

Supporting Information to Accompany “A Highly Selective and On-Off-On Responsive Lanthanide (III) based Probe for Recognition of Copper and Hydrogen Sulfide”

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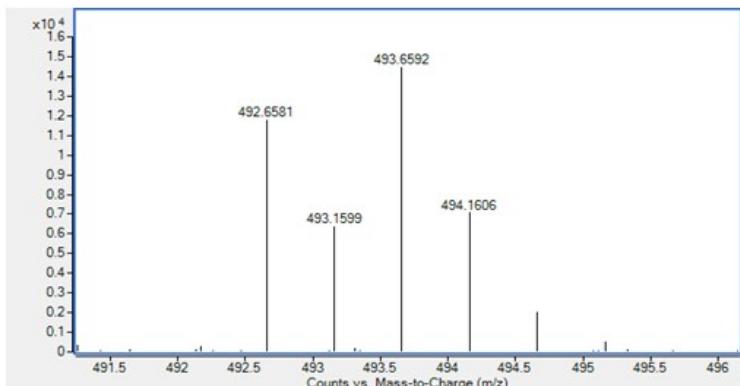


Figure S1. High resolution mass spectrum of **EuL1**.

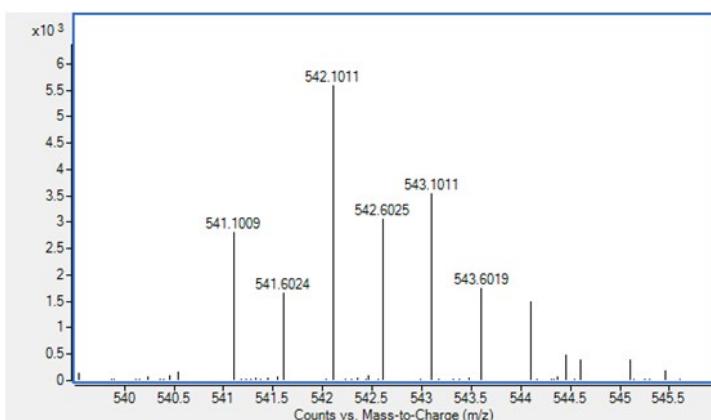


Figure S2. High resolution mass spectrum of **EuL1Cu**.

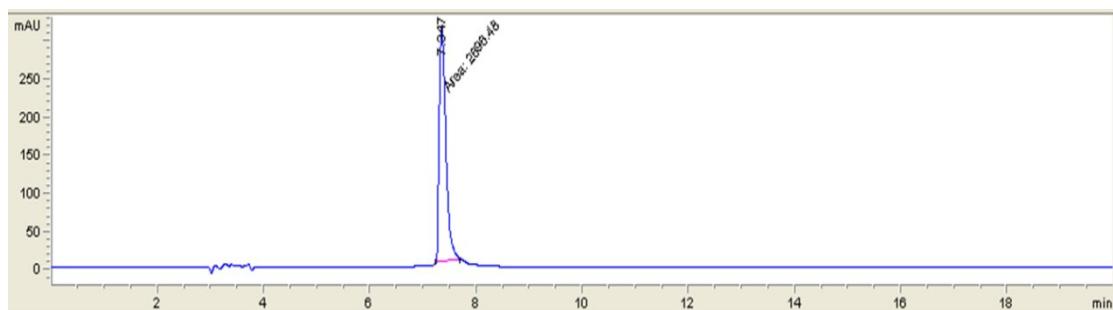


Figure S3. HPLC chromatogram of **EuL1**.

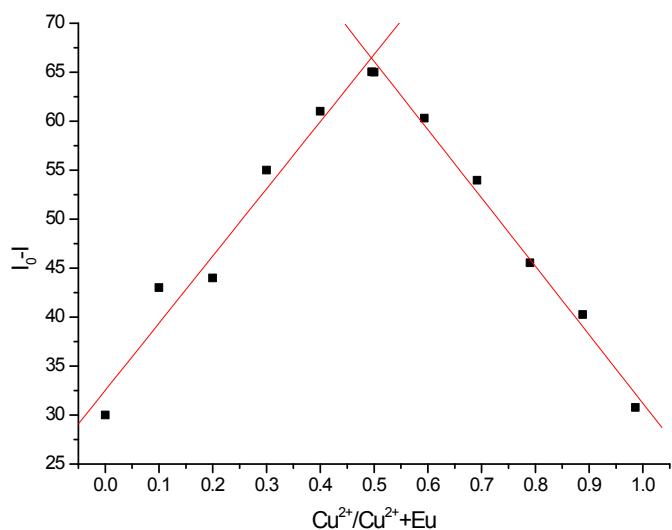


Figure S4. Job's plot of **EuL1** and Cu^{2+} ion. I and I_0 were measured at 612nm.

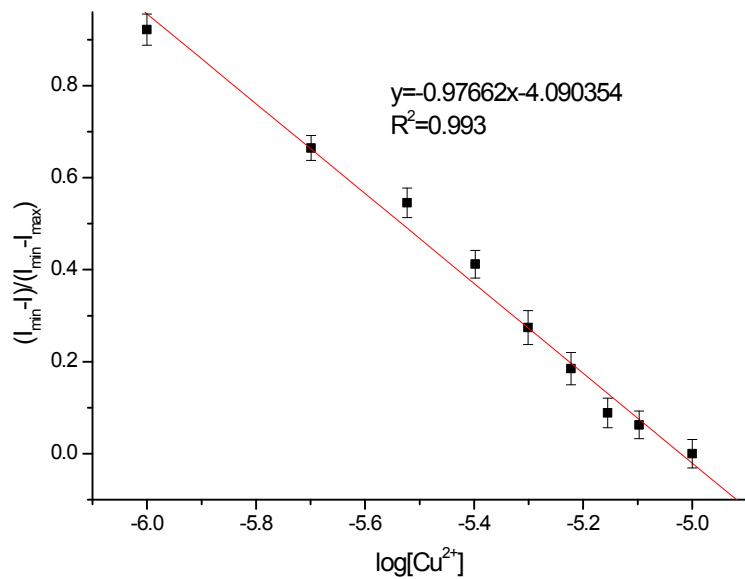


Figure S5. Luminescence response to changing Cu^{2+} ion concentration.

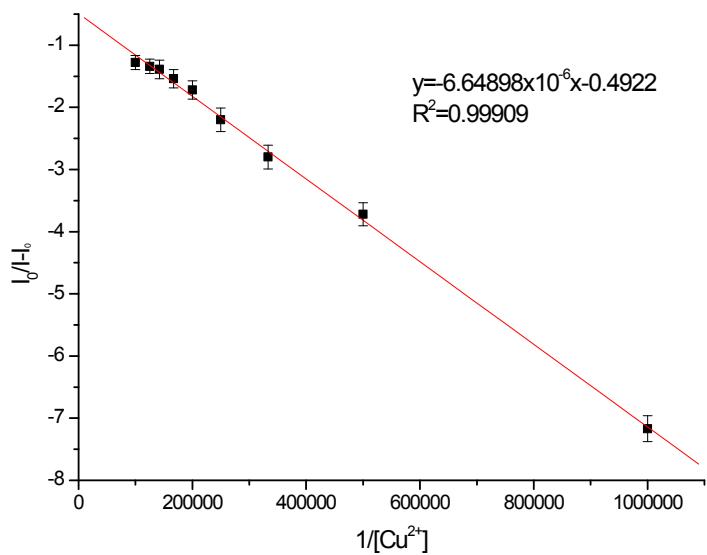


Figure S6. Fitting of fluorescence Cu²⁺ ion titration curve of **EuL1**.

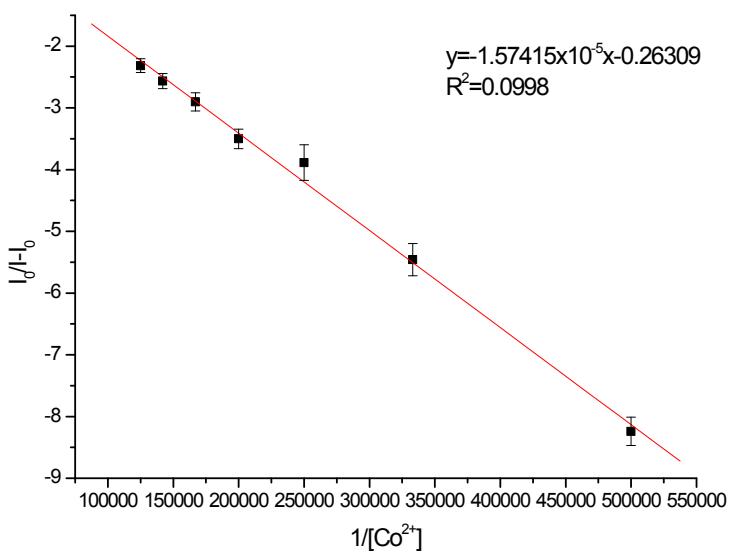


Figure S7. Fitting of fluorescence Co²⁺ ion titration curve of **EuL1**.

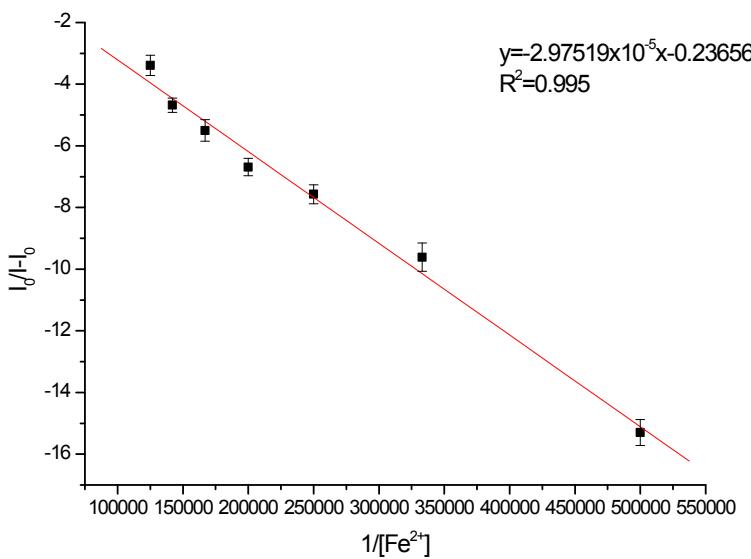


Figure S8. Fitting of fluorescence Fe²⁺ ion titration curve of **EuL1**.

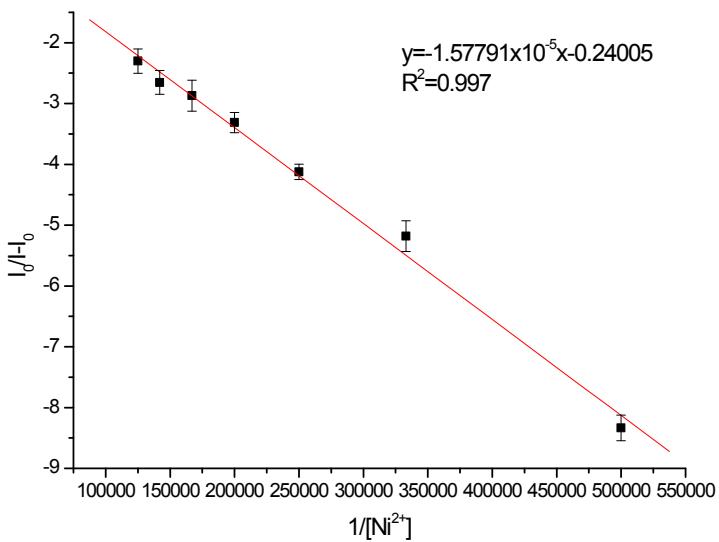


Figure S9. Fitting of fluorescence Ni²⁺ ion titration curve of **EuL1**.

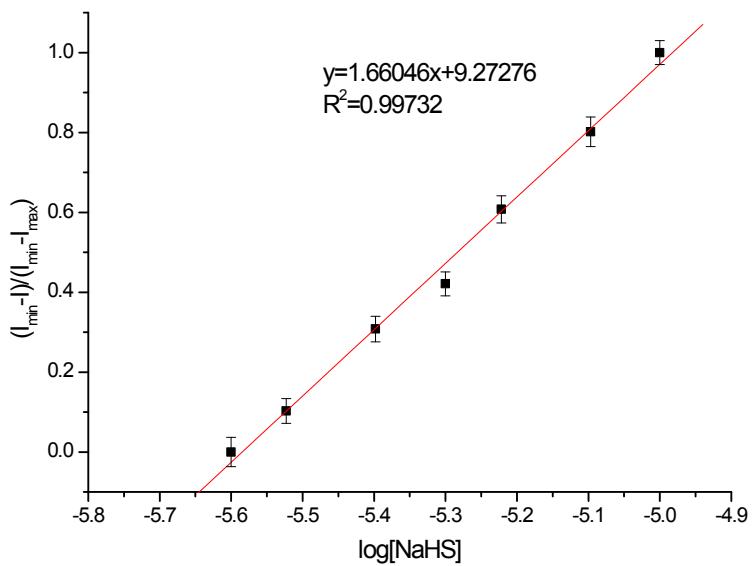


Figure S10. Luminescence response to changing NaHS concentration.

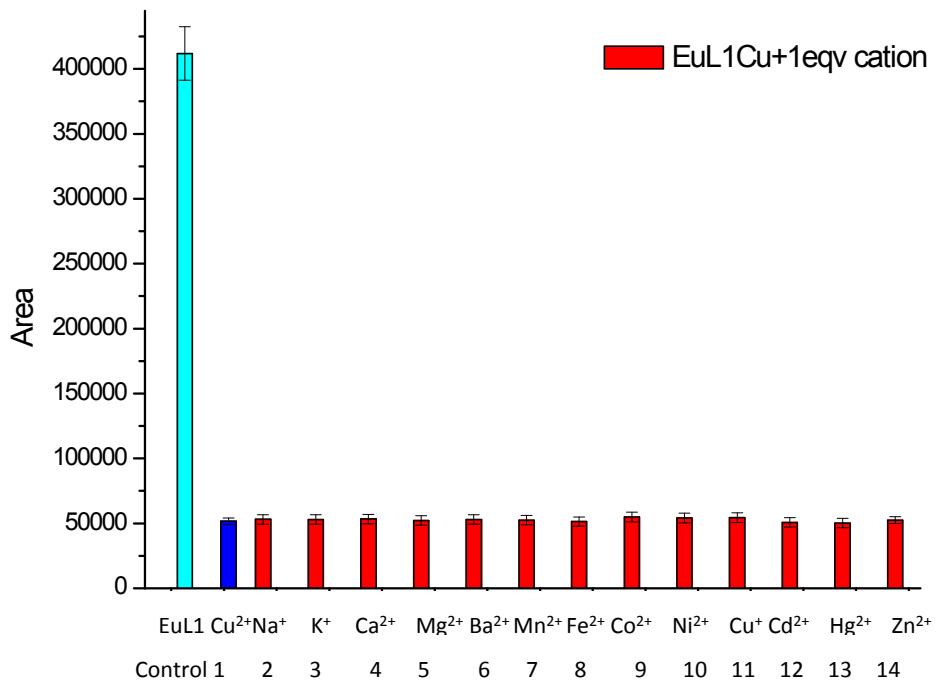


Figure S11. The luminescence intensity changes of $[\text{EuL1Cu}]$ ($10 \mu\text{M}$) in 10 mM Hepes (reverse titration for 1 to 14: Cu(II) ion was first added to **EuL1** then cation was added) (excitation: 350 nm). Control : **EuL1 only**, 1: **EuL1+1eqv Cu(II) ion** , 2: 0.1M Na(I) ion, 3: 0.1M K(I) ion, 4: 0.1mM Ca(II) ion, 5: 0.1mM Mg(II) ion, 6: 1eqv Ba(II) ion, 7: 1eqv Mn(II) ion, 8: 1eqv Fe(II) ion, 9: 1eqv Co(II) ion, 10: 1eqv Ni(II) ion, 11: 1eqv Cu(I) ion, 12: 1eqv Cd(II) ion, 13: 1eqv Hg(II) ion, 14: 1eqv Zn(II) ion.

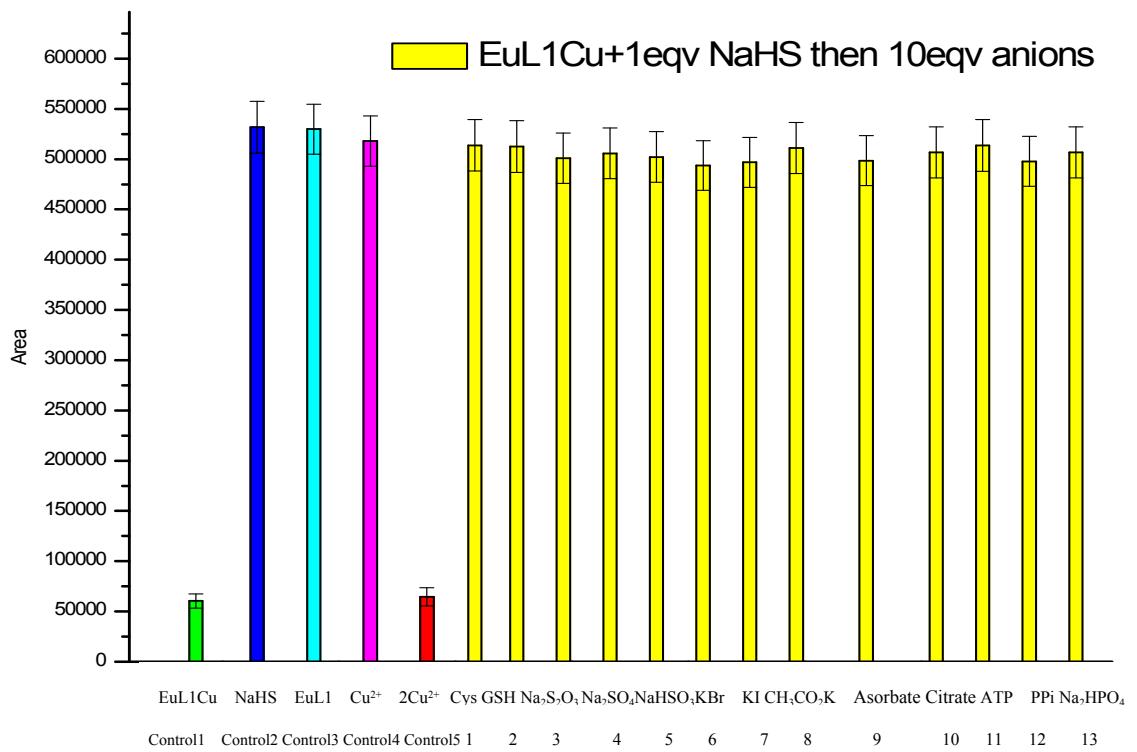


Figure S12. The luminescence intensity changes of **[EuL1Cu]** (10 μ M) in 10 mM Hepes (excitation: 350 nm). Control 1: **EuL1Cu**, Control 2: **EuL1Cu** + 1eqv NaHS, Control 3: **EuL1** + 1eqv NaHS, Control 4: **EuL1** + 1eqv NaHS+ 1eqv Cu (II) ion, Control 5: **EuL1** + 1eqv NaHS+ 2eqv Cu (II) ion, 1: Cysteine (Cys), 2: Glutathione (GSH), 3: Na₂S₂O₃,4: Na₂SO₄, 5: NaHSO₃,6: KBr, 7: KI, 8: potassium acetate, 9: sodium ascorbate, 10: Sodium citrate, 11:ATP, 12: Pyrophosphate (PPi),13: Na₂HPO₄.

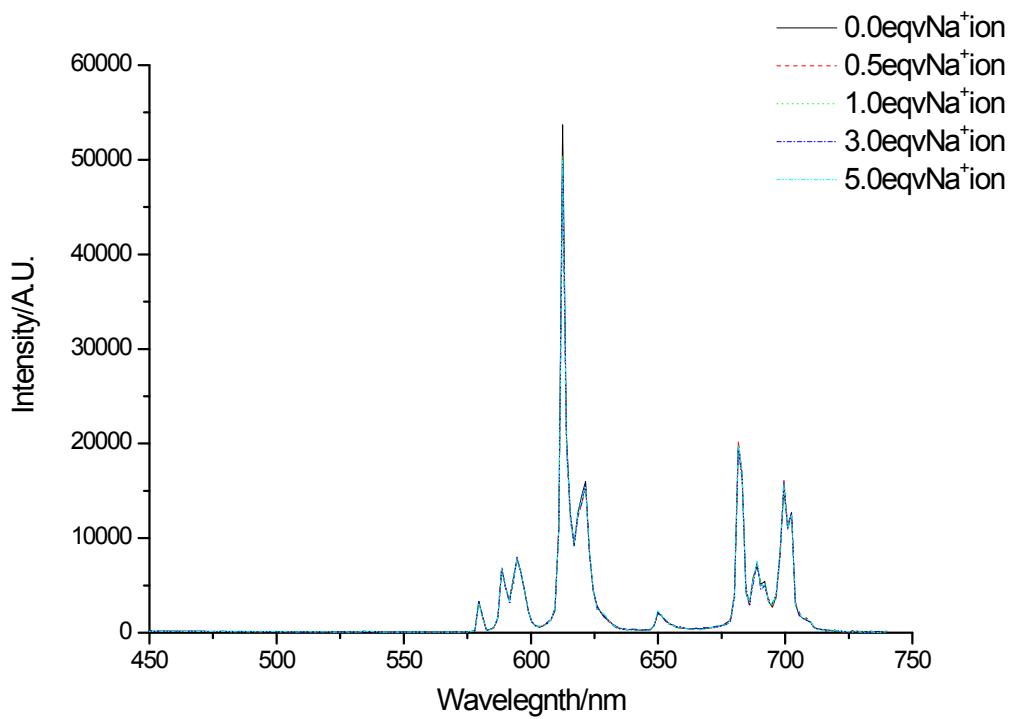


Figure S13. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of Na(I) ions with respect to **EuL1** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

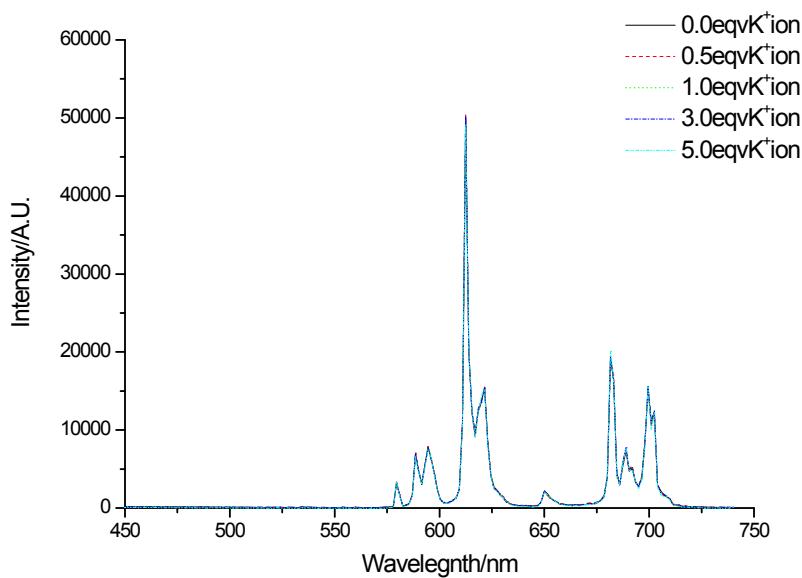


Figure S14. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of K(I) ions with respect to **EuL1** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

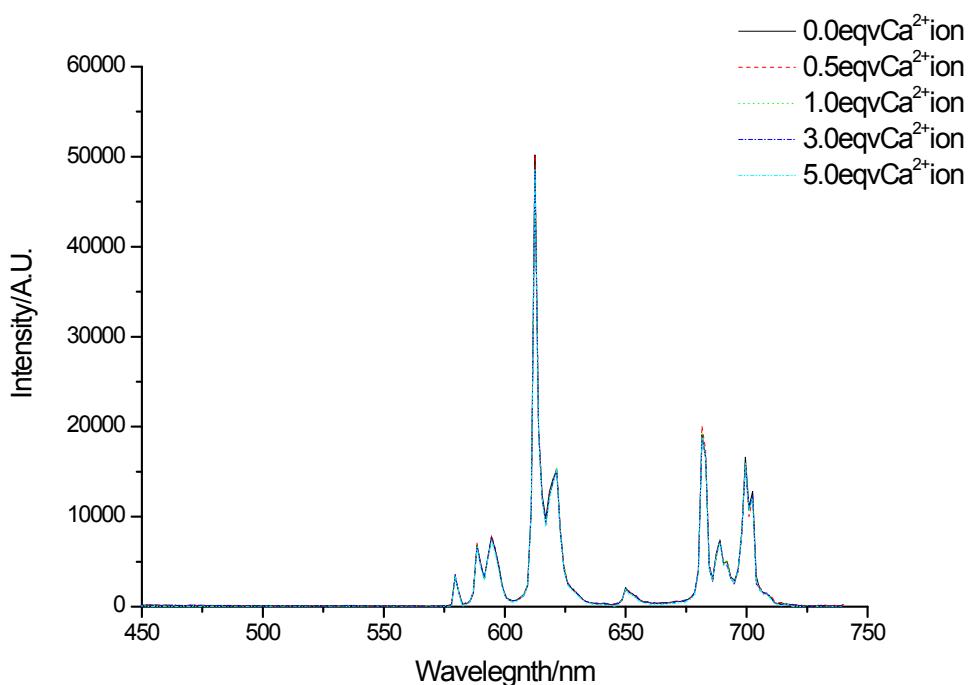


Figure S15. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of Ca (II) ions with respect to **EuL1** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

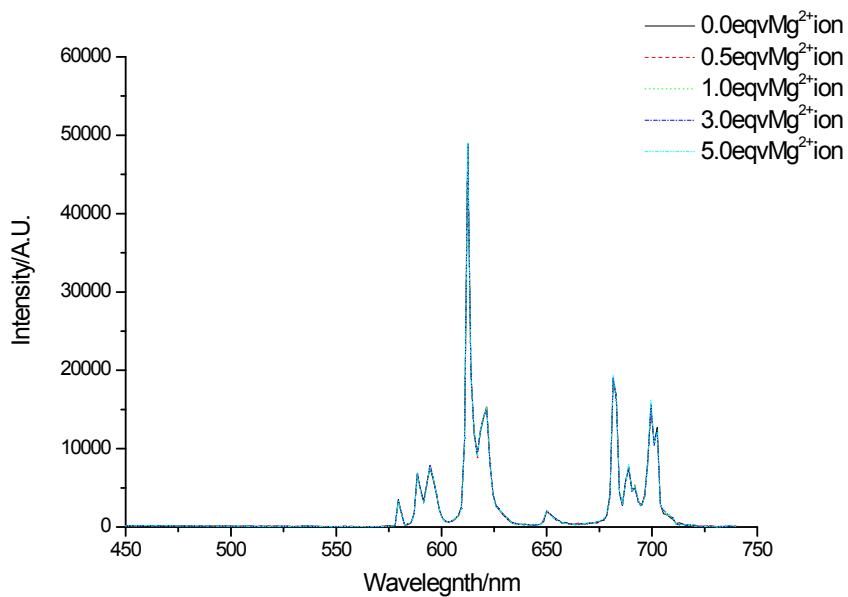


Figure S16. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of Mg (II) ions with respect to **EuL1** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

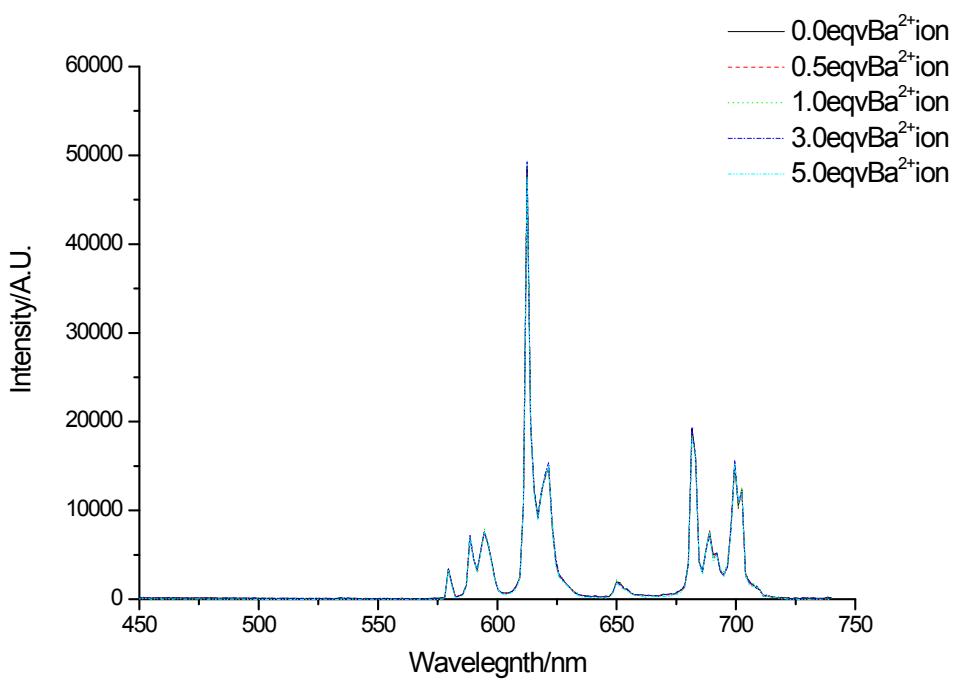


Figure S17. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of Ba (II) ions with respect to **EuL1** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

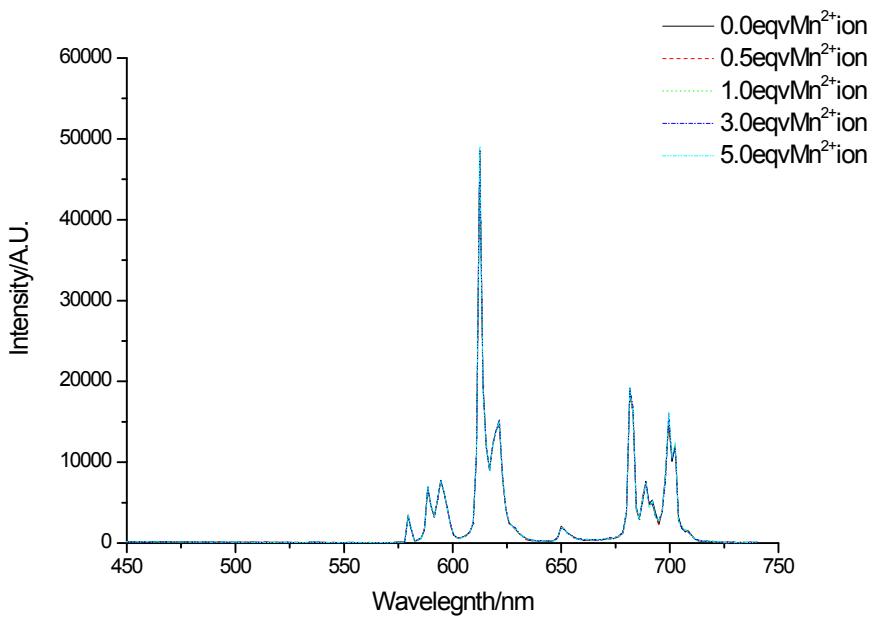


Figure S18. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of Mn (II) ions with respect to **EuL1** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

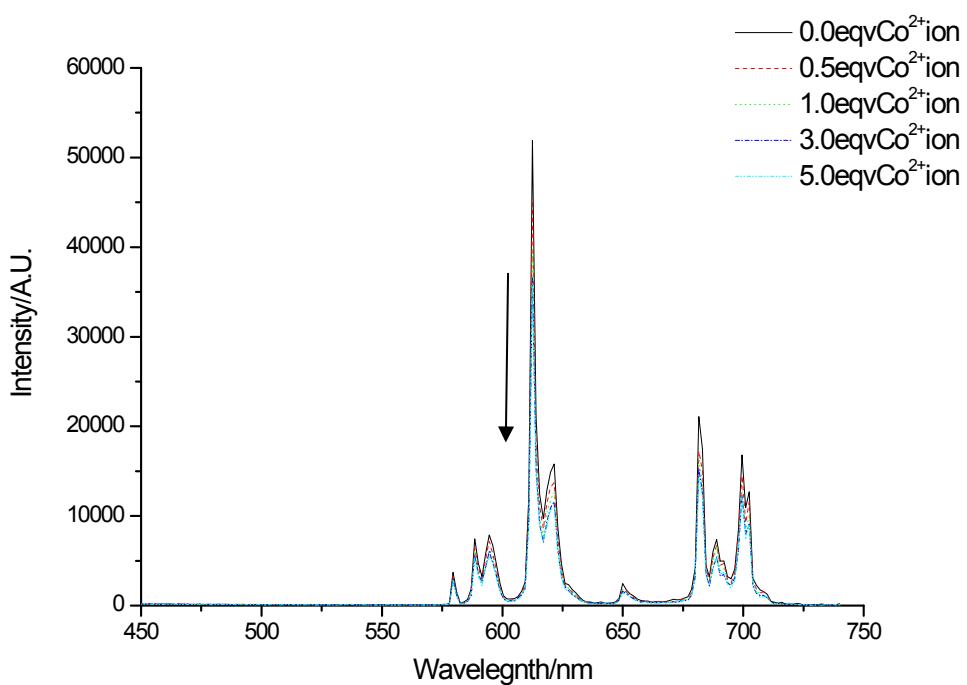


Figure S19. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of Co (II) ions with respect to **EuL1** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

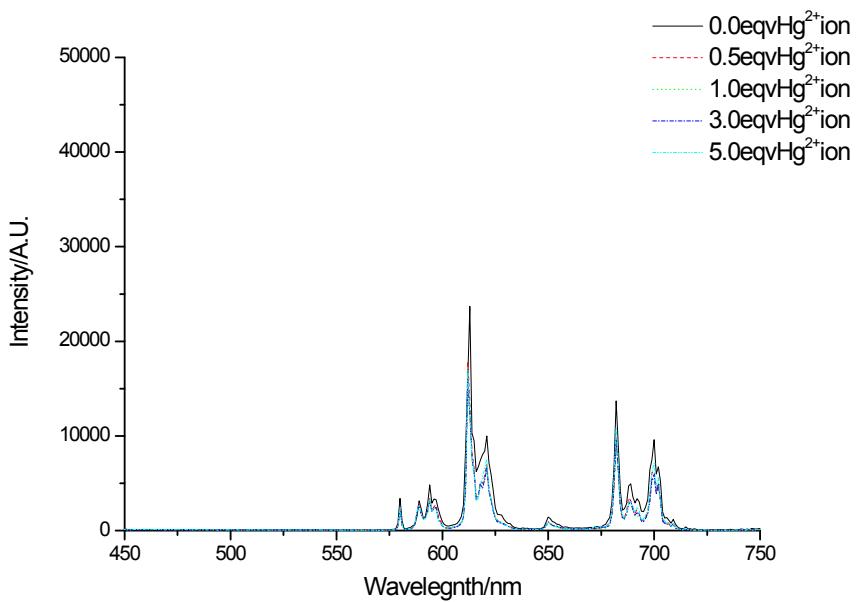


Figure S20. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of Hg (II) ions with respect to **EuL1** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

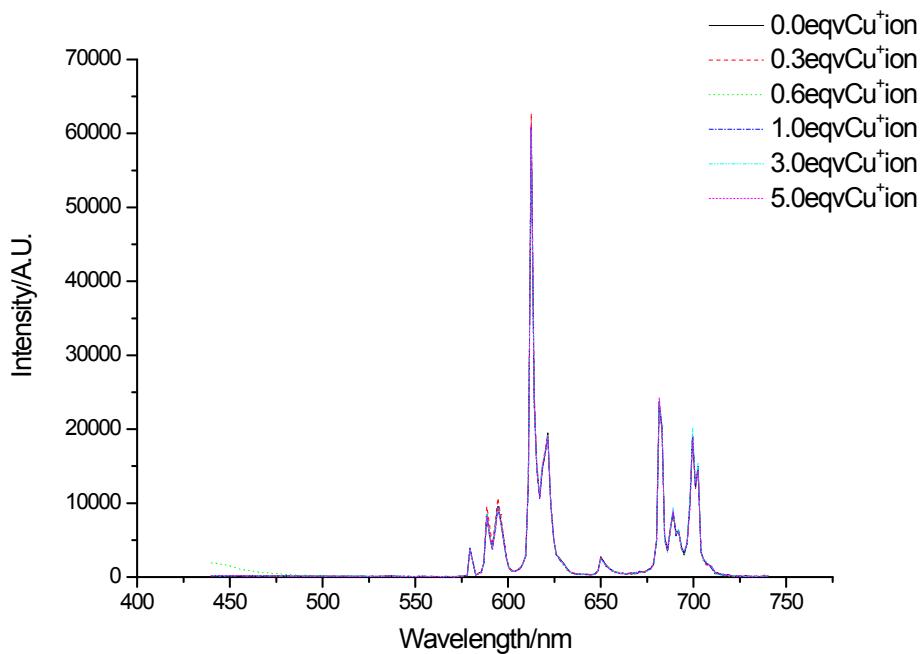


Figure S21. Emission spectra of 10 μM aqueous solution upon addition of aliquots of various equiv of Cu (I) ions with respect to **EuL1** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

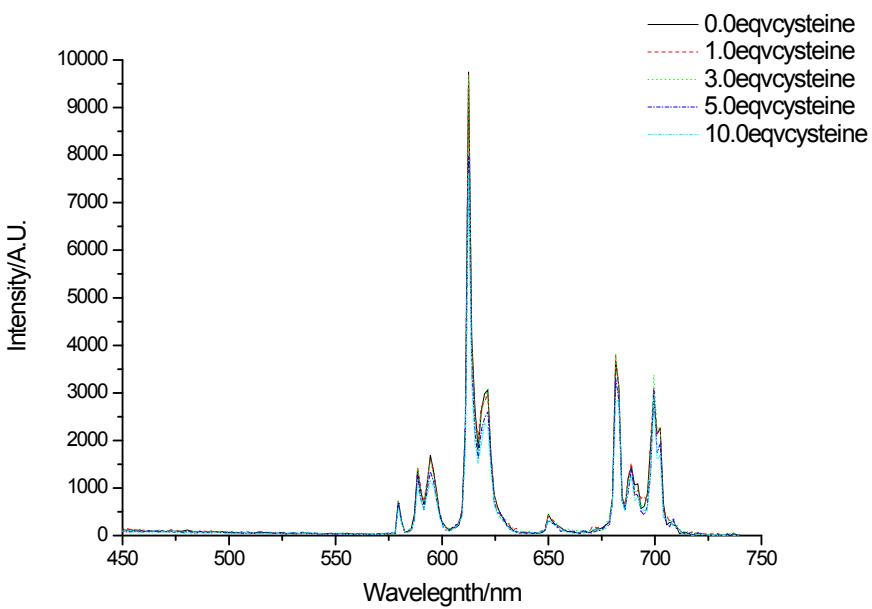


Figure S22. Emission spectra of 10 μM aqueous solution upon addition of aliquots of various equiv of Cysteine with respect to **EuL1Cu** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

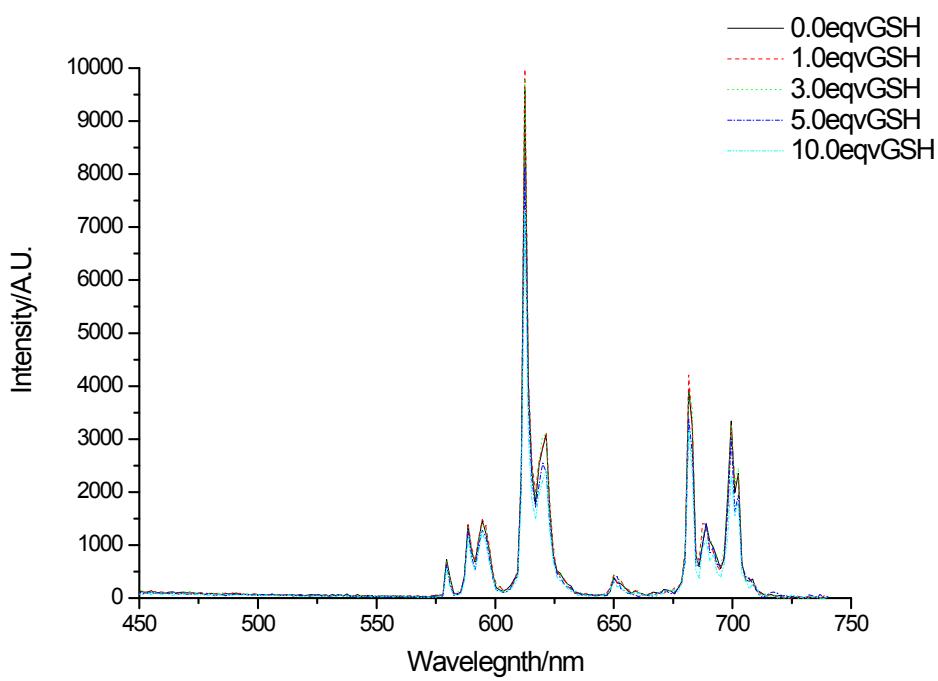


Figure S23. Emission spectra of 10 μM aqueous solution upon addition of aliquots of various equiv of GSH with respect to **EuL1Cu** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

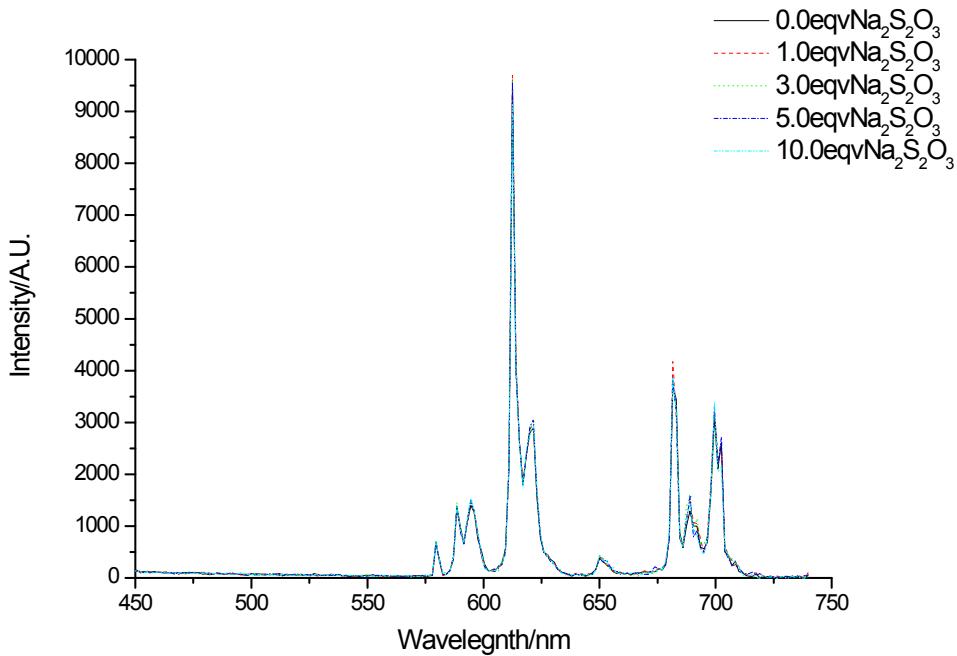


Figure S24. Emission spectra of 10 μM aqueous solution upon addition of aliquots of various equiv of Na₂S₂O₃ with respect to **EuL1Cu** (0.01M Hepes, pH=7.4, $\lambda_{\text{ex}}=350\text{nm}$) .

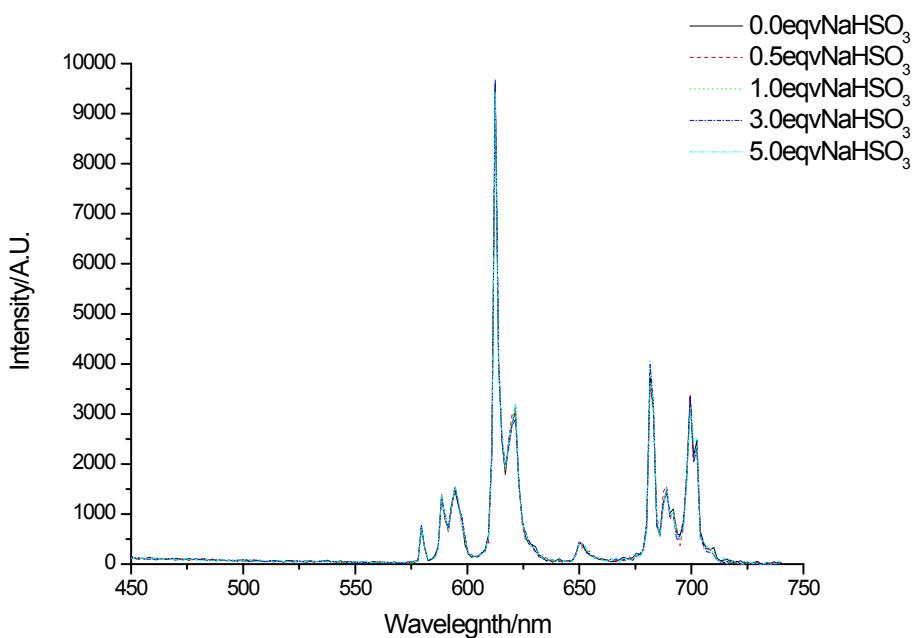


Figure S25. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of NaHSO_3 with respect to **EuL1Cu** (0.01M Hepes, $\text{pH}=7.4$, $\lambda_{\text{ex}}=350\text{nm}$) .

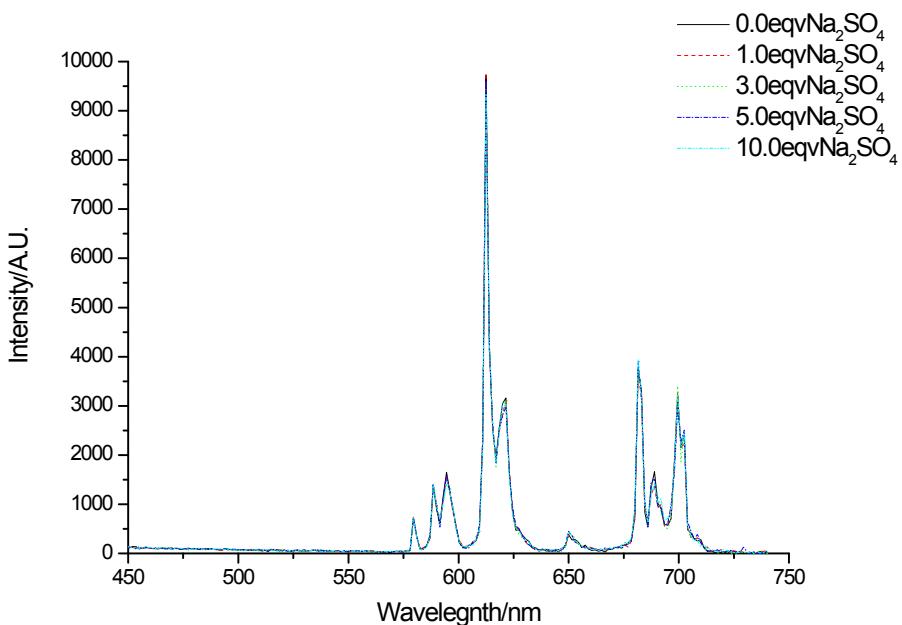


Figure S26. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of Na_2SO_4 with respect to **EuL1Cu** (0.01M Hepes, $\text{pH}=7.4$, $\lambda_{\text{ex}}=350\text{nm}$) .

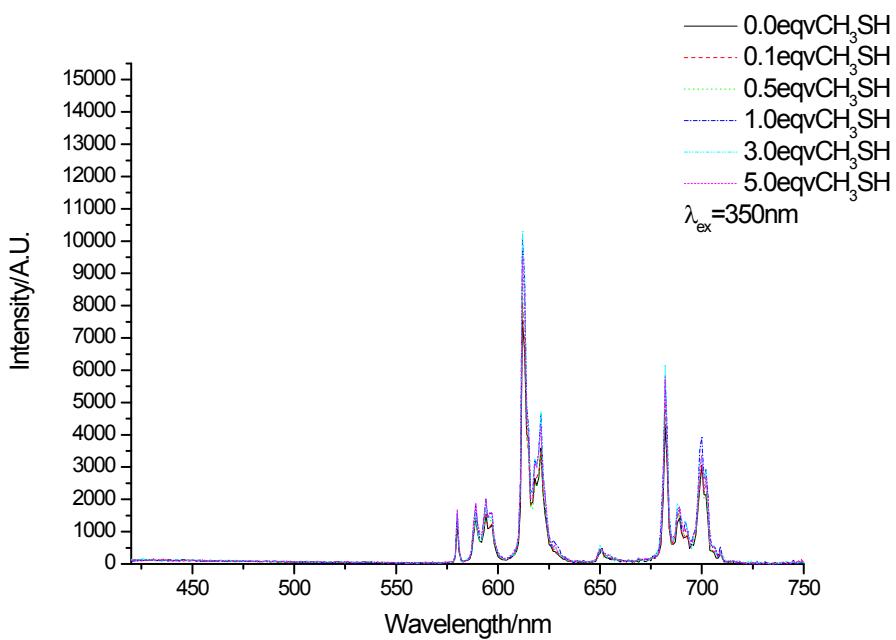


Figure S27. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of CH_3SH with respect to **EuL1Cu** (0.01M Hepes, $\text{pH}=7.4$, $\lambda_{\text{ex}}=350\text{nm}$) .

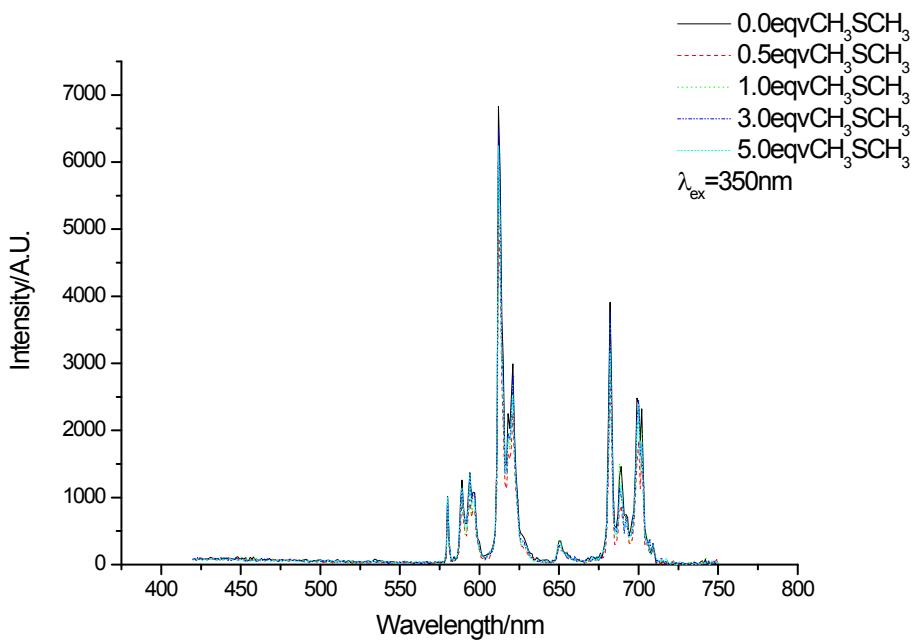
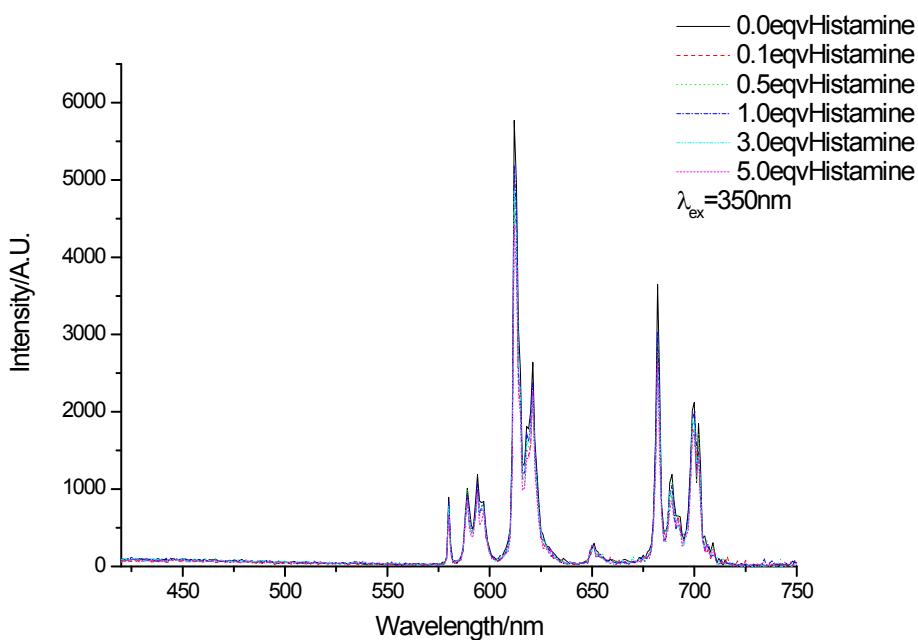


Figure S28. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of CH_3SCH_3 with respect to **EuL1Cu** (0.01M Hepes, $\text{pH}=7.4$, $\lambda_{\text{ex}}=350\text{nm}$) .



Figure

S29. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of histamine with respect to **EuL1Cu** (0.01M Hepes, $\text{pH}=7.4$, $\lambda_{\text{ex}}=350\text{nm}$) .

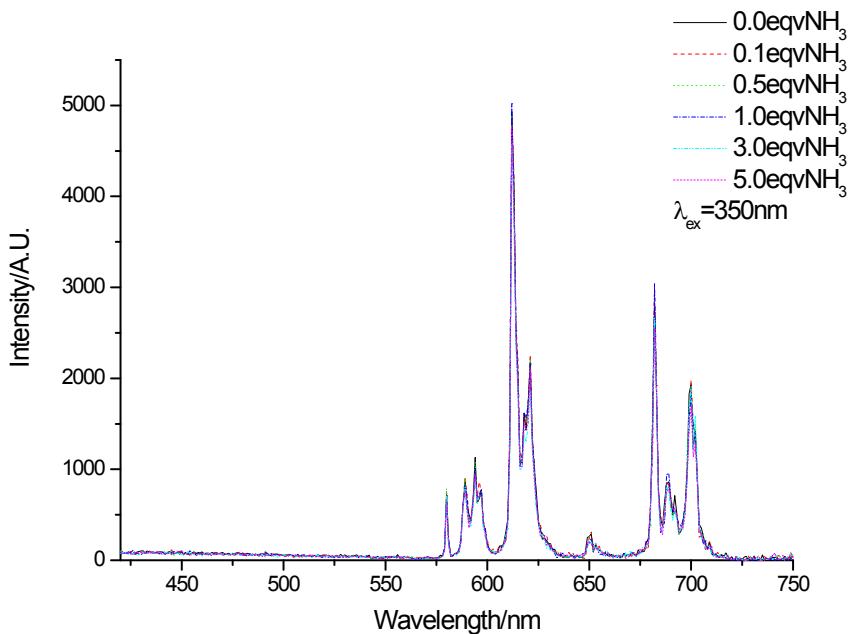


Figure S30. Emission spectra of $10 \mu\text{M}$ aqueous solution upon addition of aliquots of various equiv of NH_3 with respect to **EuL1Cu** (0.01M Hepes, $\text{pH}=7.4$, $\lambda_{\text{ex}}=350\text{nm}$) .

Cations/Anions	Titration range	Effect
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Na(I) ion	0 eqv to 5 eqv	No significant change
K (I) ion	0 eqv to 5 eqv	No significant change
Ca (II) ion	0 eqv to 5 eqv	No significant change
Mg(II) ion	0 eqv to 5 eqv	No significant change
Ba (II) ion	0 eqv to 5 eqv	No significant change
Mn (II) ion	0 eqv to 5 eqv	No significant change
Fe (II) ion	0 eqv to 5 eqv	Slightly quenched
Co (II) ion	0 eqv to 5 eqv	quenched
Ni (II) ion	0 eqv to 5 eqv	quenched
Cu (I) ion	0 eqv to 5 eqv	No significant change
Cd (II) ion	0 eqv to 5 eqv	Slightly quenched
Hg (II) ion	0 eqv to 5 eqv	Slightly quenched
Zn (II) ion	0 eqv to 5 eqv	Slightly quenched
BSA	0 eqv to 5 eqv	No significant change
ATP	0 eqv to 5 eqv	No significant change
GSH	0 eqv to 5 eqv	No significant change
Cysteine	0 eqv to 5 eqv	No significant change

Tabele S1. Summary of titration result of EuL1 with various cations/anions.

Anions	Titration range	Effect
Cysteine	0 eqv to 10 eqv	No significant change
GSH	0 eqv to 10 eqv	No significant change
NaHSO ₃	0 eqv to 10 eqv	No significant change
NaSO ₄	0 eqv to 10 eqv	No significant change
Na ₂ S ₂ O ₃	0 eqv to 10 eqv	No significant change
ATP	0 eqv to 10 eqv	No significant change
pyrophosphate	0 eqv to 10 eqv	No significant change
Na ₂ HPO ₄	0 eqv to 10 eqv	No significant change
KI	0 eqv to 10 eqv	No significant change
KBr	0 eqv to 10 eqv	No significant change
Potassium acetate	0 eqv to 10 eqv	No significant change
Sodium citrate	0 eqv to 10 eqv	No significant change
Sodium asorbate	0 eqv to 10 eqv	No significant change

Tabele S2. Summary of titration result of EuL1Cu with various anions.