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Converting an intensity-based sensor to a ratiometric sensor: luminescence colour switching of an Ir/Eu dyad upon binding of a V-series chemical warfare agent simulant

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Electronic Supporting Information

Experimental details

General details:

UV/Vis absorption spectra were measured on a Varian Cary 50 spectrophotometer. Steady-state luminescence spectra were measured on a Jobin-Yvon Fluoromax 4 fluorimeter, using 1 cm quartz cuvettes with samples sufficiently dilute to have an optical density of no more than 0.2 at the excitation wavelength. Luminescence titrations were performed in air-equilibrated MeCN at room temperature. Unless stated otherwise, calculation of 1 : 1 K values from luminescence data was performed using a program that has been described previously.¹

The following compounds were prepared according to literature procedures: Ir•L,² Eu(hfac)₃(H₂O)₂,³ and VO.⁴

Titration details:

A: Eu(hfac)₃(H₂O)₂ + DMMP

A stock solution of DMMP (1.85×10^{-1} M) in Eu(hfac)₃(H₂O)₂ (8.26×10^{-5} M in MeCN) was titrated into Eu(hfac)₃(H₂O)₂ (8.26×10^{-5} M), such that the concentration of Eu(hfac)₃(H₂O)₂ was constant throughout, to give the species Eu.(DMMP)₂. The final concentration of DMMP in this titration was 1.04×10^{-2} M. The excitation wavelength used was 340 nm, and emission was recorded between 400-700 nm. The intensities between 600 – 630 nm were integrated and plotted against [DMMP] (see above for tabulated binding constant data).

B: Eu(hfac)₃(H₂O)₂ + Et₃N

A stock solution of Et₃N (2.16×10^{-2} M) in Eu(hfac)₃(H₂O)₂ (7.27×10^{-5} M in MeCN) was titrated into Eu(hfac)₃(H₂O)₂ (7.27×10^{-5} M), such that the concentration of Eu(hfac)₃(H₂O)₂ was constant throughout, to give the species Eu.(Et₃N)₂. The final concentration of Et₃N in this titration was 5.96×10^{-3} M. The excitation wavelength used was 340 nm, and emission was recorded between 400-700 nm. The intensities between 600 – 630 nm were integrated and plotted against [Et₃N].

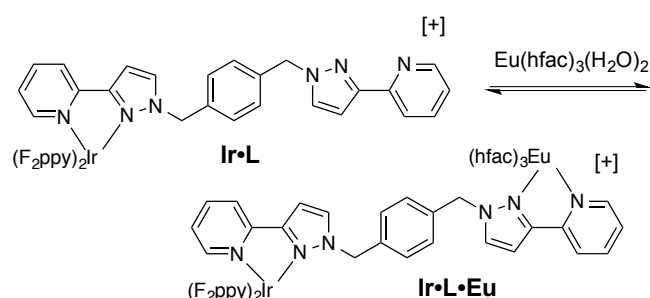
C: Eu(hfac)₃(H₂O)₂ + VO \rightleftharpoons Eu•VO + 2H₂O (*Scheme 2*)

A stock solution of VO (1.21×10^{-2} M) in Eu(hfac)₃(H₂O)₂ (7.50×10^{-5} M in MeCN) was titrated into Eu(hfac)₃(H₂O)₂ (7.50×10^{-5} M), such that the concentration of Eu(hfac)₃(H₂O)₂ was constant throughout, to give the species Eu.VO. The final concentration of VO in this titration was 4.88×10^{-3} M. The excitation wavelength used was 340 nm, and emission was recorded

between 400-700 nm. The intensities between 600 – 630 nm were integrated and plotted against [VO]. Data was fit using the following equation for multiple binding constants:⁵

$$\text{calcInt} = f + ((b_1-f)K_1[G]) + ((b_2-f)K_1K_2[K]^2) / 1 + (K_1[G]) + (K_1K_2[G]^2)$$

D: $\text{Ir}\cdot\text{L} + \text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2 \rightleftharpoons \text{Ir}\cdot\text{L}\cdot\text{Eu} + 2\text{H}_2\text{O}$ (Scheme 1)

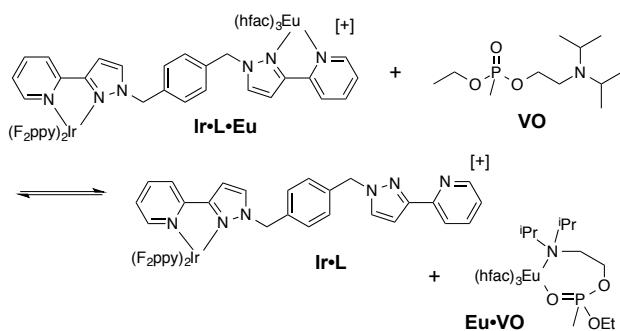


A stock solution of $\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2$ (1.16×10^{-3} M) in $\text{Ir}\cdot\text{L}$ (1.04×10^{-4} M in MeCN) was titrated into $\text{Ir}\cdot\text{L}$ (1.04×10^{-4} M), such that the concentration of $\text{Ir}\cdot\text{L}$ was constant throughout, to give the species $\text{Ir}\cdot\text{L}\cdot\text{Eu}$. The final concentration of $\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2$ in this titration was 4.97×10^{-4} M.

The excitation wavelength used was 395 nm, and emission was recorded between 405-780 nm.

The intensities between 600 – 630 nm were integrated and plotted against [Eu].

E: $\text{Ir}\cdot\text{L}\cdot\text{Eu} + \text{VO} \rightleftharpoons \text{Ir}\cdot\text{L} + \text{Eu}\cdot\text{VO}$



Initial titration:

A solution of $\text{Ir}\cdot\text{L}\cdot\text{Eu}$ was prepared with $\text{Ir}\cdot\text{L}$ (1.04×10^{-4} M) and $\text{Eu}(\text{hfac})_3$ (1.15×10^{-4} M), giving $[\text{Ir}\cdot\text{L}\cdot\text{Eu}] = K \cdot [\text{Ir}] \cdot [\text{Eu}] = (8.15 \times 10^{-5}$ M).

A stock solution of VO (1.56×10^{-2} M) in $\text{Ir}\cdot\text{L}\cdot\text{Eu}$ (8.15×10^{-5} M in MeCN) was titrated into $\text{Ir}\cdot\text{L}\cdot\text{Eu}$ (8.15×10^{-5} M), such that the concentration of $\text{Ir}\cdot\text{L}\cdot\text{Eu}$ was constant throughout, to give

the species Ir•L + Eu•VO. The final concentration of VO in this titration was 6.50×10^{-3} M. The excitation wavelength used was 395 nm, and emission was recorded between 405-780 nm.

The intensities between 600 – 630 nm were integrated and plotted against [VO].

Titration using more concentrated solutions:

A solution of Ir.L.Eu was prepared with Ir.L (3.85×10^{-4} M) and Eu(hfac)₃ (1.14×10^{-4} M), giving [Ir.L.Eu] = $k \cdot [\text{Ir}] \cdot [\text{Eu}] = (3.01 \times 10^{-4}$ M).

A stock solution of VO (1.69×10^{-2} M) in Ir.L.Eu (3.01×10^{-4} M in MeCN) was titrated into Ir.L.Eu (3.01×10^{-4} M), such that the concentration of Ir.L.Eu was constant throughout, to give the species Ir.L + Eu.VO. The final concentration of VO in this titration was 6.77×10^{-3} M. The excitation wavelength used was 395 nm, and emission was recorded between 405-780 nm.

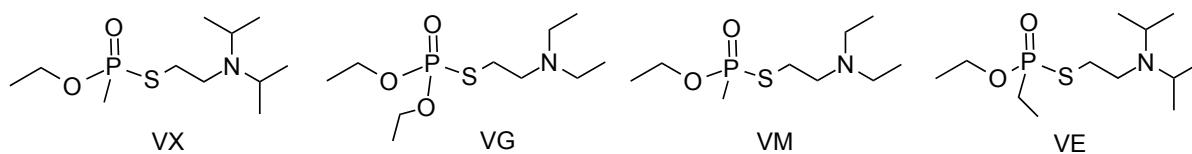
The intensities between 600 – 630 nm were integrated and plotted against [VO].

References

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Additional figures

Selected V-Series Chemical Warfare Agents



Selected G-Series Chemical Warfare Agents

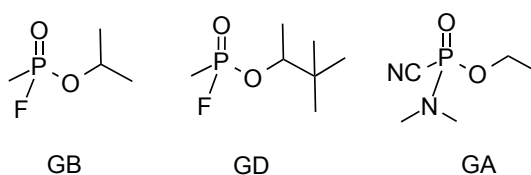


Fig. S1: Structural diagrams of some V-series and G-series OP CWAs

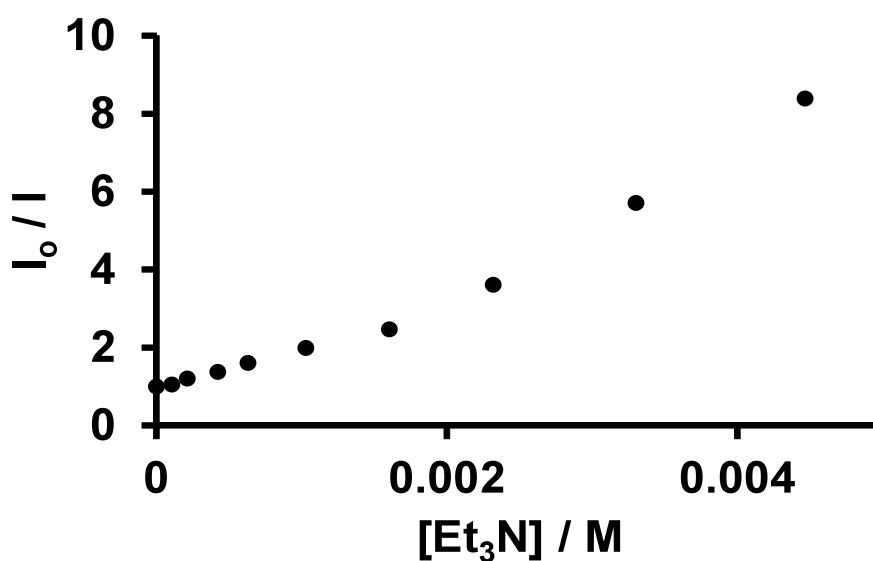


Fig. S2. Stern-Volmer plot of the luminescence data shown in Fig. 1(b) of the main text, from titration of $[\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2]$ with Et_3N in MeCN. The upward curvature indicates a combination of static and dynamic quenching; it could not be fitted well to a simple model with two quenching rate constants, as has been noted before (refs. 10 and 11, main text).

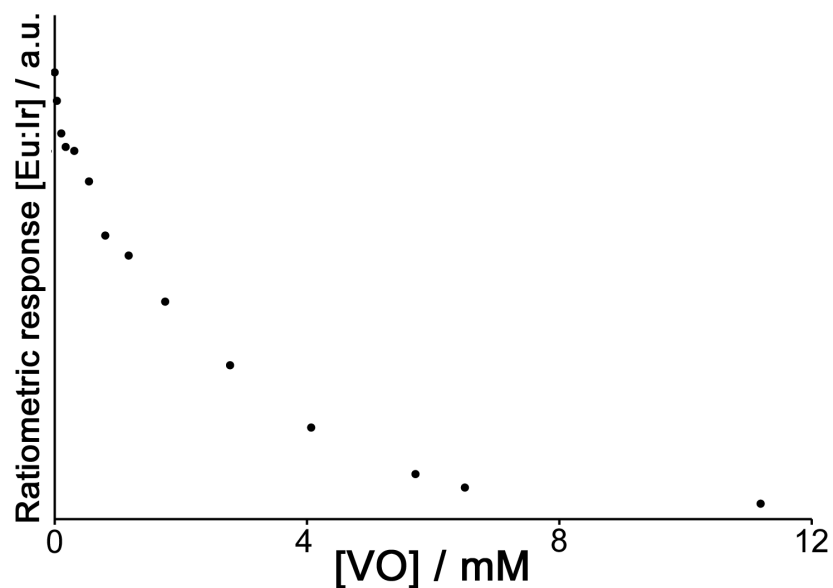


Fig. S3. Ratio of Eu:Ir emission intensity during addition of VO to Ir•L•Eu, based on the data in Fig. 4 of the main text. The Eu-based emission intensity is the integrated emission intensity of the main 612 nm band (to avoid issues associated with small changes in lineshape); the Ir-based emission intensity is just measured directly at the emission maximum.

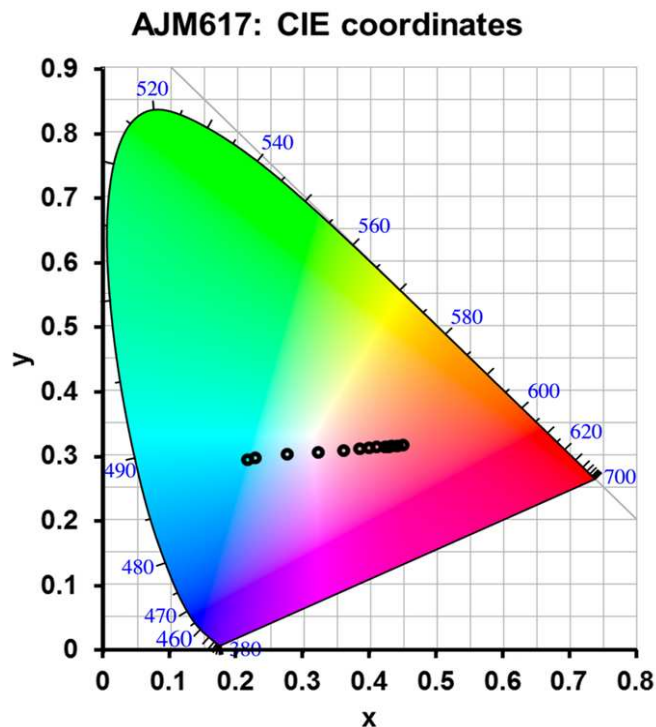


Fig. S4. Change in colour of the luminescence from red to blue (shown by circles moving from right to left) based on the data shown in Fig. 5a of the main text, recorded during titration of VO into Ir•L•Eu in MeCN.

Summary table of binding constants / quenching constants

$\text{Ir}\cdot\text{L} + \text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2$ (Scheme 1, Fig. 3)	6800 M ⁻¹
$\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2 + 2\text{DMMP}$ (Fig. 1a)	2400 M ⁻²
$\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2 + \text{Et}_3\text{N}$ (Fig. 1b)	780 M ⁻¹
$\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2 + \text{VO}$ (Fig. 2a)	70000 M ⁻¹ (rise of luminescence) 640 M ⁻¹ (decay of luminescence)
$\text{Ir}\cdot\text{L}\cdot\text{Eu} + \text{VO}$ (Scheme 2, Fig. 4)	410 M ⁻¹ (decay of luminescence)