Supporting Information

A Dual Luminescent Lanthanide Coordination Polymers for

Ratiometric Sensing and Efficient Removal of Hg²⁺

Peiyao Lv, Ying Cao, Zi Liu, Rong Wang, Baoxian Ye and Gaiping Li*

College of Chemistry, Zhengzhou University, Zhengzhou, 450001, PR China.





Figure S1. (A) SEM image of the GMP-Tb; (B) Fluorescence spectra of GMP-Tb $(\lambda_{ex}=310 \text{ nm})$. (C) The Energy-dispersive X-ray (EDX) spectra of GMP-Tb.

College of Chemistry, Zhengzhou University, Zhengzhou, 450001, PR China. E-mail: lgpingzy@zzu.edu.cn; Fax: +86 0371 67763654; Tel: +86 0371 67781757



Figure S2. Fluorescence spectra of luminol (50 μ M) in the presence of different concentrations of Tb³⁺ from 0 to 5 mM (λ_{ex} = 310 nm).



Figure S3 (A) UV-vis spectra of GMP, luminol, Tb³⁺ and GMP-Tb-luminol, respectively; (B) FTIR spectra of luminol (curve a), GMP (curve b) and GMP-Tb-luminol (curve c), respectively.

To verify the formation of GMP-Tb-luminol, the UV–vis spectra of luminol, GMP, and GMP-Tb-luminol were examined. As shown in Figure S3A, GMP displayed an obvious absorption peak at 260 nm, which was assigned to the π – π * transition of adenine base.¹ The absorption peaks at 300 nm and 347 nm were attributed to luminol.² The GMP-Tb-luminol exhibited broaden UV absorption peak at 260 nm and 347 nm, respectively. The above phenomenon indicated the coordination between GMP and luminol with Tb³⁺.³

The formation of GMP-Tb-luminol was also confirmed by FT-IR spectra (Figure S3B). The peaks at 3420 and 3330 cm⁻¹ of luminol belonged to the N–H stretching vibrations.³ The peaks at 1053 and 1620 cm⁻¹ of luminol (curve a) were attributed to NH₂ rocking vibrations and C=O stretching vibrations,⁴ respectively. For GMP, the

peaks at 1083, 1240, 1475, and 1688 cm⁻¹, (curve b) belonged to the symmetric (vsPO₂), the phosphate antisymmetric (vasPO₂), N₇-C₈ stretching (vN₇-C₈) and P-OH stretching band (vP-OH) band in the guanine subunit, respectively. ^{5, 6} For GMP-Tb-luminol, the corresponding peaks at 1083, 1240, 1475 and 1688 cm⁻¹ (curve c) of GMP slightly shifted, indicated that the nucleobase moieties and phosphate groups of GMP were involved in the coordination process. ⁷ Meanwhile, the typical peaks of the amino group in the luminol spectrum at 3330 and 3420 cm⁻¹ disappeared. The peak of luminol at 1053 cm⁻¹ shifted. The above phenomenon indicated a reflection of the covalent interaction between the Tb³⁺ and amino group.⁸ In addition, for GMP-Tb-luminol, the peak at around 1622 cm⁻¹ corresponding to the stretching vibrations of C=O slightly shifted, which provided evidence of the successful preparation of GMP-Tb-luminol.⁹ All of these results demonstrated that the dual ligand, dual emission GMP-Tb-luminol CPs was obtained.



Figure S4. Time-dependent fluorescence intensity ratio (I_{430}/I_{548}) of the GMP-Tbluminol after addition of 40 μ M Hg²⁺.



Figure S5. Effects of luminol concentration on the fluorescence intensity ratio



 $(I_{430}\!/I_{548})$ of GMP-Tb-luminol in the presence of 10 μM Hg^{2+} ($\lambda_{ex}\!=$ 310 nm).

Figure S6. The fluorescence intensity ratio (I_{430}/I_{548}) of GMP-Tb-luminol in the absence (black column) and presence (red column) of Hg²⁺ (10 μ M) at different excitation wavelengths.



Figure S7. (A) Fluorescent spectra of the GMP-Tb-luminol (depurated) with different concentrations of Hg²⁺ (λ_{ex} =310 nm); (B) Plot of the ratios I₄₃₀/I₅₄₈ versus the concentration of Hg²⁺.



Figure S8. The emission spectra of GMP-Tb-luminol, GMP-Tb-luminol + Hg^{2+} , GMP-Tb-luminol + Cu^{2+} , GMP-Tb-luminol + PPi, GMP-Tb-luminol + PPi + Cu^{2+} and GMP-Tb-luminol + PPi + Hg^{2+} (Hg^{2+} : 40 μ M; Cu^{2+} : 40 μ M; PPi: 0.5 mM).

References

1. F. Pu, E. Ju, J. Ren and X. Qu, Adv. Mater. 2014, 26, 1111-1117.

 K. S. Ahn, J. H. Lee, J. M. Park, N. C. Han and W. Y. Lee, Biosens. Bioelectron., 2016, 75, 82-87.

3. F. Barni, S. W. Lewis, A. Berti, G. M. Miskelly and G. Lago, Talanta, 2007, 72, 896-913.

4. Y. B. Miao, N. Gan, H. X. Ren, T. Li and Y. Chen, Talanta, 2016, 147, 296-301.

5. H. H. Zeng, L. Zhang, L.Q. Rong, R.P. Liang and J.D. Qiu, Biosens. Bioelectron., 2017, 89, 721-727.

6. N. Liu, J. Hao, K. Cai, M. Zeng, Z. Huang, L. Chen, B. Peng, P. Li, L. Wang and Y. Song, Luminescence, 2018, 33, 119-124.

7. H. H. Zeng, W.B. Qiu, L. Zhang, R.P. Liang and J.D. Qiu, Anal. Chem., Anal. Chem., 2016, 88, 6342-6348

8. Y.J. Tong, L.D. Yu, L.L. Wu, S.P. Cao, Y.L. Guo, R.P. Liang and J.D. Qiu, ACS Sustainable Chem. Eng., 2018, 6, 9333-9341.

9. H. Cui, W. Wang, C.F. Duan, Y.P. Dong and J.Z. Guo, Chem. - Eur. J., 2007, 13, 6975-6984.