Detection of aqueous and gaseous hydrogen sulfide with lanthanide-macrocycle binary complexes

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Table of Contents

Mass spectra

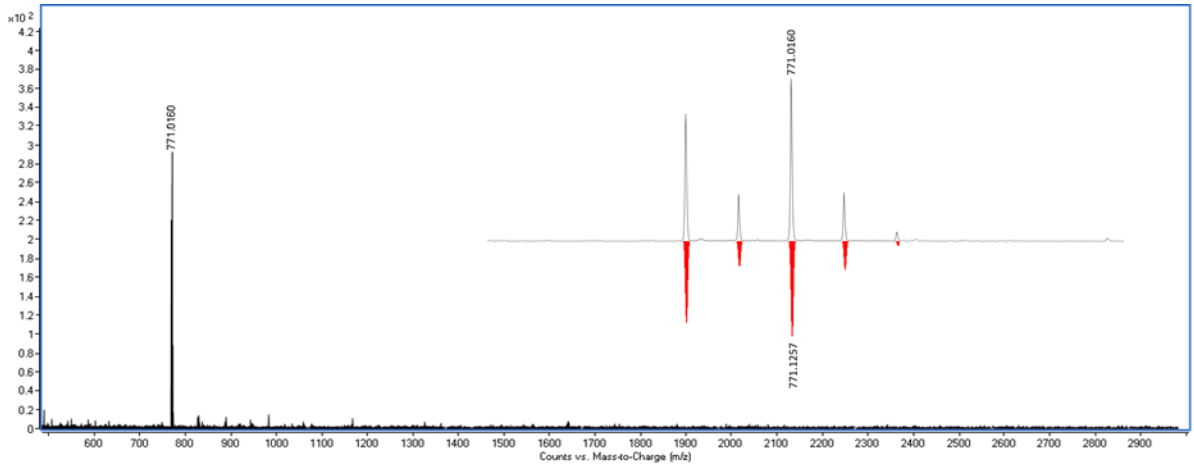

Figure S1. HRMS of [Eu.**2**].Na, insert: expanded MS with the matching predicted isotope pattern displayed in red.

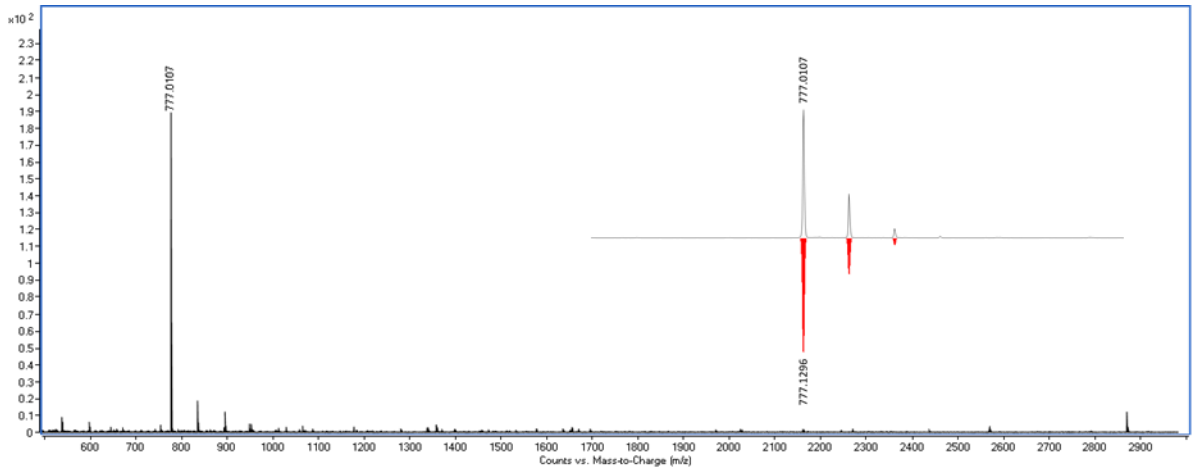

Figure S2. HRMS of [Tb.**2**].Na, insert: expanded MS with the matching predicted isotope pattern displayed in red.

NMR spectra

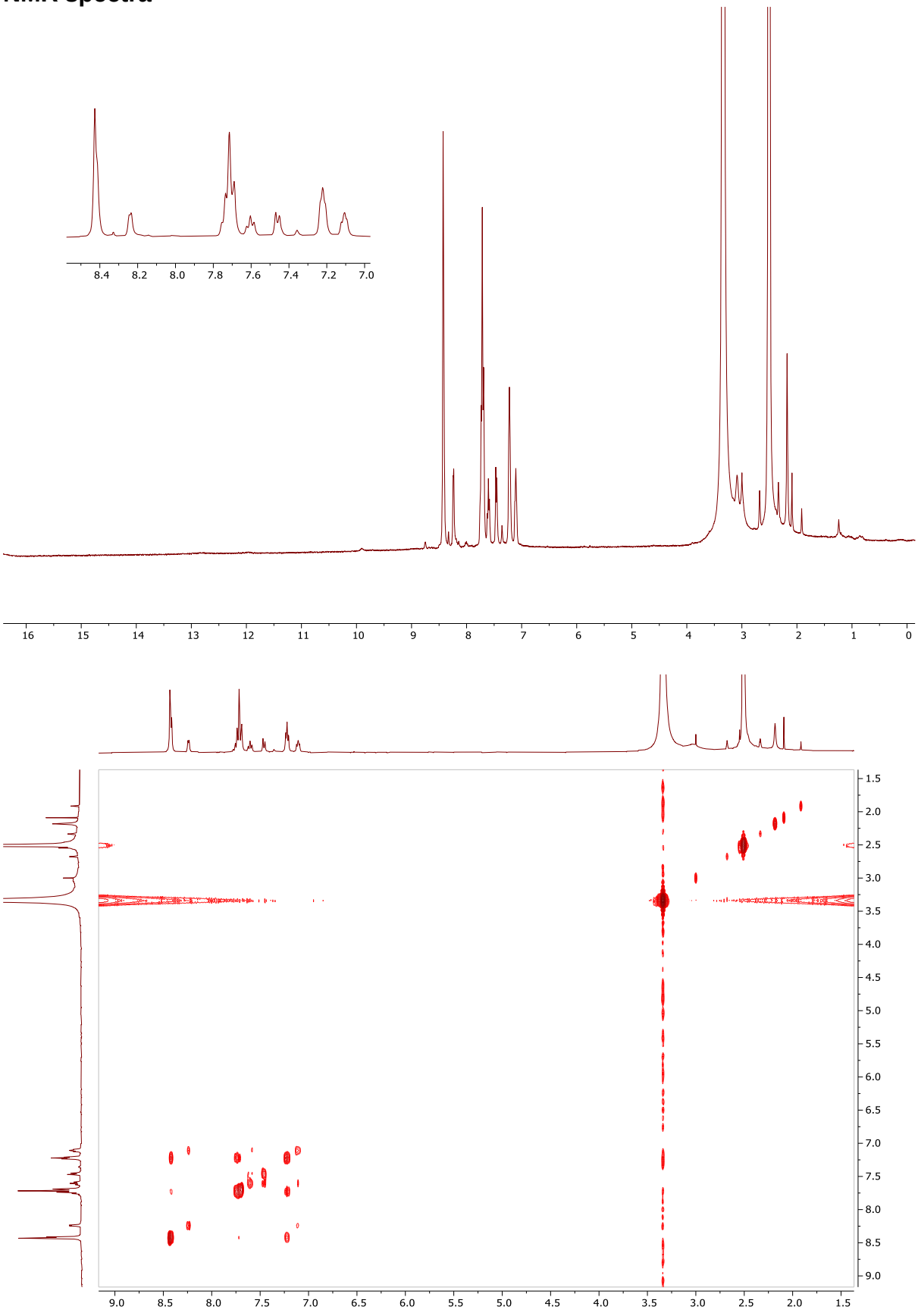

Figure S3. ^{1}H NMR spectrum of [Eu.**2**] (400 MHz, DMSO-d_6), (top), with expansion shown, and the ^{1}H/^{1}H COSY NMR spectrum of [Eu.**2**] (bottom).

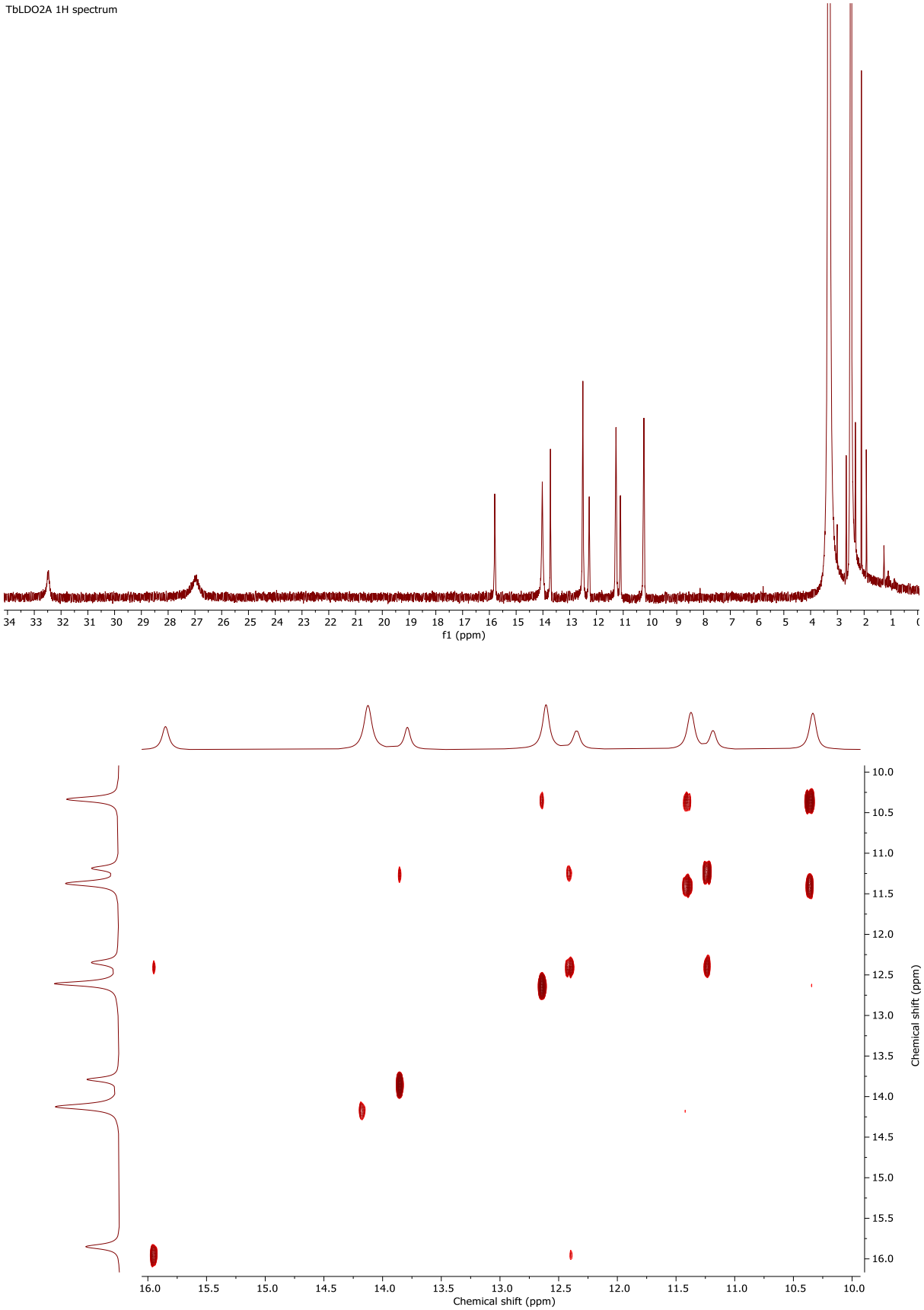

Figure S4. ^{1}H NMR spectrum of [Tb.**2**] (400 MHz, DMSO-d_6) (top) and ^{1}H/^{1}H COSY NMR spectrum (10-16 ppm) of [Tb.**2**] (bottom).

Solution luminescence studies:

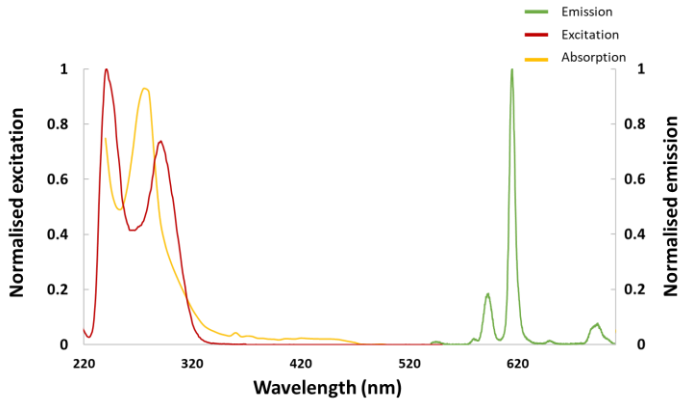

Figure S5. Absorption (yellow line), excitation (red line, λ_{em} = 615 nm), and emission (green line, λ_{ex} = 250 nm) spectra of 10 µM Eu.**2**, in 10 mM Tris-HCl buffer, pH 7.4

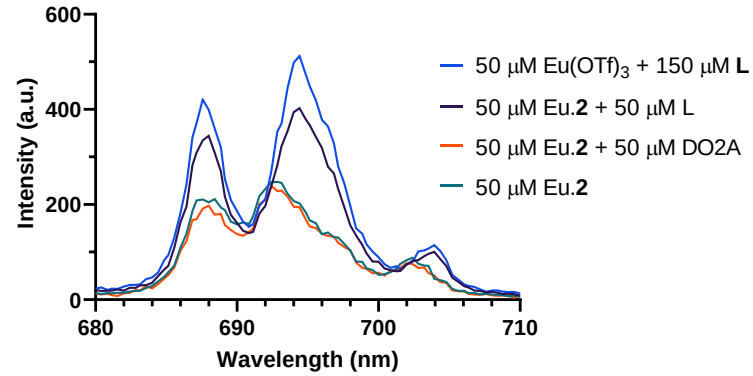

Figure S6. The time-gated emission spectra (680-710 nm, λ_{ex} = 250 nm) spectra of 50 µM Eu.**2** ([Eu(DO2A)(triazole-DPA)]$^-$), with i) alone, ii) 1 equivalent of DO2A, iii) 1 equivalent of **L**, or iv) 50 µM $[Eu\mathbf{L}_3]^{3-}$ formed *in situ*. All solutions are in 10 mM Tris-HCl buffer, pH 7.4; excitation slit width 10 nm, emission slit width 1.5 nm.

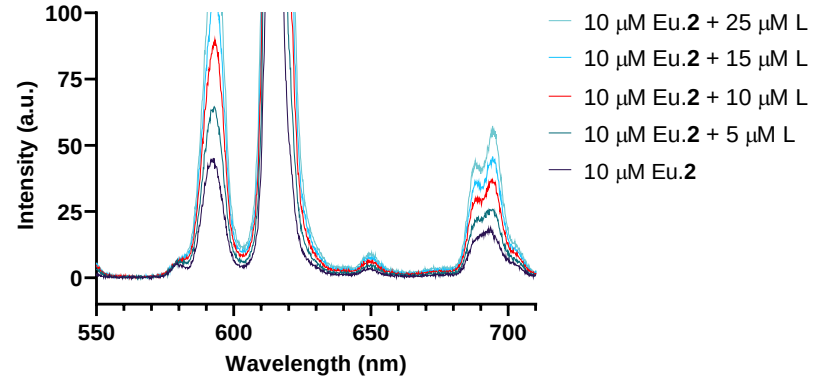

Figure S7. The time-gated emission spectra (λ_{ex} = 250 nm) spectra of 10 µM Eu.**2** ([Eu(DO2A)(triazole-DPA)]$^-$), with varying amounts of **L** (triazole-DPA), in 10 mM Tris-HCl buffer, pH 7.4, excitation slit width 5 nm, emission slit width 5 nm.

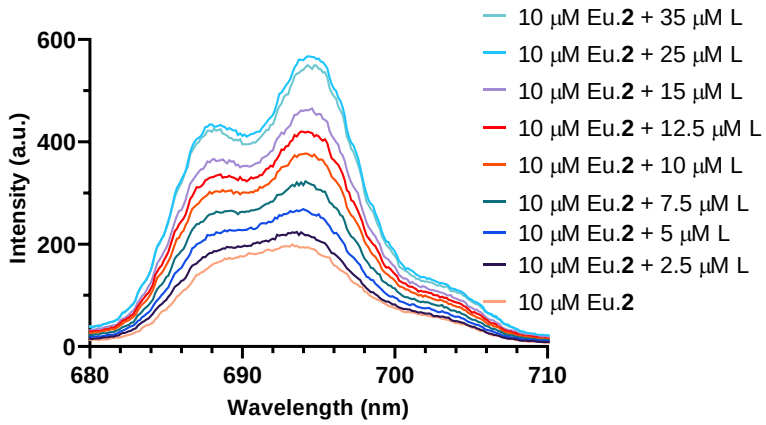

Figure S8. Selected region of the time-gated emission spectra (680-710 nm, λ_{ex} = 250 nm) spectra of 10 μM Eu.**2** ([Eu(DO2A)(triazole-DPA)]$^-$), with varying amounts of **L** (triazole-DPA), in 10 mM Tris-HCl buffer, pH 7.4, excitation slit width 5 nm, emission slit width 5 nm.

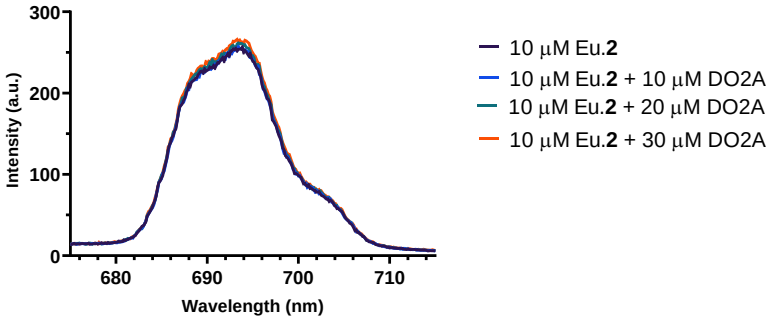

Figure S9. Selected region of the time-gated emission spectra (675-715 nm, λ_{ex} = 250 nm) spectra of 10 μM Eu.**2** ([Eu(DO2A)(triazole-DPA)]$^-$), with varying amounts of DO2A, in 10 mM Tris-HCl buffer, pH 7.4, excitation slit width 5 nm, emission slit width 5 nm.

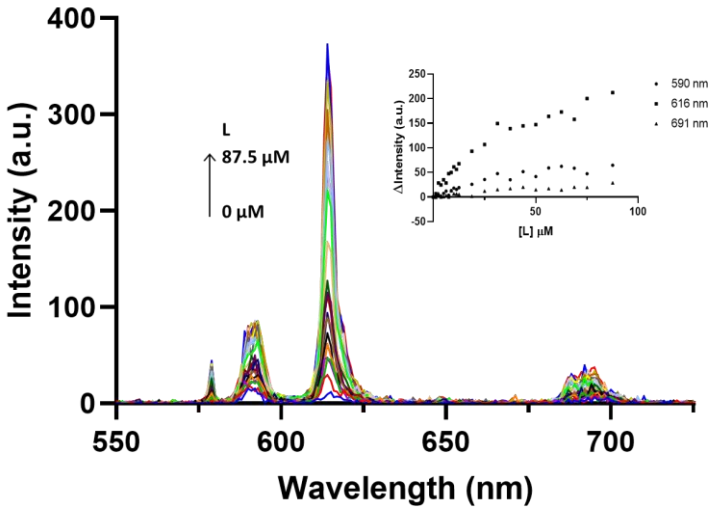

Figure S10. The time-gated emission spectra (λ_{ex} = 250 nm) of [Eu(DO2A)]$^+$ (50 μM) with the addition of various amounts of **L** (0 to 87.5 μM), insert Luminescent intensity changes detected at the wavelengths noted; spectra measured in 10 mM Tris HCl buffer (pH 7.4). The association constant was determined by fitting to binding models using a custom written python program BindFit available at www.supramolecular.org; http://app.supramolecular.org/bindfit/view/f71fe141-81eb-4b7a-8899-e3e020bbe69c.

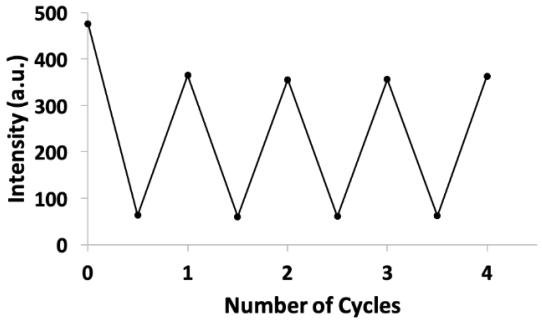

Figure S11. Luminescence intensity of Eu.**2** (10 μM) in 10 mM Tris-HCl buffer, pH 7.4, containing <5% DMSO upon the alternate addition of Cu^{2+} ions (10 μM) and Na_2S (10 μM) at 615 nm; spectra measured in 10 mM Tris HCl buffer (pH 7.4) with λ_{ex} = 250 nm, (n = 1).

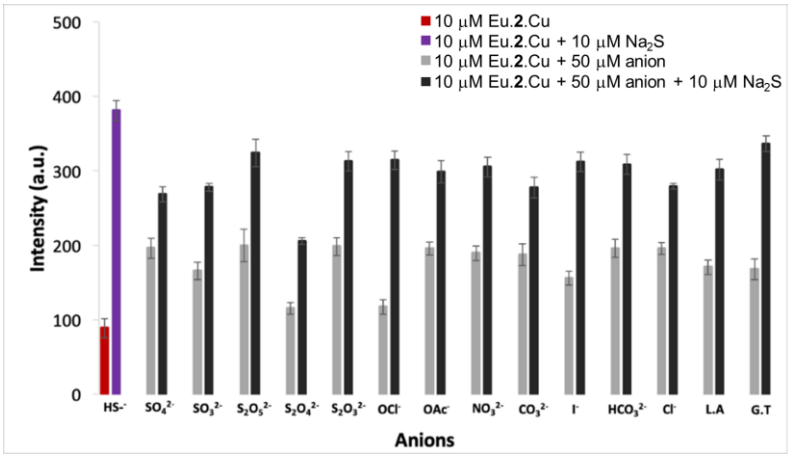

Figure S12. Eu.**2**.Cu (10 μM) in the presence of various anions; Red bar: Eu.**2**.Cu (10 μM); purple bar: Eu.**2**.Cu (10 μM) + Na_2S (10 μM); (light grey bars: Eu.**2**.Cu (10 μM) + anion (50 μM); Black bars: Eu.**2**.Cu (10 μM) + anion (50 μM) + Na_2S (10 μM); spectra measured in 10 mM Tris-HCl buffer (pH 7.4), containing <5% DMSO, λ_{ex} = 250 nm, λ_{em} = 615 nm and showing the average of triplicate results (n=3). L.A = lipoic acid, G.T. = glutathione.

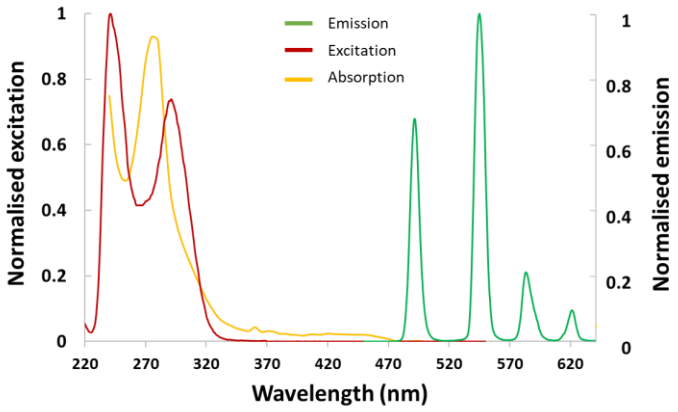

Figure S13. Absorption (yellow line), excitation (red line, λ_{em} = 545 nm), and emission (green line, λ_{ex} = 250 nm) spectra of **Tb.2** (10 μM), in 10 mM Tris-HCl buffer, pH 7.4, containing <5% DMSO.

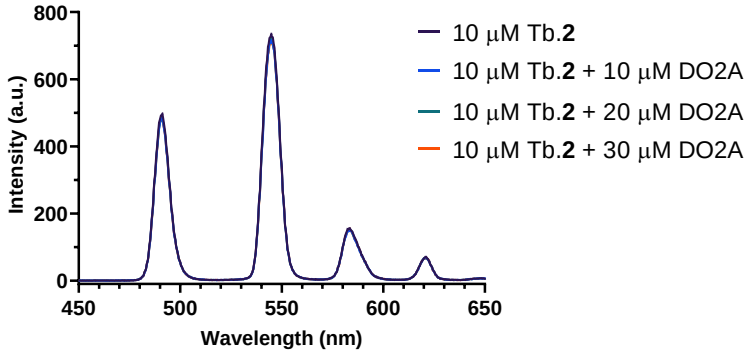

Figure S14. The time-gated emission spectra (570-600 nm, λ_{ex} = 250 nm) spectra of 50 μM Tb.**2** ([Tb(DO2A)(triazole-DPA)]$^{-}$), with i) alone, ii) 1 equivalent of DO2A, iii) 1 equivalent of **L**, or iv) 50 μM [Tb**L**$_3$]$^{3-}$ formed *in situ*. All solutions are in 10 mM Tris-HCl buffer, pH 7.4; excitation slit width 10 nm, emission slit width 1.5 nm.

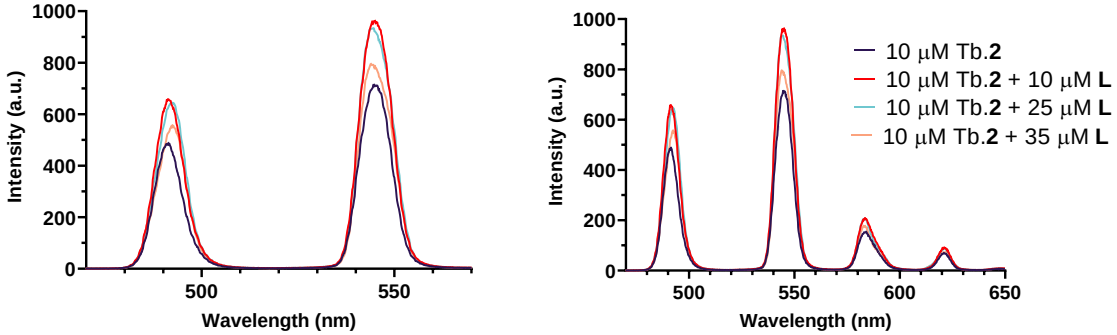

Figure S15. The time-gated emission spectra (470-570 nm and 450-650 nm, λ_{ex} = 250 nm) spectra of 10 μM Tb**.2** ([Tb(DO2A)(triazole-DPA)]$^{-}$), with varying amounts of **L** (triazole-DPA), in 10 mM Tris-HCl buffer, pH 7.4, excitation slit width 5 nm, emission slit width 5 nm. There is a shift with the addition of excess **L** (light blue and orange lines), indicative of formation of [TbL$_3$]$^{3-}$

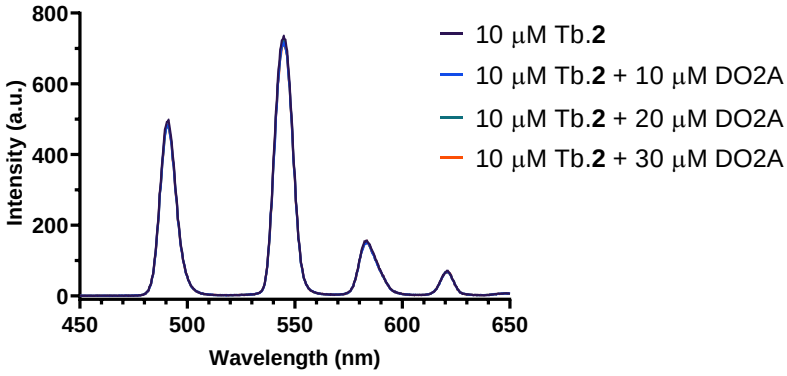

Figure S16. The time-gated emission spectra (λ_{ex} = 250 nm) spectra of 10 μM Tb**.2** ([Tb(DO2A)(triazole-DPA)]$^{-}$), with varying amounts of DO2A, in 10 mM Tris-HCl buffer, pH 7.4, excitation slit width 5 nm, emission slit width 5 nm. The intensity of signals does not change with addition of excess DO2A.

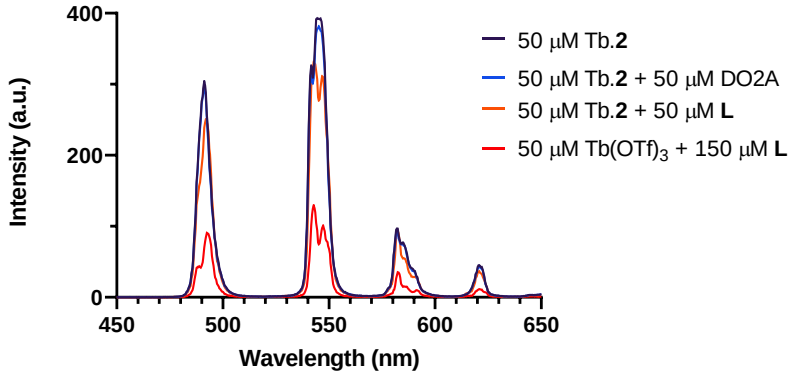

Figure S17. The time-gated emission spectra (450-650 nm, λ_{ex} = 250 nm) spectra of 50 μM Tb.**2** ([Tb(DO2A)(triazole-DPA)]$^{-}$), with i) alone, ii) 1 equivalent of DO2A, iii) 1 equivalent of **L**, or iv) 50 μM [Tb**L**$_3$]$^{3-}$ formed *in situ*. All solutions are in 10 mM Tris-HCl buffer, pH 7.4; excitation slit width 10 nm, emission slit width 1.5 nm.

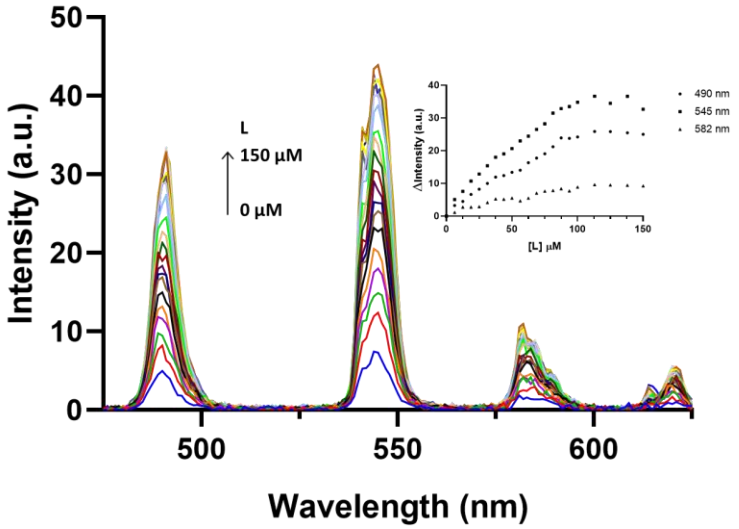

Figure S18. The time-gated emission spectra (λ_{ex} = 250 nm) of [Tb(DO2A)]$^{+}$ (50 μM) with the addition of various amounts of **L** (0 to 150 μM), insert Luminescent intensity changes detected at the selected wavelengths noted; spectra measured in 10 mM Tris HCl buffer (pH 7.4). The association constant was determined by fitting to binding models using a custom written python program BindFit available at www.supramolecular.org; http://app.supramolecular.org/bindfit/view/509e824f-0d66-4c66-9089-62c0d549f76e.

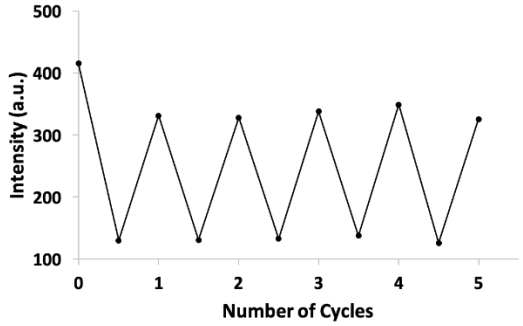

Figure S19. Luminescence intensity of Tb.**2** (10 μM) in 10 mM Tris-HCl buffer, pH 7.4, containing <5% DMSO upon the alternate addition of Cu^{2+} ions (10 μM) and Na_2S (10 μM) at 545 nm; spectra measured in 10 mM Tris HCl buffer (pH 7.4) with λ_{ex} = 250 nm, (n = 1).

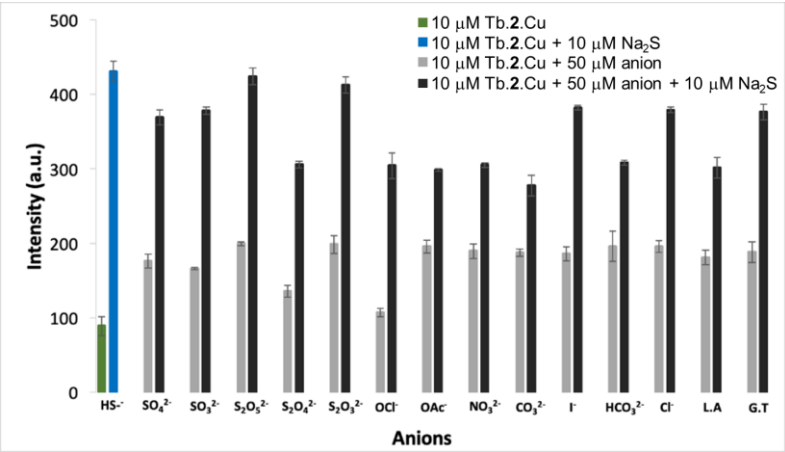

Figure S20. Tb.**2**.Cu (10 μM) in the presence of various anions; Green bar: Tb.**2**.Cu (10 μM); Blue bar: Tb.**2**.Cu (10 μM) + Na_2S (10 μM); (Grey bars: Tb.**2**.Cu (10 μM) + anion (50 μM); Black bars: Tb.**2**.Cu (10 μM) + anion (50 μM) + Na_2S (10 μM); spectra measured in 10 mM Tris-HCl buffer (pH 7.4), containing <5% DMSO, λ_{ex} = 250 nm, λ_{em} = 545 nm and showing the average of triplicate results (n=3). L.A = lipoic acid, G.T. = glutathione.

Paper-based luminescence studies:

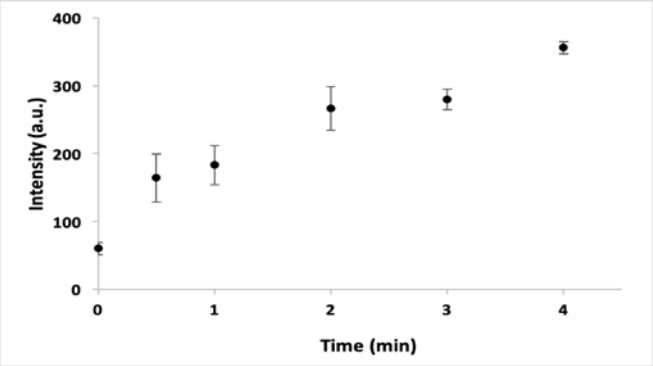

Figure S21. Change in luminescence intensity of filter paper discs impregnated with [**Eu.2**.Cu^{2+}]$^{+}$ at 615 nm upon exposure to 6 ppm gaseous $H_2S_{(g)}$ over time (0.5 – 4 min), 23 °C. Showing the average of triplicate results (n=3).

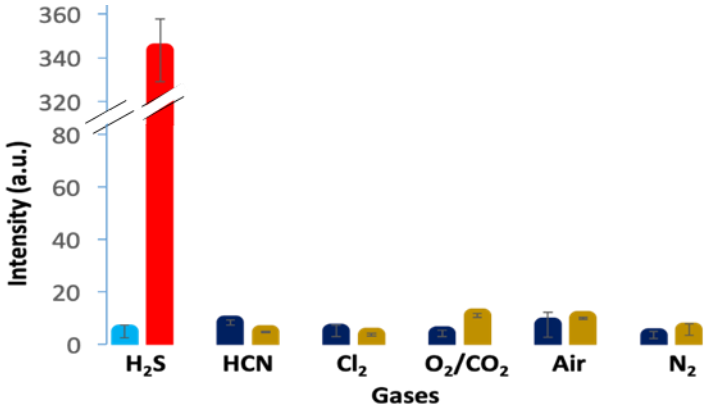

Figure S22. a) Time-delayed emission spectra of filter paper discs impregnated with Eu.**2**.Cu in the presence of various gases; Light blue bar: Eu.**2**.Cu; Red bar: Eu.**2**.Cu + H_2S (4 ppm, 0.5 L/min for 4 min); Dark blue bars: Eu.**2**.Cu prior to exposure; Brown bars: after exposure to the respective gases [HCN (4 ppm, 0.5 L/min for 4 min), Cl_2 (4 ppm, 0.5 L/min for 4 min), O_2/CO_2 (4 min exposure), Air (4 min exposure), N_2 (4 min exposure); spectra measured at λ_{ex} = 250 nm, λ_{em} = 615 nm and showing the average of triplicate results (n=3).