

ESI for Nanoscale

Luminescent Europium-Dipicolinic Acid Nanohybrid for the Rapid and Selective Sensing of Pyrophosphate and Alkaline Phosphatase Activity

Jiahui Zhao^{a,b}, Shuang Wang^{a,c}, Shasha Lu^{a,c}, Jian Sun^{*,a}, and Xiurong Yang^{*,a}

^aState Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun, Jilin 130022, China

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

^cUniversity of Science and Technology of China, Hefei, Anhui 230026, China

*Fax: +86 431 85689278. E-mail: xryang@ciac.ac.cn

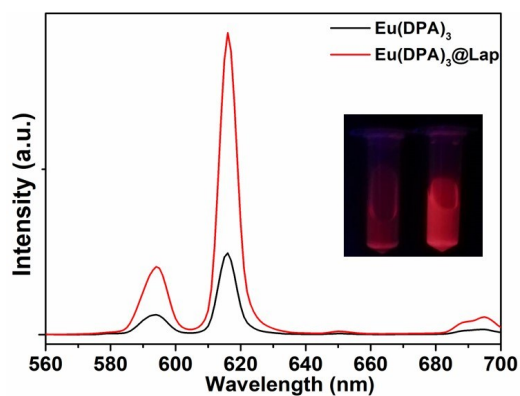
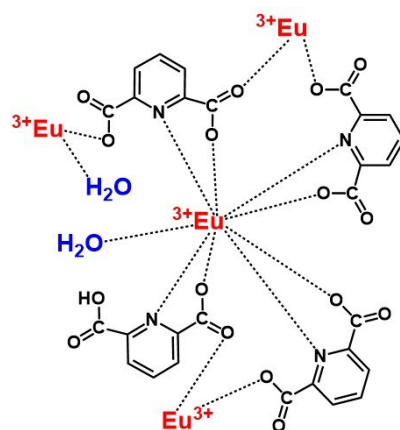


Figure S1. Luminescence emission spectra of 1.5 mM $\text{Eu}(\text{DPA})_3$ complex (black line) and 1.48 mM $\text{Eu}(\text{DPA})_3@Lap$ nanohybrid (red line).



Scheme S1. The possible schematic structure of $\text{Eu}(\text{DPA})_3$ complex in aqueous solution.

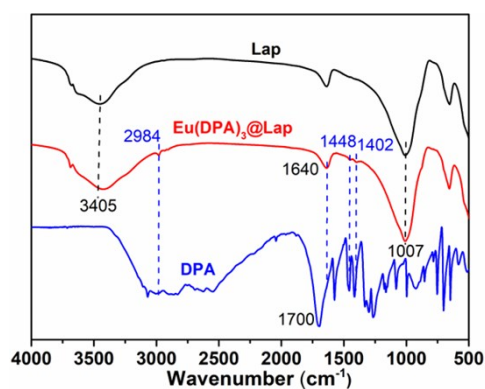


Figure S2. FTIR spectra of Lap, DPA and $\text{Eu}(\text{DPA})_3@Lap$.

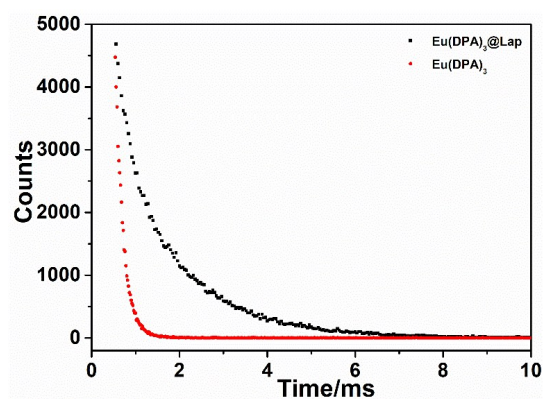


Figure S3. Luminescence decays of the as-prepared Eu(DPA)₃@Lap nanohybrid (black line) and Eu(DPA)₃ (red line) complex in aqueous solution, respectively.

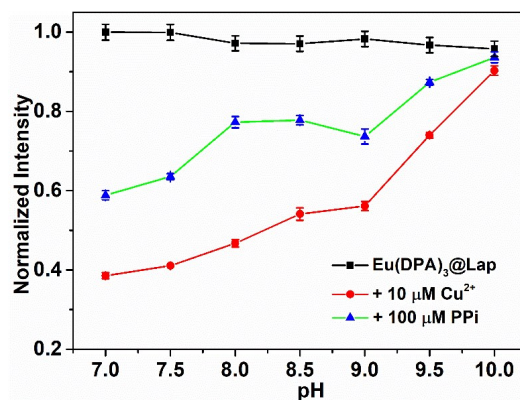


Figure S4. Normalized luminescence intensities at 616 nm of the proposed sensing system with different pH values for recognition of Cu²⁺ (red lines) and PPI (green lines).

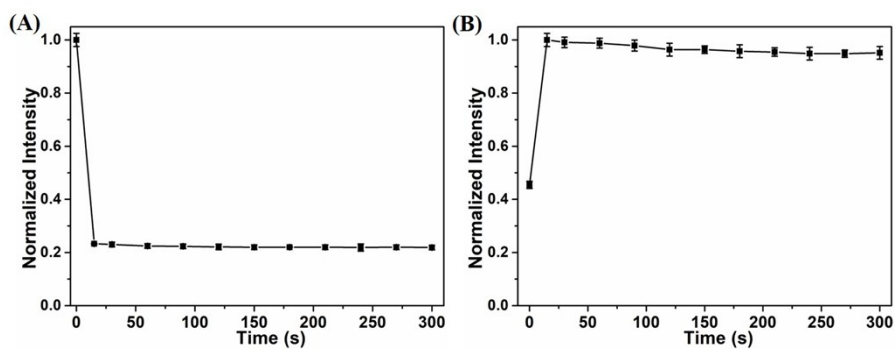


Figure S5. Normalized luminescence intensities at 616 nm of the proposed sensing system as a function of incubation time for recognition of (A) Cu²⁺ and (B) PPI.

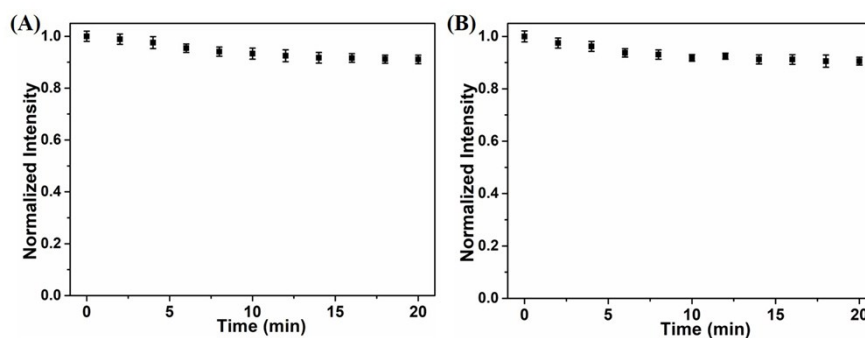


Figure S6. Normalized luminescence intensities at 616 nm of the $\text{Eu}(\text{DPA})_3@Lap$ solution as a function of exposure time to UV light of 270 nm in the (A) absence and (B) presence of Cu^{2+} .

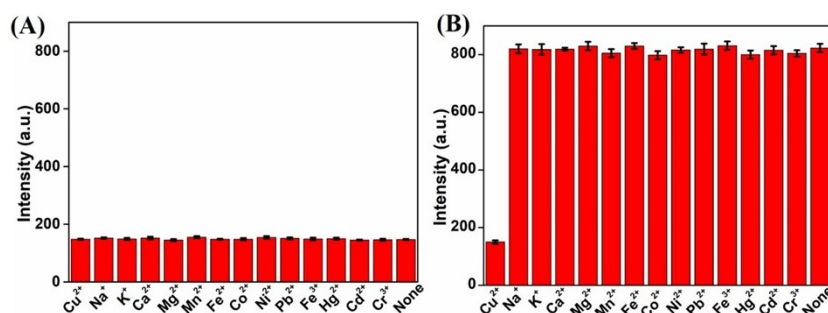


Figure S7. Luminescence responses of the proposed system in the coexistence of the control cations in the (A) presence and (B) absence of Cu^{2+} . All measurements were performed in DEA buffer (20 mM, pH 8.0), containing Mg^{2+} (500 μM), $\text{Eu}(\text{DPA})_3@Lap$ nanohybrid (30 μM) and Cu^{2+} (10 μM).

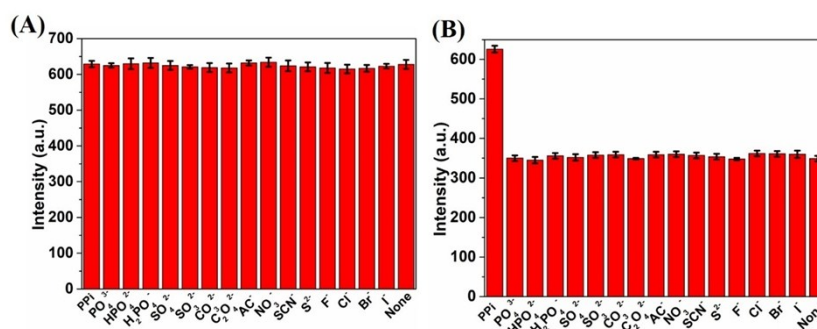


Figure S8. Luminescence responses of the sensing system in the coexistence of the control anions in the (A) presence and (B) absence of PPI. All measurements were performed in DEA buffer (20 mM, pH 8.0), containing Mg^{2+} (500 μM), $\text{Eu}(\text{DPA})_3@Lap$ nanohybrid (30 μM), Cu^{2+} (10 μM) and PPI (100 μM).

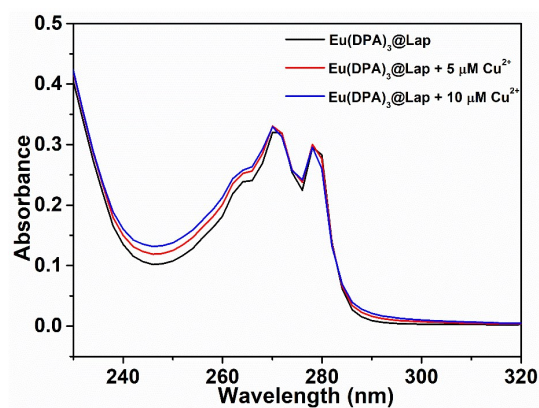


Figure S9. The UV-vis absorption spectra of as-prepared Eu(DPA)₃@Lap nanohybrid in the absence and presence of Cu²⁺, respectively.

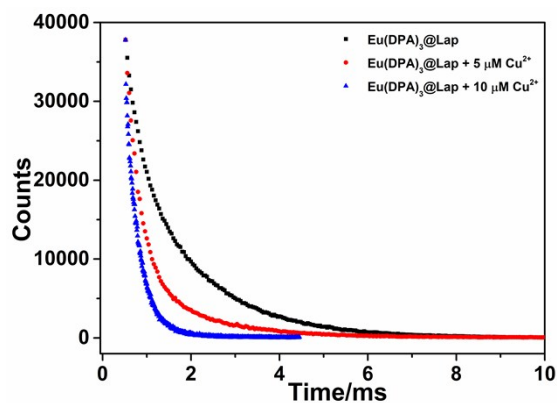


Figure S10. Luminescence lifetimes of the as-prepared Eu(DPA)₃@Lap nanohybrid in the presence of Cu²⁺ (0, 5, 10 μM) in aqueous solution, respectively.

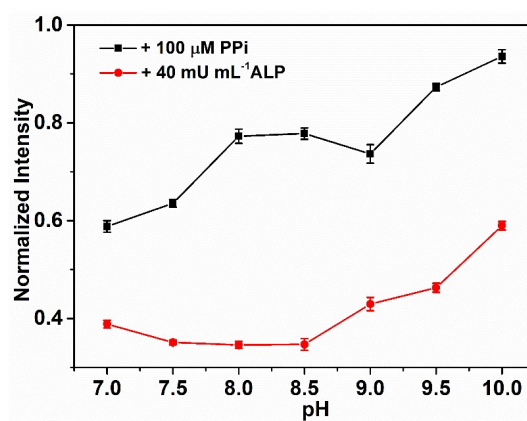
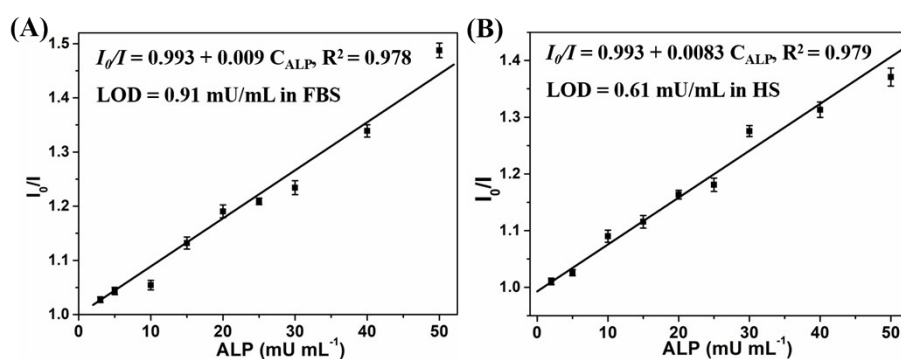


Figure S11. Normalized luminescence intensities at 616 nm of the proposed sensing system as a function of different pH values for ALP incubation.

Table S1. Comparison of the current work with other reported methods for the detection of ALP.

Method	Sensing system	LOD (mU/mL)	Linear range (mU/mL)	Ref.
Colorimetry	Redox active nanoceria	0.04	0.13 - 2	1
Fluorometry	PPECO ₂ -Cu ²⁺	20	66.6 - 1200	2
Fluorometry	CdS QDs	0.5	1.6 - 50	3
Fluorometry	Chalcone derivative	0.15	0.5 - 150	4
Fluorometry	SiNPs	0.2	0.66 - 30	5
luminescence	NaGdF ₄ :Yb/Tm upconversion nanoparticles	19	62.5 - 87.5	6
Fluorometry	fluorescein-polyethylene terephthalate fibers	0.3	0.73 - 3.05	7
Fluorometry	near-infrared probe	0.07	0.23 - 100	8
Fluorometry	DNA/AgNCs	5	30 - 240	9
Luminescence	Eu(DPA) ₃ @Lap nanohybrid	0.15	0.5 - 60	This work

**Figure S12.** The linear detection range in 2% fetal bovine serum (FBS) and human serum (HS).**Table S2.** Results of recovery efficiency in the analysis of serum samples.

Sample	Spiked (mU/mL)	Found (mU/mL)	Recovery
Fetal bovine serum (2%)	0	2.52 ± 0.23	-
	5	7.05 ± 0.40	90.6%
	20	19.1 ± 0.78	83.0%
	40	35.8 ± 1.39	83.2%
Human serum (2%)	0	1.45 ± 0.43	-
	5	6.87 ± 0.38	108.4%
	20	19.2 ± 0.84	88.8%
	40	37.5 ± 2.35	90.1%

References

1. A. Hayat, G. Bulbul and S. Andreescu, *Biosens. Bioelectron.*, 2014, **56**, 334.
2. Y. Liu and K. S. Schanze, *Anal. Chem.*, 2008, **80**, 8605.
3. N. Malashikhina, G. Garai-Ibabe and V. Pavlov, *Anal. Chem.*, 2013, **85**, 6866.
4. Z. G. Song, R. T. K. Kwok, E. G. Zhao, Z. K. He, Y. N. Hong, J. W. Y. Lam, B. Liu and B. Z. Tang, *ACS Appl. Mater. Inter.*, 2014, **6**, 17245.
5. J. Sun, T. Hu, C. Chen, D. Zhao, F. Yang and R. X. Yang, *Anal. Chem.*, 2016, **88**, 9789.
6. F. Wang, C. Zhang, Q. Xue, H. Li and Y. Xian, *Biosens. Bioelectron.*, 2017, **95**, 21.
7. L. Zhao, S. Xie, X. Song, J. Wei, Z. Zhang and X. Li, *Biosens. Bioelectron.*, 2017, **91**, 217.
8. J. Sun, H. Mei and F. Gao, *Biosens. Bioelectron.*, 2017, **91**, 70.
9. J. L. Ma, B. C. Yin, X. Wu and B. C. Ye, *Anal. Chem.*, 2016, **88**, 9219.