

Interactions of the G-series organophosphorus chemical warfare agent sarin and various simulants with luminescent lanthanide complexes

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Reagents

GB was > 91% pure (NMR). All non-CWA reagents were obtained from Sigma-Aldrich (Australia) and were used as received without further purification.

Solvents

DMF was distilled under nitrogen and stored over sieves before use. Acetonitrile was purchased dry from Sigma-Aldrich (Australia).

Instrumentation

Solution fluorescence studies were performed on an OceanOptics portable USB 2000 fluorimeter with fibre optic cables and PX---2 pulsed xenon light source (Integration Time (sec): 100000, Spectra Averaged: 10, Boxcar Smoothing: 0). UV-Vis studies were performed on a Thermo Scientific Evolution 201 UV-Vis spectrophotometer (absorbance, band width = 2nm, Integration time 0.05 seconds, data interval 1.00 nm, scan speed 1200 nm/min).

General titration methodology

Solutions of the lanthanide complexes (1×10^{-3} mol dm⁻³) were prepared in dry dimethylformamide / dry acetonitrile (1:9) before dilution to 1×10^{-5} mol dm⁻³ in acetonitrile. Diluted solutions of the complexes were prepared fresh each day from the 1×10^{-3} mol dm⁻³ stock solutions before titration. Blank additions of acetonitrile were performed to account for any fluorescence changes resulting from concentration differences. Guest (CWA and simulant) solutions were prepared in dry acetonitrile and added to the lanthanide complex solution in a septa fitted cuvette. The concentration of the guest solution was varied during the course of the titrations to ensure $[H_{\text{initial}}]$ was as close to $[H_{\text{final}}]$ as possible. The solution was left stirring without irradiation for at least 2 minutes after each addition of guest before a spectrum was obtained.

GB NMR spectrum

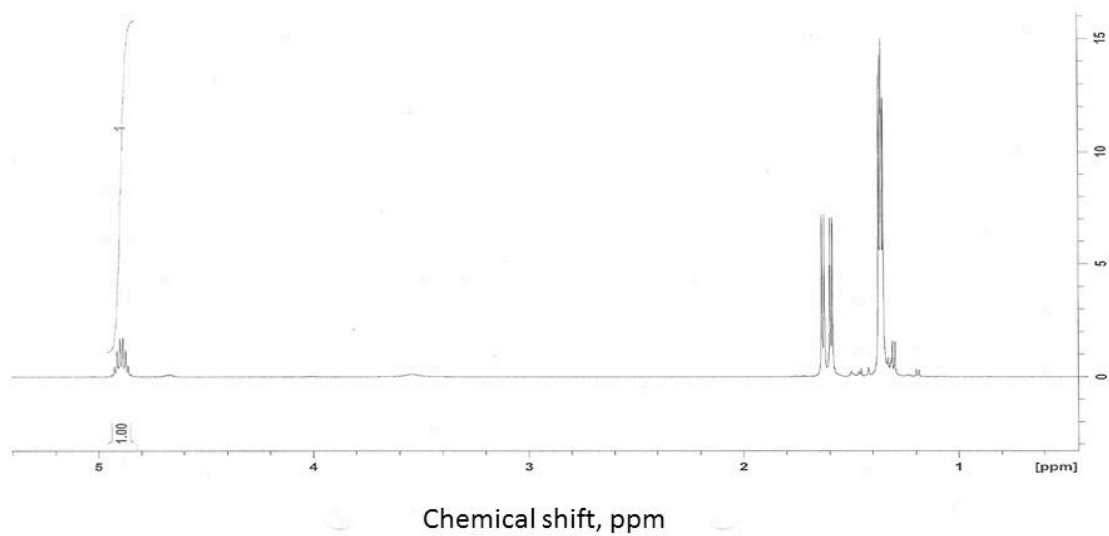


Figure S1. ^1H NMR spectrum of GB in CDCl_3 .

GB titration data

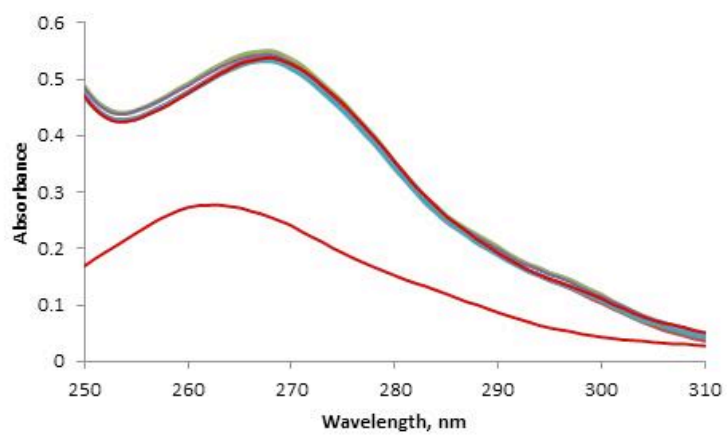


Figure S2: Selected spectra from the titration of 1 with GB: complex, 1.0, 3.0, 5.0 and 10.0 mol equiv GB. The low absorbance red trace is the spectrum of free phen; $[\text{complex}]_{\text{initial}} = 1 \times 10^{-5} \text{ mol dm}^{-3}$, 293 K.

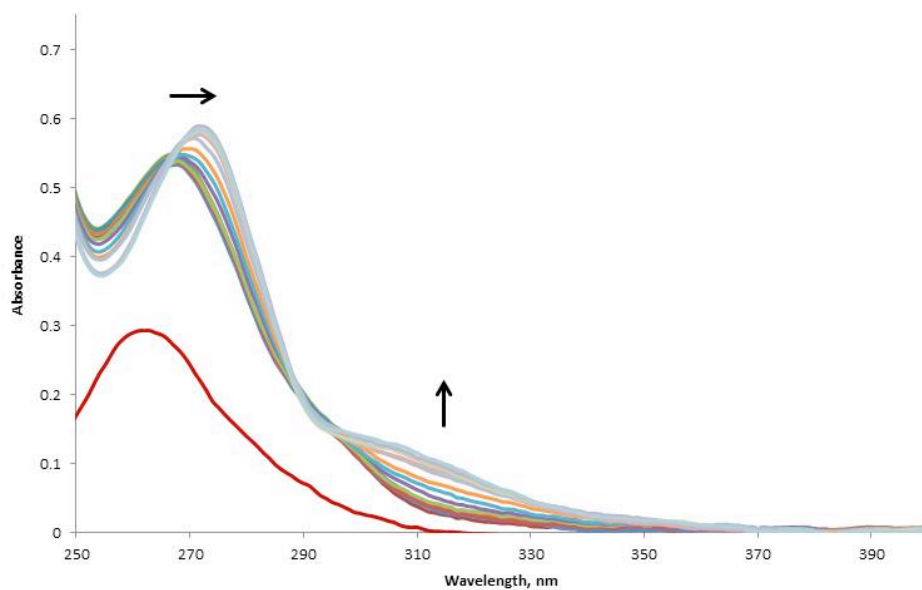


Figure S3. UV/vis spectral data for the addition of up to 200 molar equivalents of GB to a solution of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ (1×10^{-5} M) in MeCN. The red line is the absorption profile of 1,10-phenanthroline only.

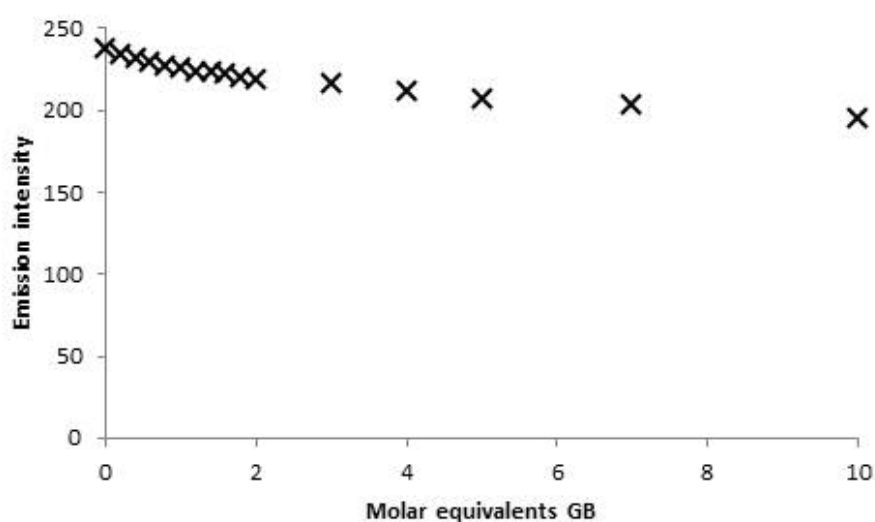


Figure S4. The luminescent emission intensity quenching ($\lambda_{\text{em}} = 545$ nm) observed upon titration of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ with GB (x) in MeCN.

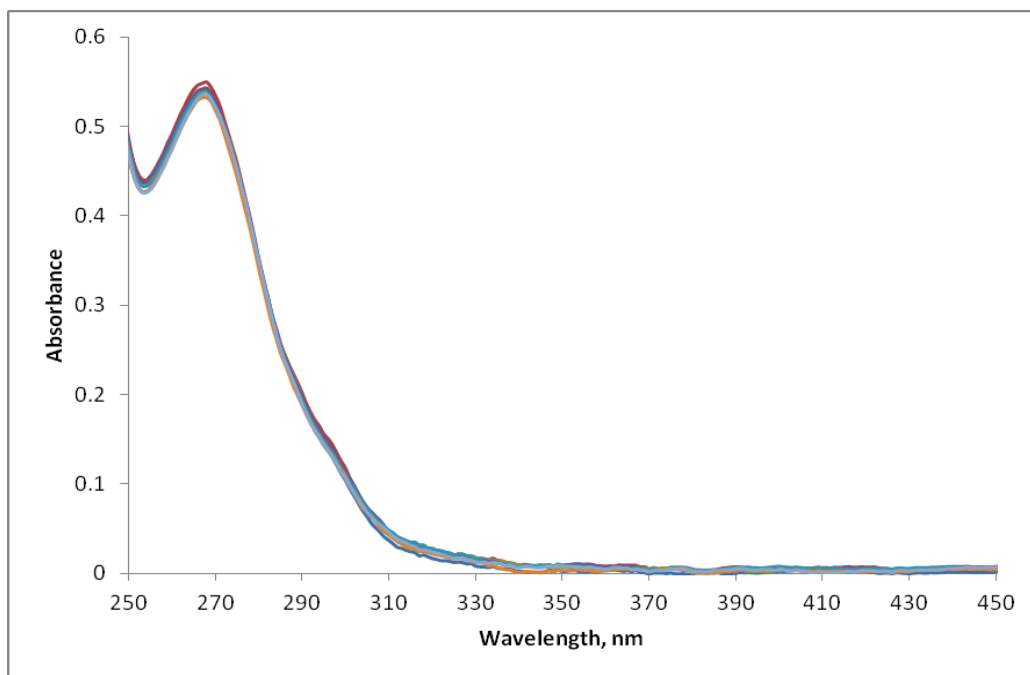


Figure S5. UV/vis spectral data for the addition of up to 10 molar equivalents of GB to a solution of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ (1×10^{-5} M) in MeCN.

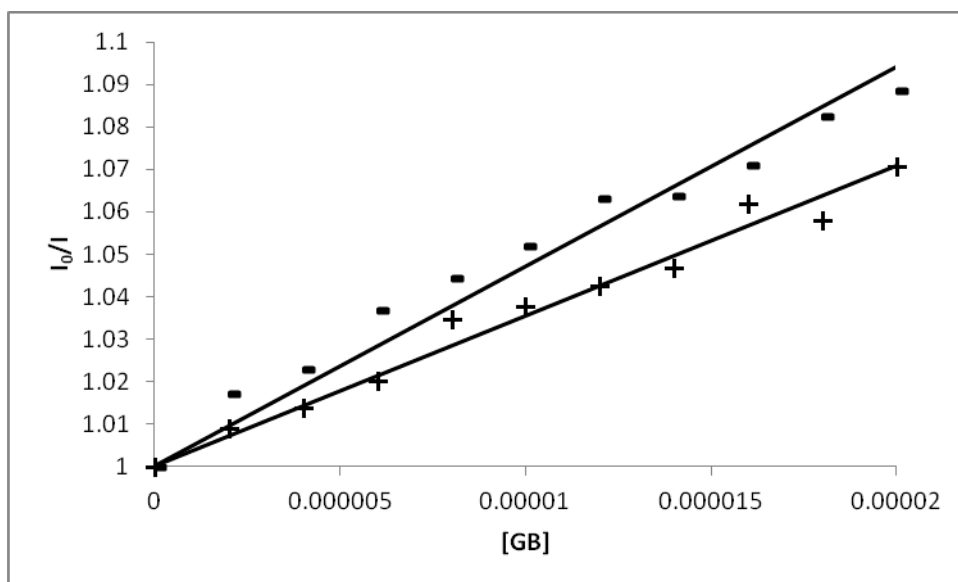


Figure S6. Stern-Volmer plot generated from the titration of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ with GB in acetonitrile.

DMMP titration data

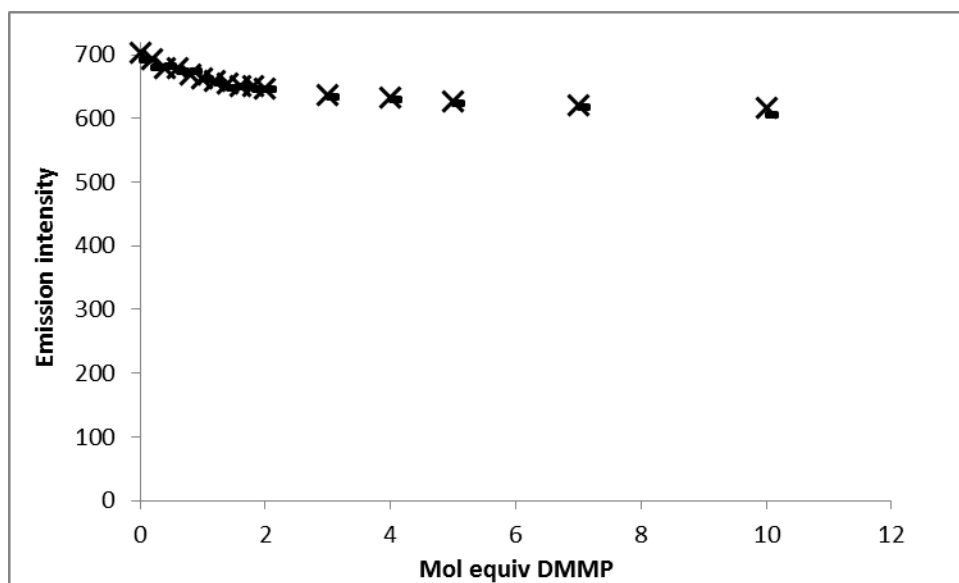


Figure S7. Luminescence emission quenching ($\lambda_{em} = 617 \text{ nm}$) of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ upon addition of DMMP. Titration done in duplicate and both sets of data are shown (X, -).

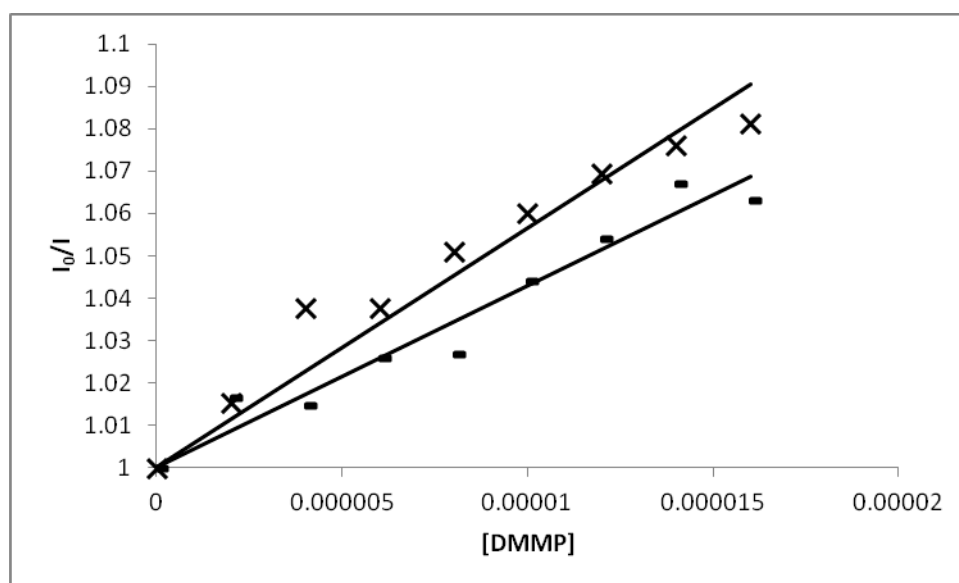


Figure S8. Stern-Volmer plot generated from the titration of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ with DMMP in acetonitrile. Results from duplicate titrations (X, -).

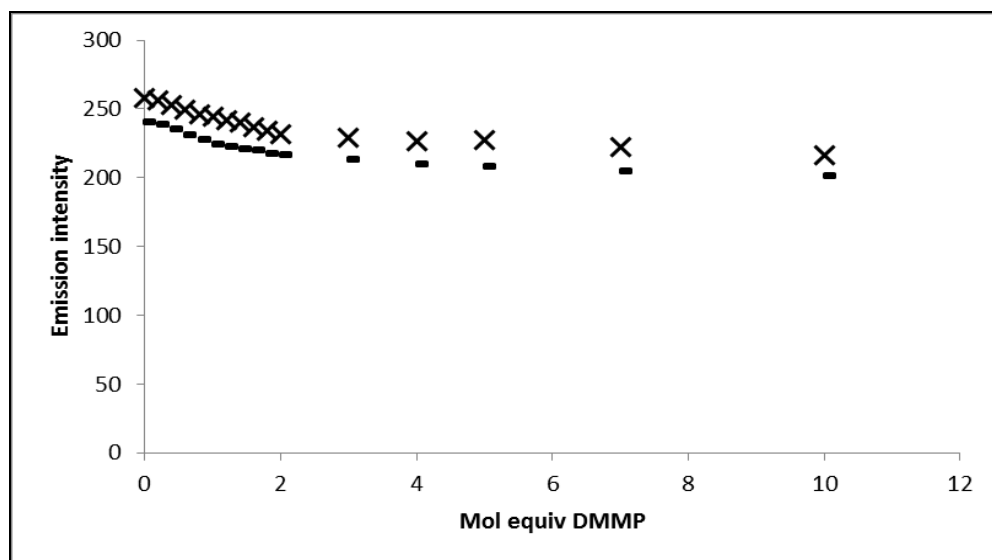


Figure S9. Luminescence emission quenching ($\lambda_{em} = 545 \text{ nm}$) of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ upon addition of DMMP. Titration done in duplicate and both sets of data are shown (X, -).

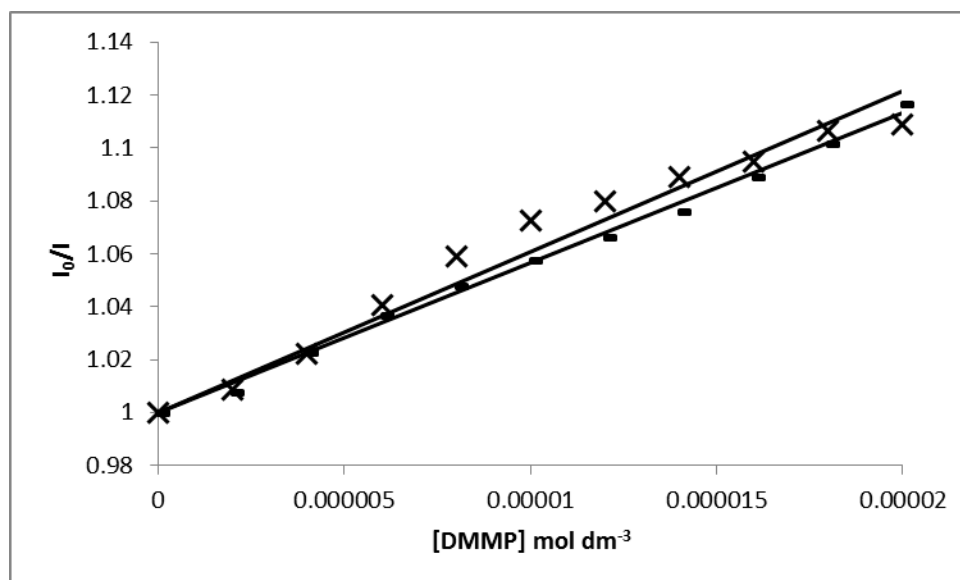


Figure S10. Stern-Volmer plot generated from the titration of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ with DMMP in acetonitrile. Results from duplicate titrations (X, -).

DCP titration data

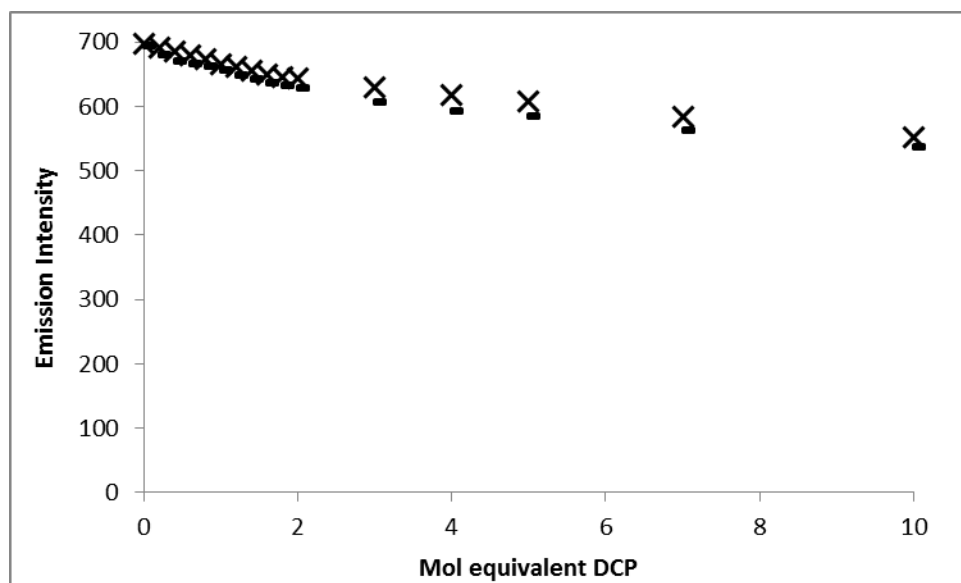


Figure S11. Luminescence emission quenching ($\lambda_{em} = 617$ nm) of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ upon addition of DCP. Titration done in duplicate and both sets of data are shown (X, -).

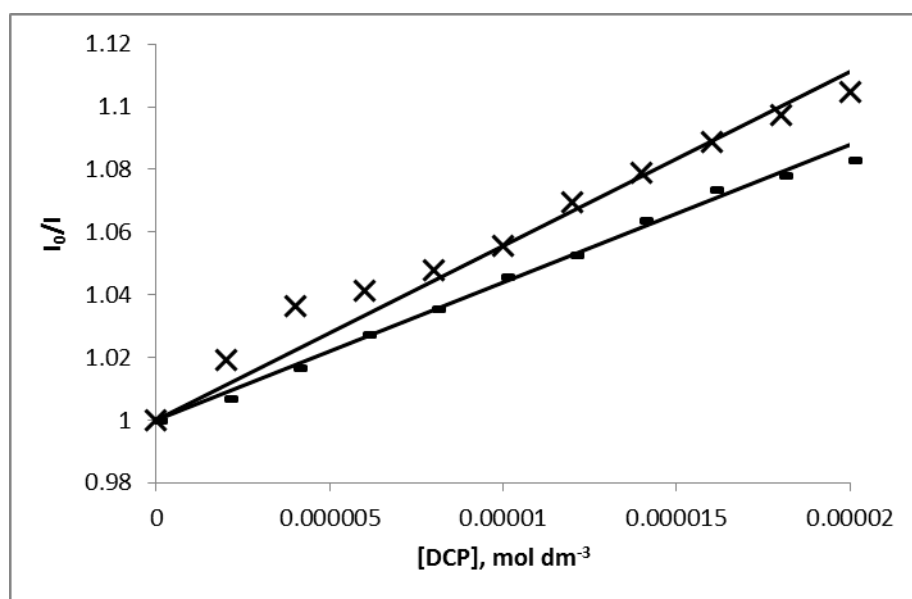


Figure S12. Stern-Volmer plot generated from the titration of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ with DCP in acetonitrile. Results from duplicate titrations (X, -).

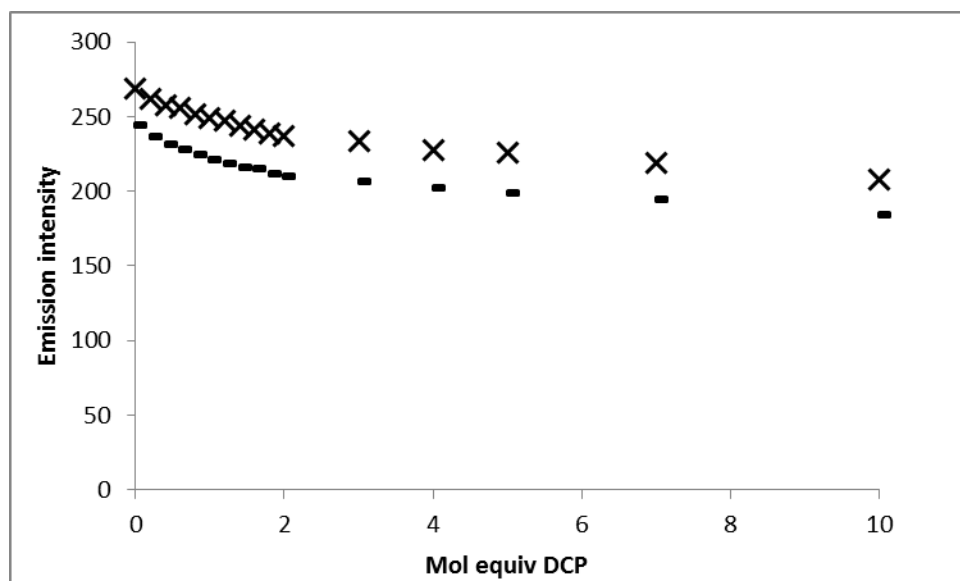


Figure S13. Luminescence emission quenching ($\lambda_{em} = 545 \text{ nm}$) of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ upon addition of DCP. Titration done in duplicate and both sets of data are shown (X, -).

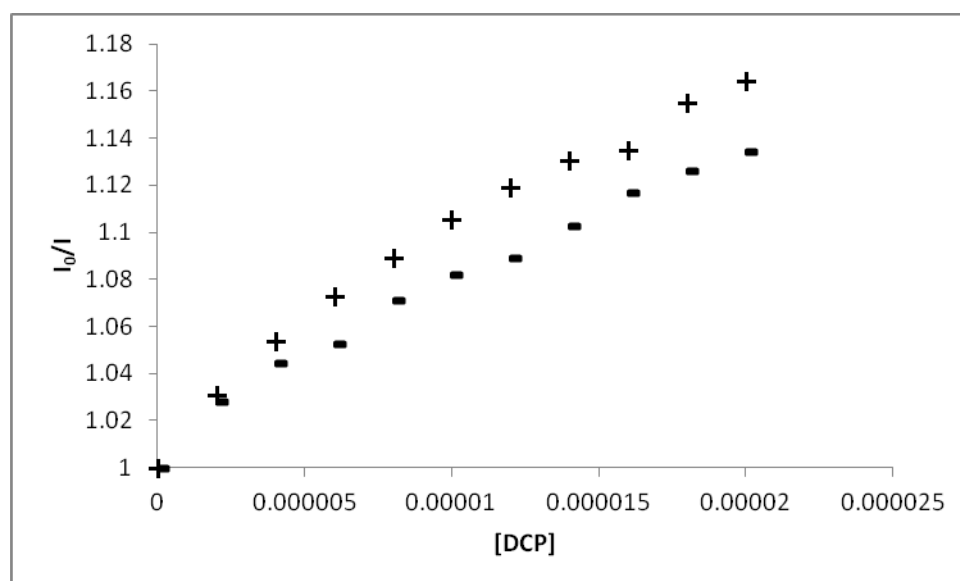


Figure S14. Stern-Volmer plot generated from the titration of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ with DCP in acetonitrile. Results from duplicate titrations (X, -).

TBAF titration data

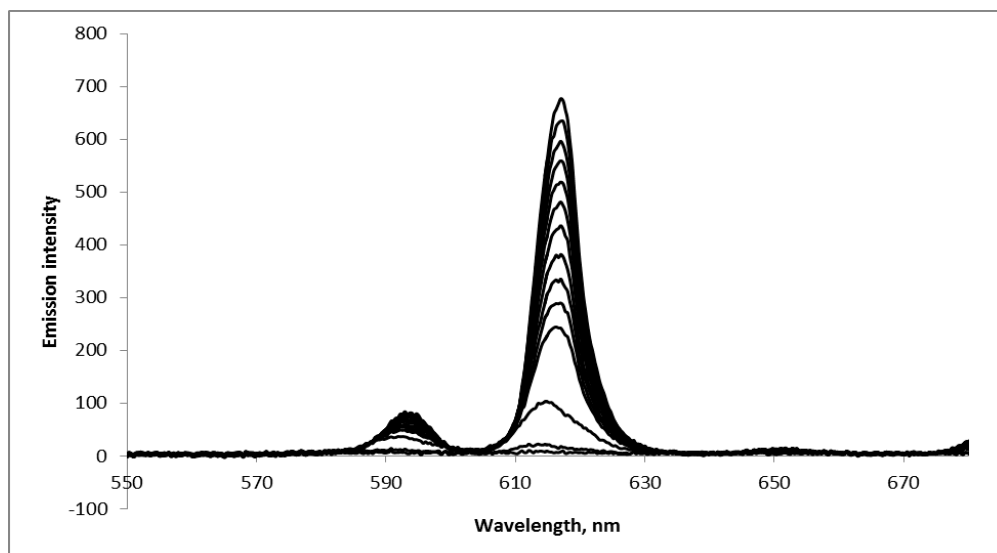


Figure S15. Luminescence emission quenching of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ in acetonitrile upon addition of up to 5 molar equivalents of TBAF.

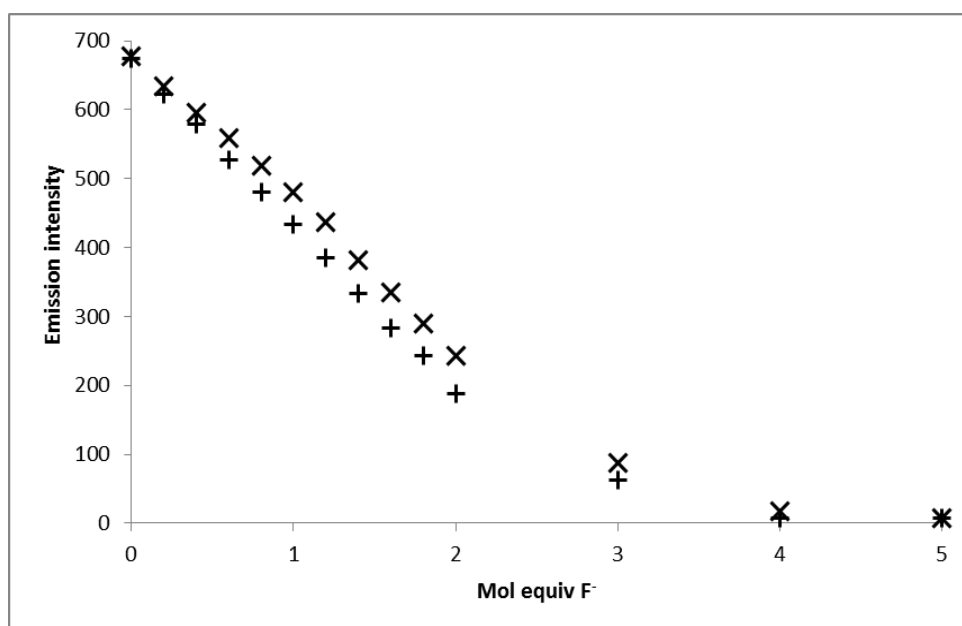


Figure S16. Luminescence emission quenching ($\lambda_{\text{em}} = 617 \text{ nm}$) of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ in acetonitrile upon addition of TBAF. Titration done in duplicate and both sets of data are shown (X, +).

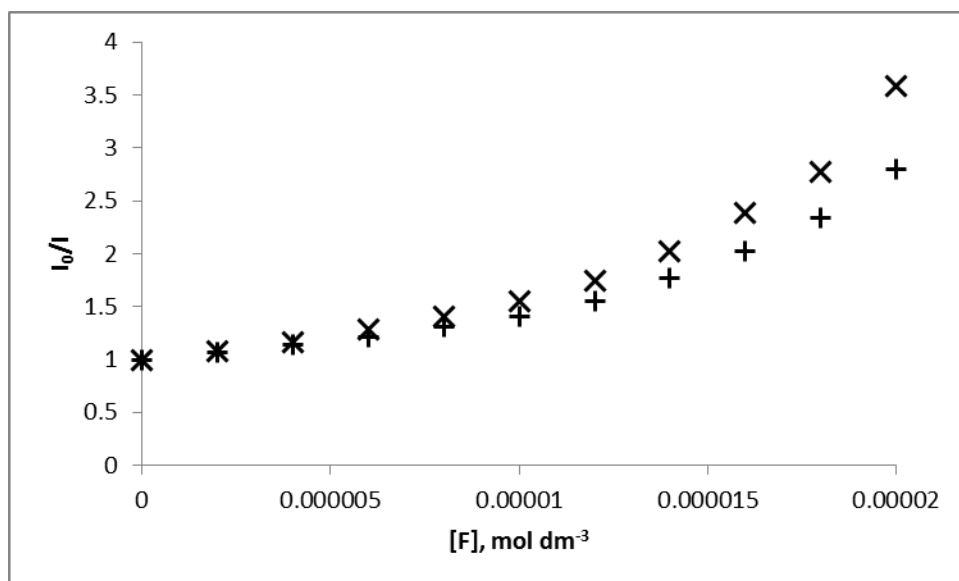


Figure S17. Stern-Volmer plot generated from the titration of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ with TBAF in acetonitrile. Results from duplicate titrations (X, +).

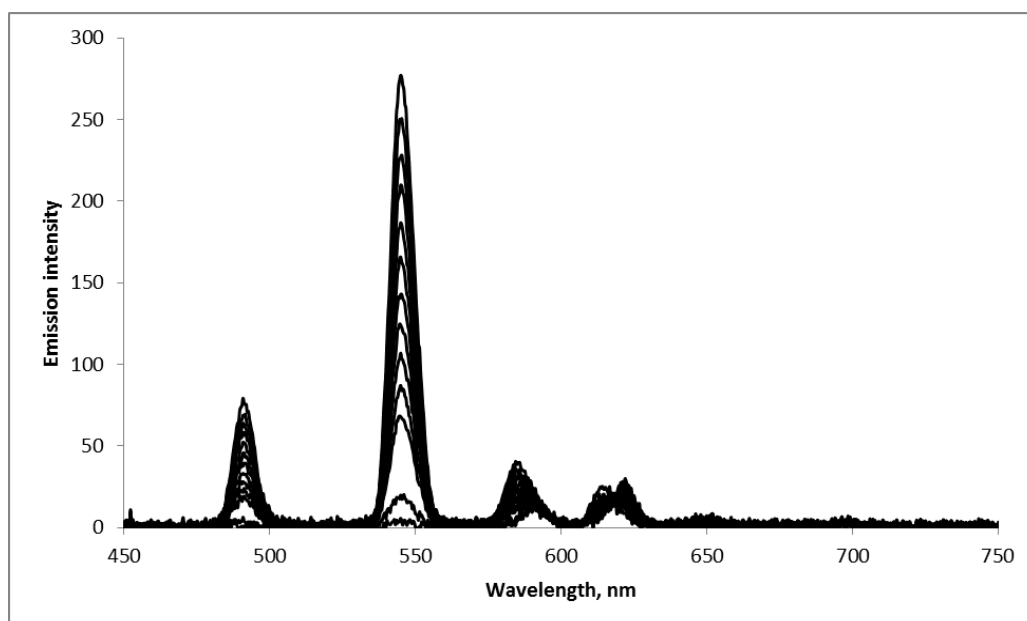


Figure S18. Luminescence emission quenching of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ in acetonitrile upon addition of up to 4 molar equivalents of TBAF.

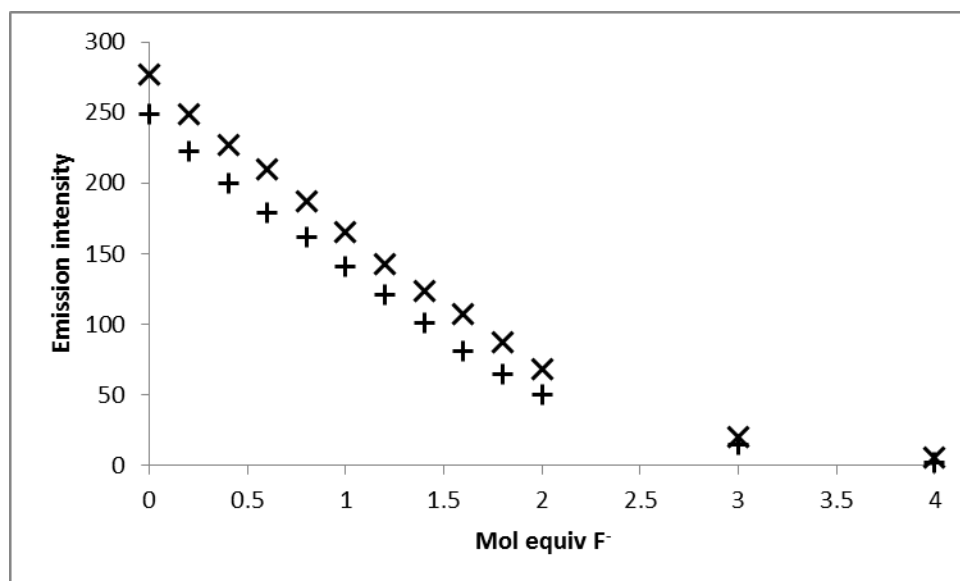


Figure S19. Luminescence emission quenching ($\lambda_{em} = 545 \text{ nm}$) of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ in acetonitrile upon addition of TBAF. Titration done in duplicate and both sets of data are shown (X, +).

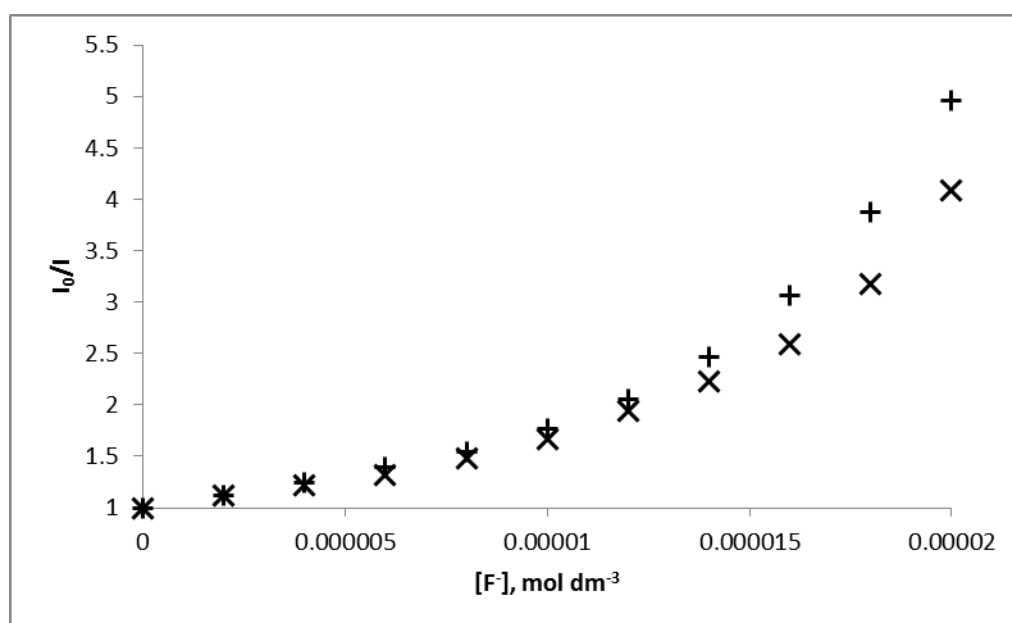


Figure S20. Stern-Volmer plot generated from the titration of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ with TBAF in acetonitrile. Results from duplicate titrations (X, +).

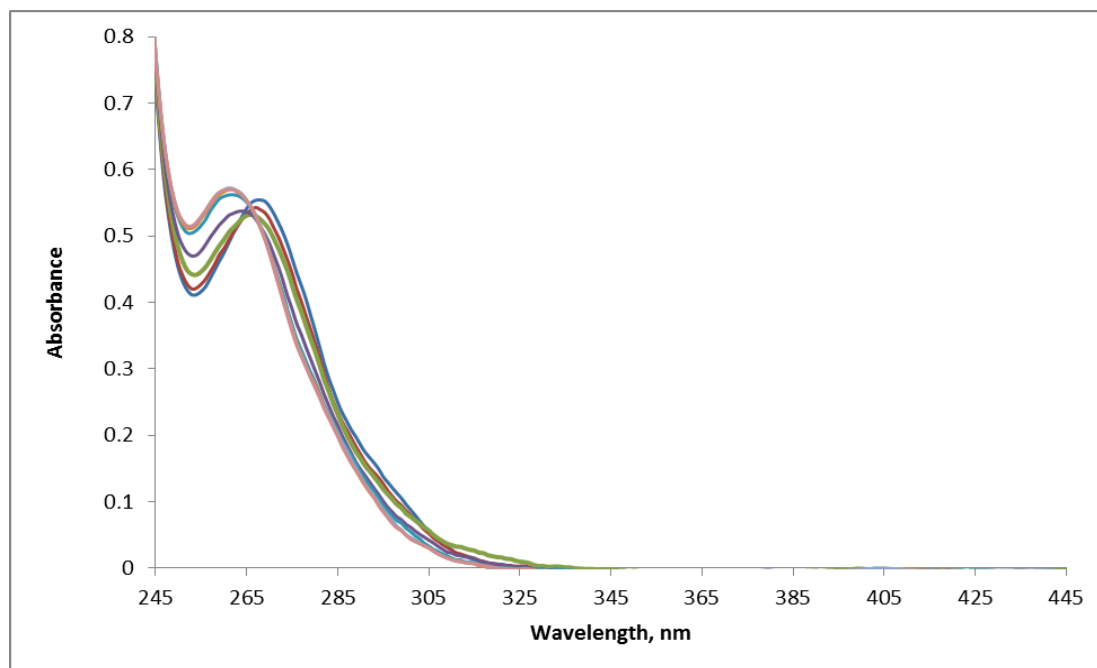


Figure S21. UV-Vis spectral plot generated from the titration of $\text{Tb}(\text{phen})_2(\text{NO}_3)_3$ with TBAF in acetonitrile. Spectra recorded at 0,1,2,3,4,5,7 and 10 molar equivalents of TBAF.