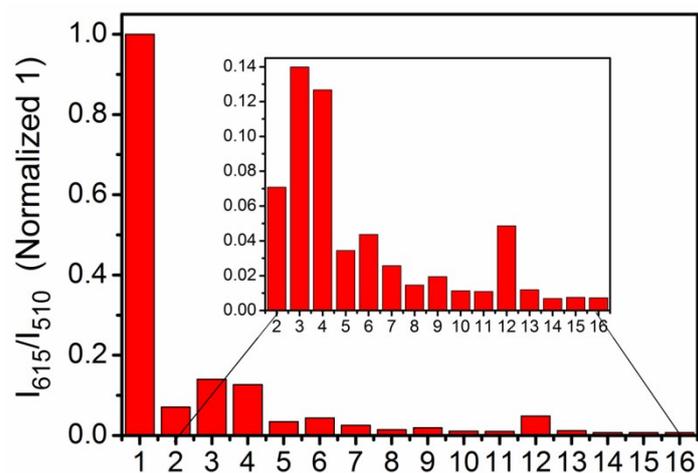


Fig. S1. Luminescence response of probe with molar ratio of ASAP: EuCl_3 : pyranine = 4000: 4000: 1 in the presence of different interfering aromatic ligands. Effect of various interfering aromatic ligands at I_{615}/I_{510} in the presence of 2 mM acrylate. (1) DPA, (2) 2,3-PA, (3) 2,4-PA, (4) 2,5-PA, (5) 3,4-PA, (6) 3,5-PA, (7) o-PA, (8) m-PA, (9) p-PA, (10) NA, (11) isonicotinic acid, (12) picolinic acid, (13) BA, (14) glu, (15) asp, (16) NAD.

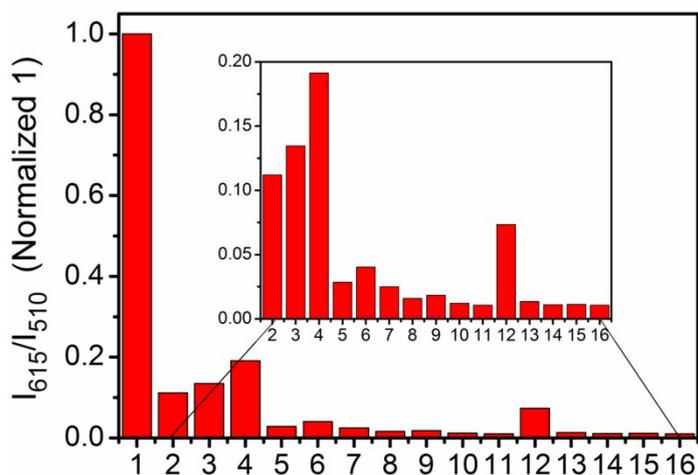


Fig. S2. Luminescence response of probe with molar ratio of ASAP: EuCl_3 : pyranine = 8000: 4000: 1 in the presence of different interfering aromatic ligands. Effect of various interfering aromatic ligands at I_{615}/I_{510} in the presence of 4 mM acrylate. (1) DPA, (2) 2,3-PA, (3) 2,4-PA, (4) 2,5-PA, (5) 3,4-PA, (6) 3,5-PA, (7) o-PA, (8) m-PA,

(9) p-PA, (10) NA, (11) isonicotinic acid, (12) picolinic acid, (13) BA, (14) glu, (15) asp, (16) NAD.

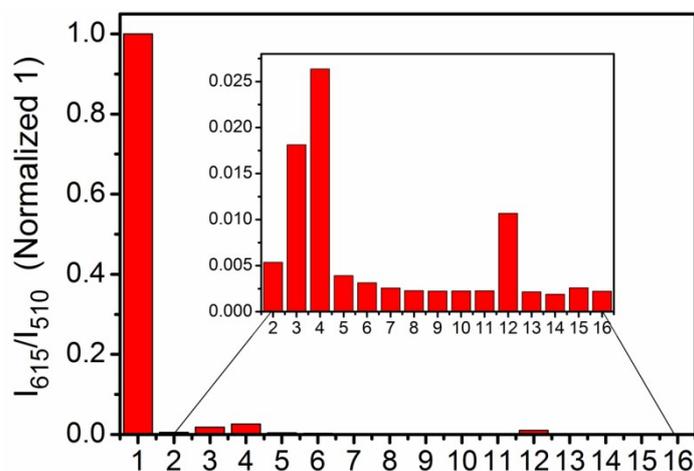


Fig. S3. Luminescence response of probe with molar ratio of ASAP: EuCl_3 : pyranine = 12000: 4000: 1 in the presence of different interfering aromatic ligands. Effect of various interfering aromatic ligands at I_{615}/I_{510} in the presence of 6 mM acrylate. (1) DPA, (2) 2,3-PA, (3) 2,4-PA, (4) 2,5-PA, (5) 3,4-PA, (6) 3,5-PA, (7) o-PA, (8) m-PA, (9) p-PA, (10) NA, (11) isonicotinic acid, (12) picolinic acid, (13) BA, (14) glu, (15) asp, (16) NAD.

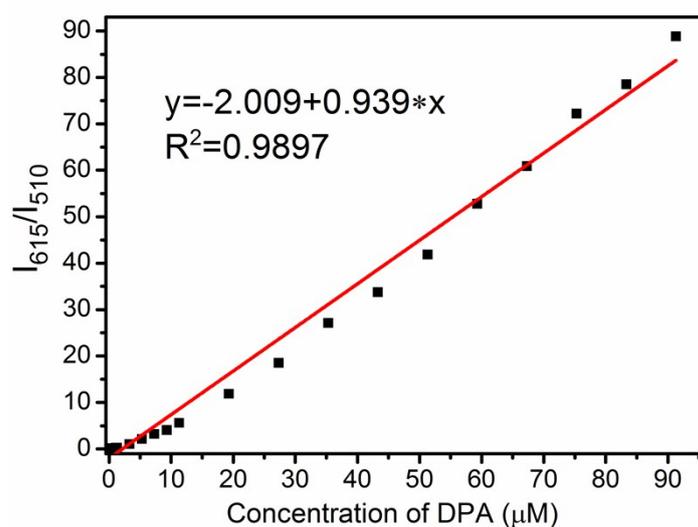


Fig. S4. The luminescence intensity ratio of the peaks at I_{615}/I_{510} of probe with molar ratio of ASAP: EuCl_3 : pyranine = 20000: 4000: 1 as a function of DPA concentration

from 0 to 90 μM in the presence of 10 mM acrylate.

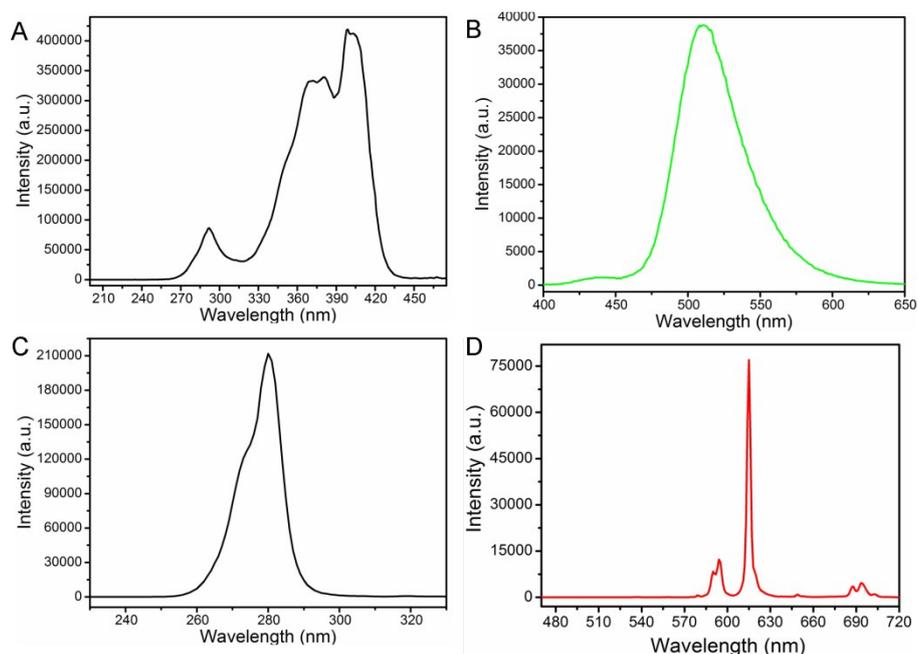


Fig. S5. The luminescence excitation monitored at 510 nm (A) and emission excited at 280 nm (B) spectra of pyranine in the presence of ASAP; the luminescence excitation monitored at 615 nm (C) and emission excited at 280 nm (D) spectra of $\text{Eu}(\text{DPA})_3$ in the presence of ASAP.

The excitation spectrum of pyranine showed two broad bands in the range of 270-310 nm and 330-430 nm (**Fig. S5A**). The excitation spectrum of $\text{Eu}(\text{DPA})_3$ showed a broad band in the range of 260-300 nm, which was corresponding to the absorption of DPA ligands (**Fig. S5C**). These results indicate pyranine and Eu^{3+} can be excited simultaneously with 280 nm.

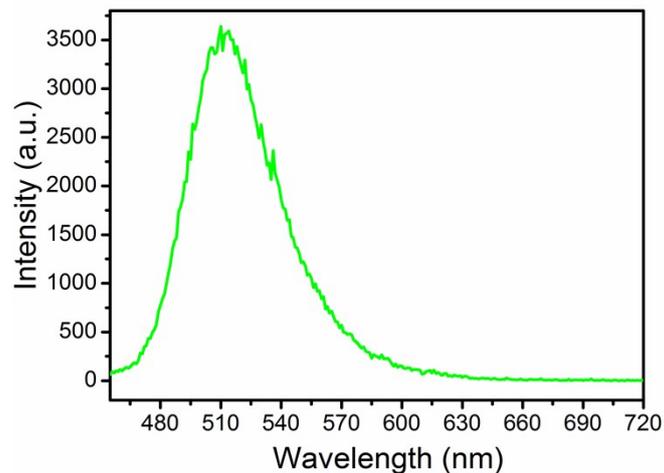


Fig. S6. Luminescence emission spectra of the probe solution before adding DPA in pH = 7 HCl-Tris buffer solution.

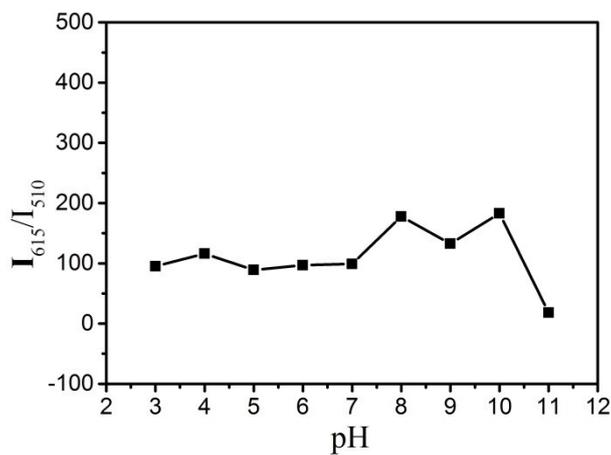


Fig. S7. Effect of solution pH on the luminescence intensity I_{615}/I_{510} of ratiometric probe solution upon adding 90 μM DPA ($\lambda_{\text{ex}} = 280 \text{ nm}$).

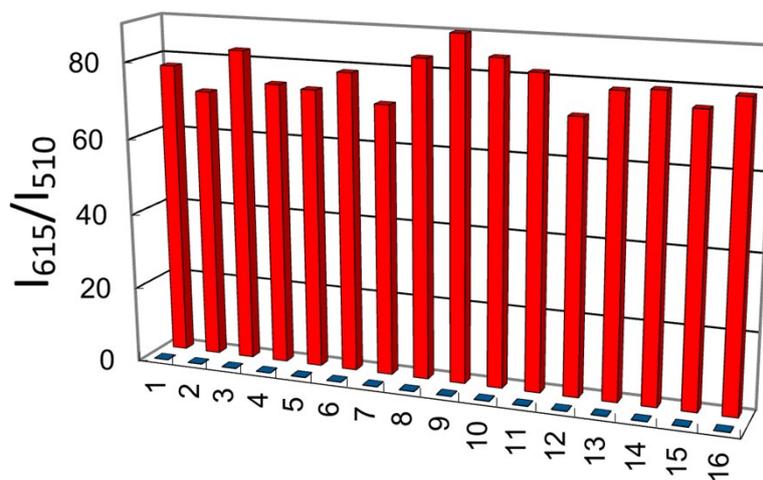


Fig. S8. Luminescence response of the probe solution in the presence of various

cations and anions. The blue bars represent adding 90 μM common cations and anions to the probe solution. The red bars represent subsequent adding 90 μM DPA to the mixture ($\lambda_{\text{ex}} = 280 \text{ nm}$). (1) blank, (2) Ca^{2+} , (3) Na^+ , (4) Mg^{2+} , (5) Al^{3+} , (6) K^+ , (7) F^- , (8) Cl^- , (9) NO_3^- , (10) SO_4^{2-} , (11) CO_3^{2-} , (12) HCO_3^- , (13) PO_4^{3-} , (14) HPO_4^{2-} , (15) H_2PO_4^- , (16) CH_3COO^- .

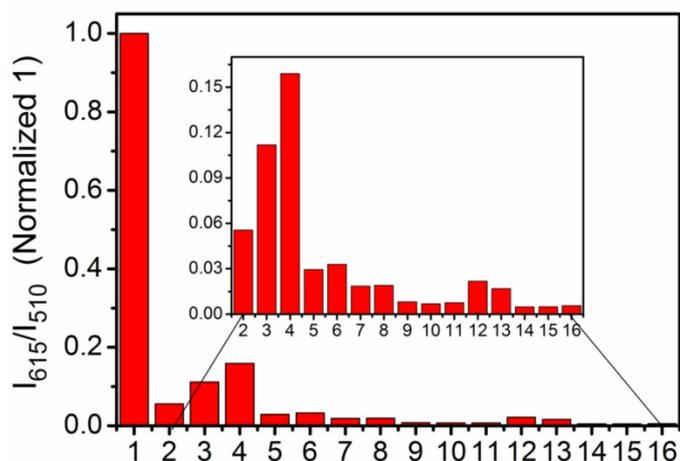


Fig. S9. Luminescence response of probe prepared by mixing EuCl_3 , poly (vinyl alcohol) and pyranine in the presence of different interfering aromatic ligands. (1) DPA, (2) 2,3-PA, (3) 2,4-PA, (4) 2,5-PA, (5) 3,4-PA, (6) 3,5-PA, (7) o-PA, (8) m-PA, (9) p-PA, (10) NA, (11) isonicotinic acid, (12) picolinic acid, (13) BA, (14) glu, (15) asp, (16) NAD.

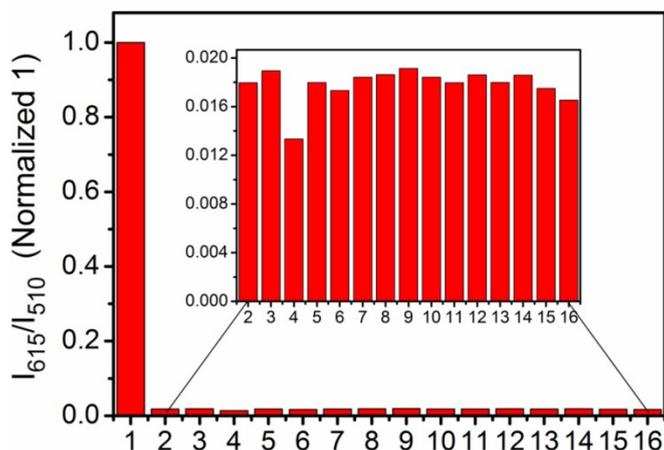


Fig. S10. Luminescence response of probe prepared by mixing EuCl_3 , sodium

acrylate and pyranine in the presence of different interfering aromatic ligands. (1) DPA, (2) 2,3-PA, (3) 2,4-PA, (4) 2,5-PA, (5) 3,4-PA, (6) 3,5-PA, (7) o-PA, (8) m-PA, (9) p-PA, (10) NA, (11) isonicotinic acid, (12) picolinic acid, (13) BA, (14) glu, (15) asp, (16) NAD.

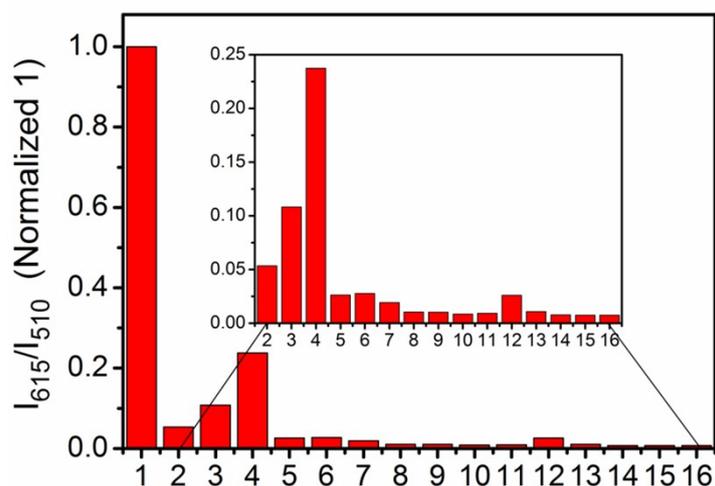


Fig. S11. Luminescence response of probe prepared by mixing EuCl_3 , sodium allylsulfonate and pyranine in the presence of different interfering aromatic ligands. (1) DPA, (2) 2,3-PA, (3) 2,4-PA, (4) 2,5-PA, (5) 3,4-PA, (6) 3,5-PA, (7) o-PA, (8) m-PA, (9) p-PA, (10) NA, (11) isonicotinic acid, (12) picolinic acid, (13) BA, (14) glu, (15) asp, (16) NAD.

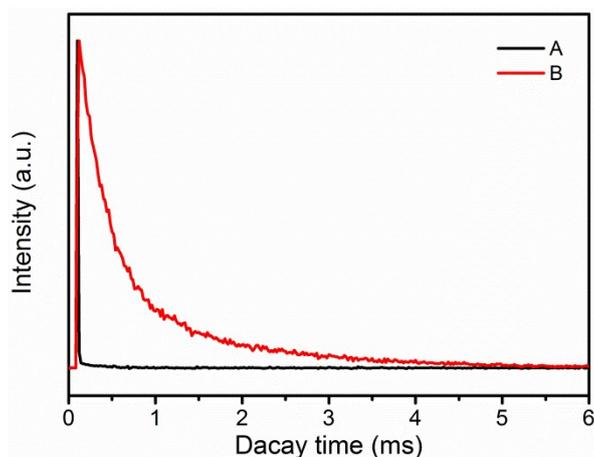


Fig. S12. The decay curves of the probe solution before (A) and after (B) adding 90 μM DPA (excited at 280 nm and monitored at 612 nm).

Table S1 Comparison of different methods for the detection of DPA

Method	Linear range	Detection limit	Reference
Luminescence	0.005-1.2 μM	5 nM	9b
Luminescence	0-80 μM	8.9 μM	9d
Luminescence	0-7 μM	54 nM	9e
Luminescence	20 nM-20 μM	10 nM	14
Luminescence	0-50 nM	10 nM	18
Luminescence	0-90 μM	10.3 nM	This work

Table S2 Luminescence lifetime τ and the number of water molecules coordinated to Eu^{3+}

Sample	τ_{H} (μs)	τ_{D} (μs)	q
Before adding 90 μM DPA	6.68	-	-
After adding 90 μM DPA	526.66	282.55	1.55
In the absence of ASAP	199.43	189.63	5.10