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Supplementary Information for:

Sensing a *Bacillis Anthracis* Biomarker with well-known OLED Emitter $EuTta_3Phen$

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General Experimental:

Synthesis of $Eu(Tta)_3Phen$ was synthesized as previously described (and outlined below). Dry solvents were obtained from a solvent purification system (Innovation Technologies) free of stabilizers. All organic reagents were purchased from Aldrich Chemical Company and used without further purification. ^{1}H-NMR spectral analyses were performed on a JEOL ECS-400MHz NMR spectrometer THF-d_8 as the solvent purchased from Goss Scientific and used directly from ampules. Mass determinations were performed by Southampton Mass Spectrometry Service based out of Southampton University. The spectra were taken using a MaXis HPLC-ESI spectrometer equipped with a Time of Flight analyser. UV- Vis spectra were taken on a Shimadzu UV-1800 Spectrometer using 1 cm quartz cells, while fluorimetry data was collected on an Edinburgh Instruments FS5 Fluorescence emission spectrophotometer using 1 cm quartz cells. All titration experiments were performed using Hamilton airtight microsyringes. Elemental analyses were performed by the London Metropolitan University Elemental Analysis Service.

Experimental Procedures:

*Preparation $Eu(Tta)_3Phen$ (**1**).*[1]

Europium(III) chloride hexahydrate (0.500g, 1.37 mmol) was dissolved in the minimum amount of methanol (~20 mL). A solution of *thenoyltrifluoroacetone (TtaH)* (0.850g, 3.83mmol) in methanol (6 ml) was added and left to stir for half an hour. The transparent solution was neutralized using 5% NaOH solution, followed by dropwise addition of a *1,10-phenanthroline (Phen)* solution (0.243 g, 1.35 mmol) in methanol (3 mL). The milky mixture was allowed to stir for half an hour. The solution was then vacuum-filtered and washed repeatedly with methanol. The filtered sample was left on a high-vacuum line to dry the sample overnight before being sealed with parafilm, wrapped in foil and placed in a draw to eliminate potential sample photo-degradation. ^{1}H NMR (400 MHz, THF-d_8) δ 10.39 (bs), 9.67 (bs), 8.61 (bs), 7.07 (bs), 6.33 (bs), 5.83 (bs), 2.38 (bs). CHN-Anal. calc'd for $C_{37}H_{24}F_9N_2O_7S_3Eu$: C, 43.24; H, 2.35; N, 2.73; found C, 43.61; H, 2.04; N, 2.71.

*Preparation of $La(Tta)_3Phen$ (**2**).*[1]

*A modified procedure from **1**, Lanthanum(III) Nitrate hydrate* (0.590g, 1.3 mmol) was dissolved in the minimum amount of methanol (~20 mL). A solution of *thenoyltrifluoroacetone (TtaH)* (0.850g, 3.83mmol) in methanol (6 ml) was added and left to stir for half an hour. The transparent solution was neutralized using 5% NaOH solution, followed by dropwise addition of a *1,10-phenanthroline (Phen)* solution (0.243 g, 1.35 mmol) in methanol (3 mL). The milky mixture was allowed to stir for half an hour. The solution was then vacuum-filtered and washed repeatedly with methanol. The filtered sample was left on a high-vacuum line to dry the sample overnight. ^{1}H NMR (400 MHz, THF-d_8) δ 9.71 (bs,

2H), 8.36 (bs, 2H), 7.80 (bs, 3H), 7.71 (bs, 2H), 7.46 (bs, 2H), 7.45 (bs, 3H), 6.89 (bs, 3H), 6.01 (bs, 3H); ^{13}C NMR (400 MHz, THF-d_8) δ 180.1, 151.1, 146.3, 145.6, 136.8, 131.5, 129.0, 128.9, 127.4, 126.3, 123.2, 120.8, 90.7. CHN-Anal. calc'd for $C_{37}H_{24}F_9N_2O_7S_3La$: C, 43.80; H, 2.38; N, 2.76; found C, 43.34; H, 2.25; N, 3.22.

UV-Vis absorption Studies:

Series of spectra were collected assessing the absorption spectra of **1** and the response imparted by the respective addition of H_2O, TBA·H_2PO_4, and/or dipicolinic acid in small aliquots, as noted.

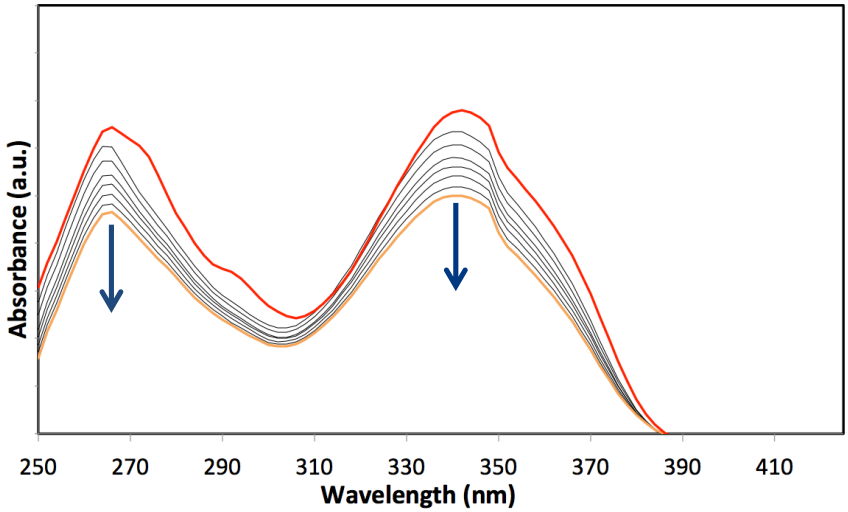

Figure S1. Eu(Tta)$_3$Phen **1** (1x10^{-5} M; THF) titrated with 5% aliquots of deionised H_2O at 298 K.

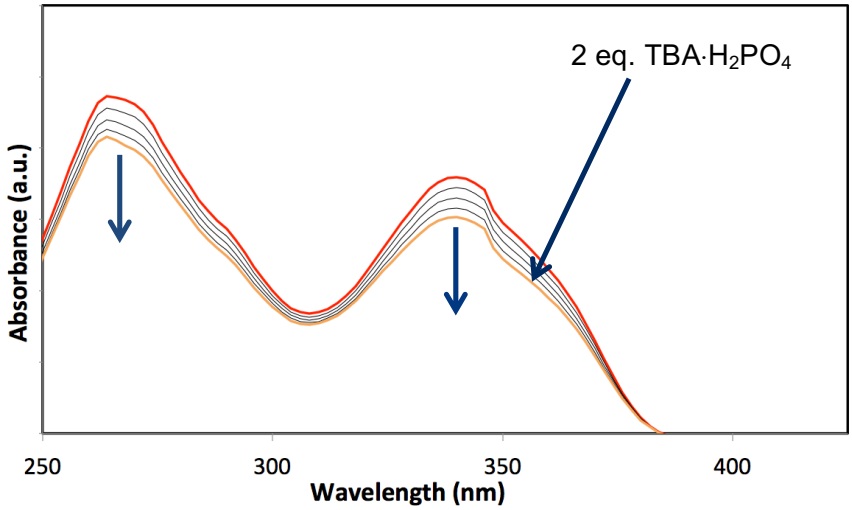

Figure S2. Eu(Tta)$_3$Phen **1** (1x10^{-5} M; THF) titrated with 0.5 equivalent aliquots of TBA·H_2PO_4 (2.0x10^{-4}M) at 298 K.

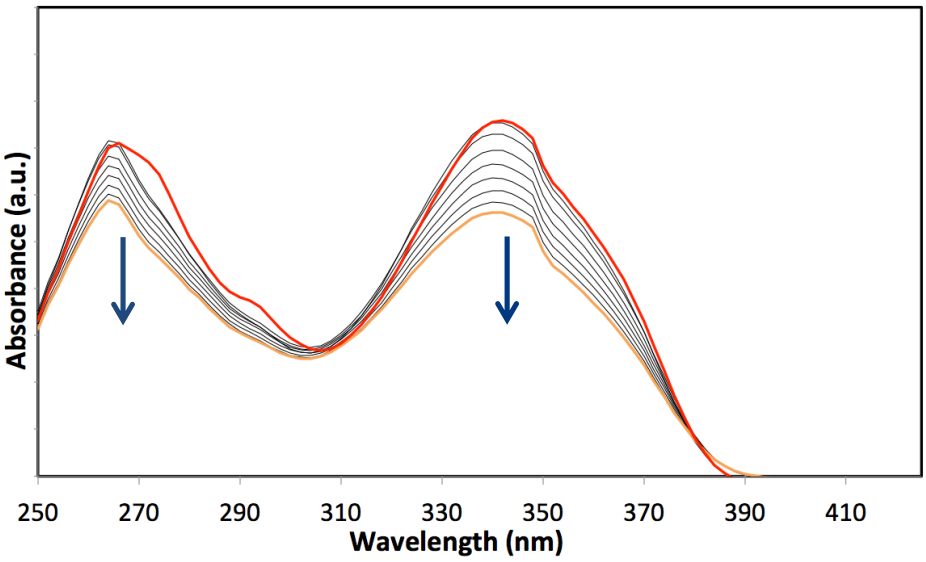

Figure S3. $Eu(Tta)_3Phen$ ($1x10^{-5}$ M; THF, 2% water) titrated with aliquots of TBA H_2PO_4 ($2.0x10^{-4}$M) at 298 K.

Fluorescence Emission Studies:

Series of spectra were collected assessing the emission of **1** and the emissive-response imparted by the respective addition of H_2O, $TBA{\cdot}H_2PO_4$, and/or dipicolinic acid in small aliquots, as noted.

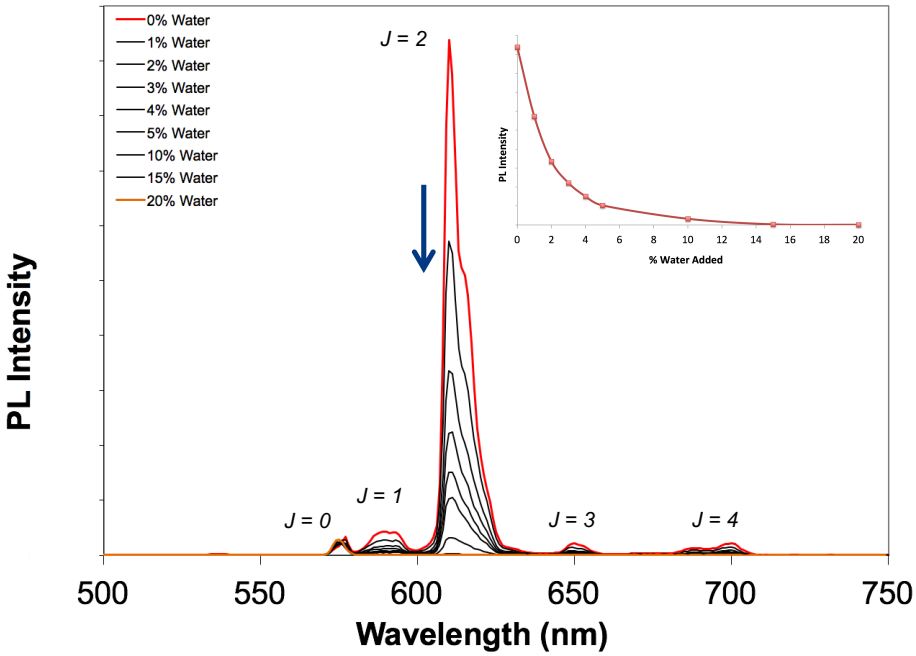

Figure S4. $Eu(Tta)_3Phen$ **1** ($1x10^{-5}$ M; THF) titrated with successive addition of deionised H_2O, as indicated, at 298 K (λ_{ex} = 340 nm).

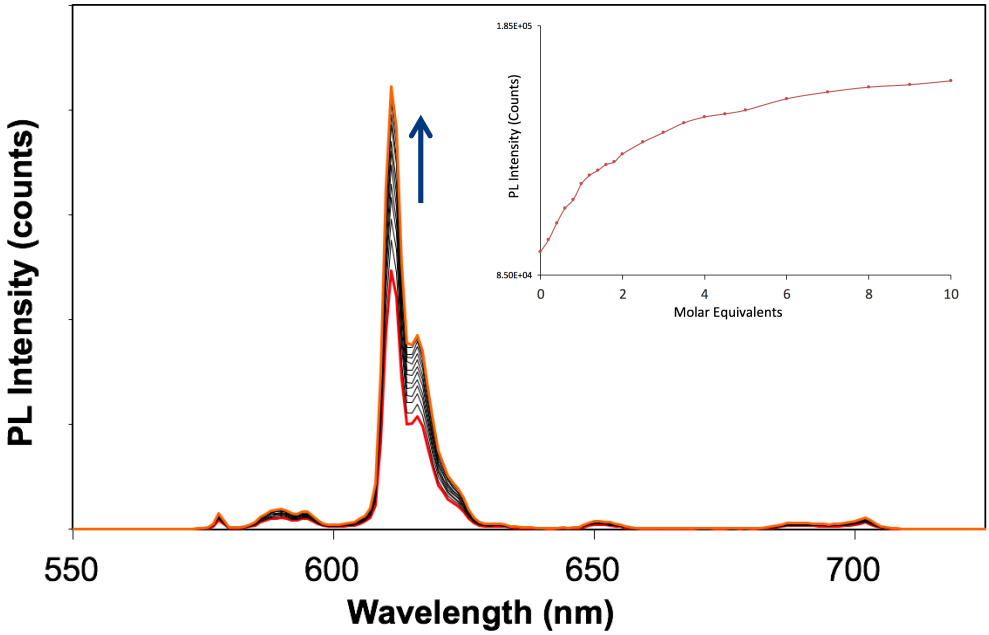

Figure S5. Eu(Tta)$_3$Phen **1** (1x10^{-5} M; THF) titrated with successive aliquots of TBA·H_2PO_4 (2.0x10^{-4}M), up to 10.0 molar equivalents (298 K; λ_{ex} = 340 nm).

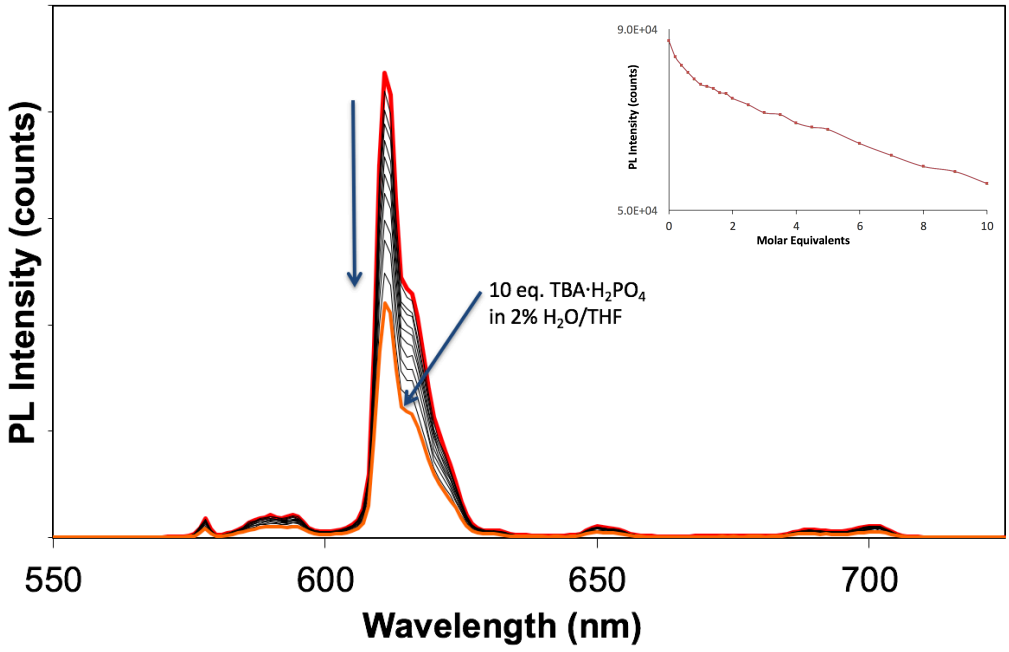

Figure S6. Eu(Tta)$_3$Phen **1** (1x10^{-5} M; THF, 2% water) titrated with successive aliquots of TBA·H_2PO_4 (2.0x10^{-4}M), up to 10.0 molar equivalents at 298 K (λ_{ex} = 340 nm).

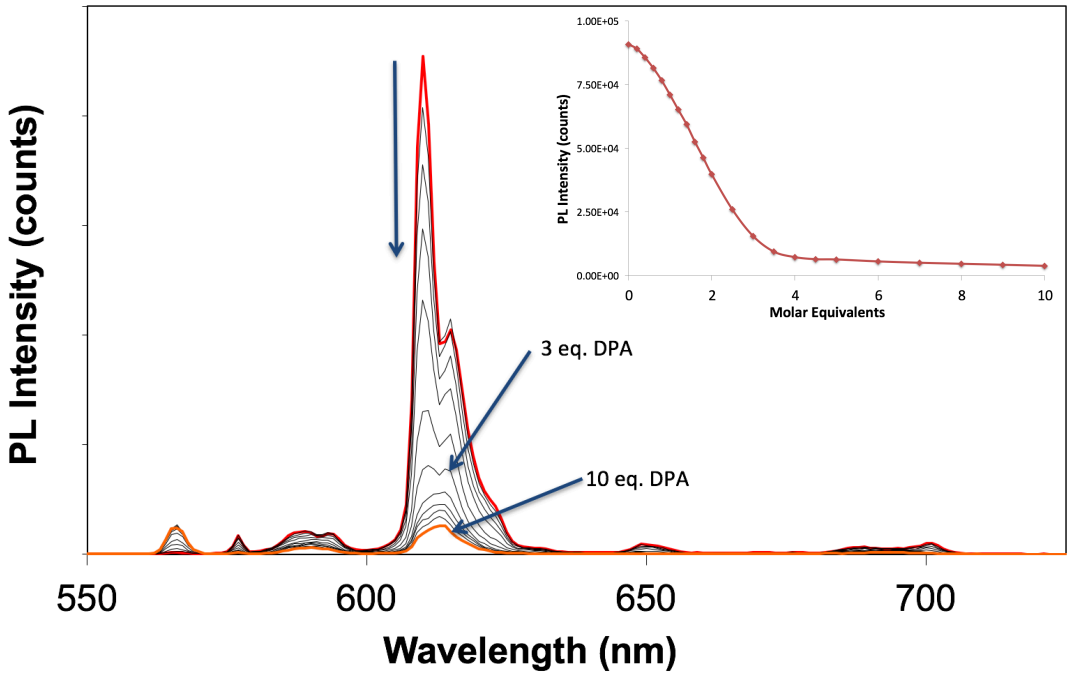

Figure S7. Eu(Tta)$_3$Phen **1** (1x10^{-5} M; THF) titrated with successive aliquots of DPA (2.0x10^{-4}M), up to 10.0 molar equivalents at 298 K (λ_{ex} = 340 nm).

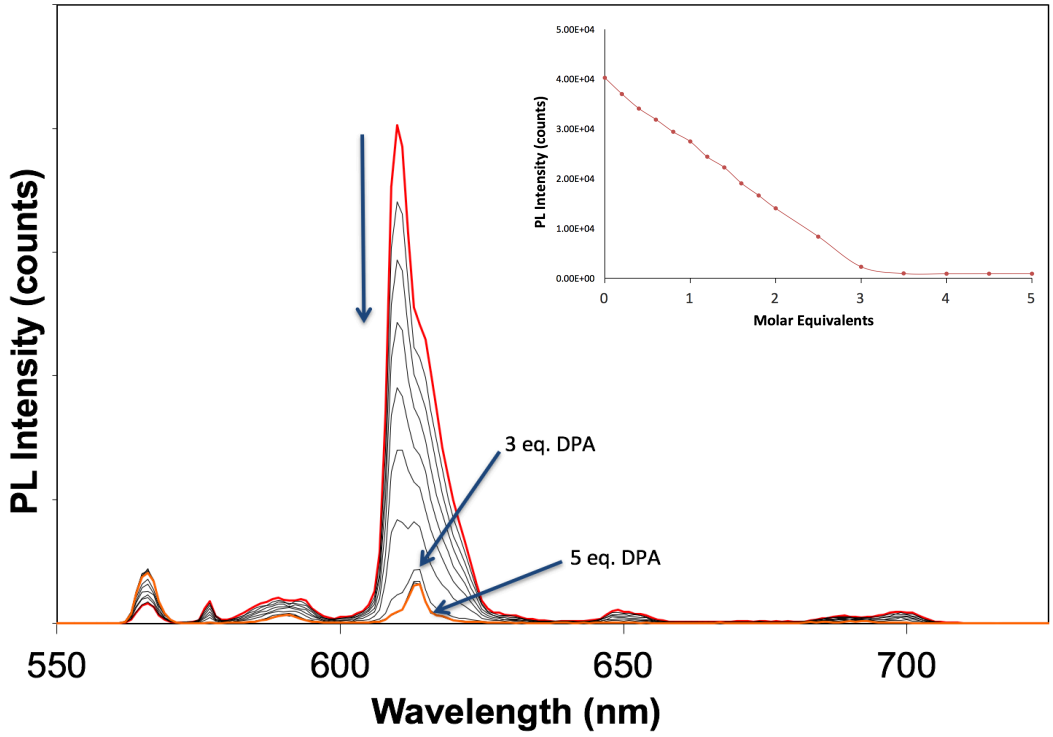

Figure S8. Eu(Tta)$_3$Phen **1** (1x10^{-5} M; THF, 2% water) titrated with successive aliquots of DPA (2.0x10^{-4}M), up to 5.0 molar equivalents at 298 K (λ_{ex} = 340 nm).

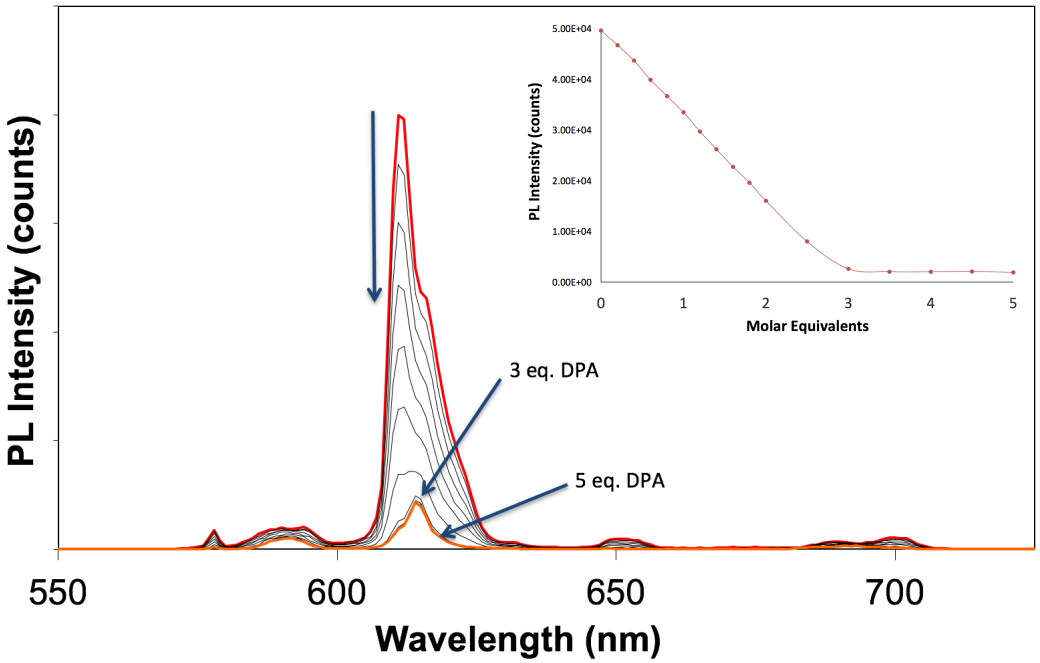

Figure S8. Eu(Tta)$_3$Phen **1** and TBA·H_2PO_4 (1x10^{-5} M and 5.0x10^{-6} M respectively in THF with 2% water) titrated with successive aliquots of DPA (2.0x10^{-4}M), up to 5.0 molar equivalents at 298 K (λ_{ex} = 340 nm).

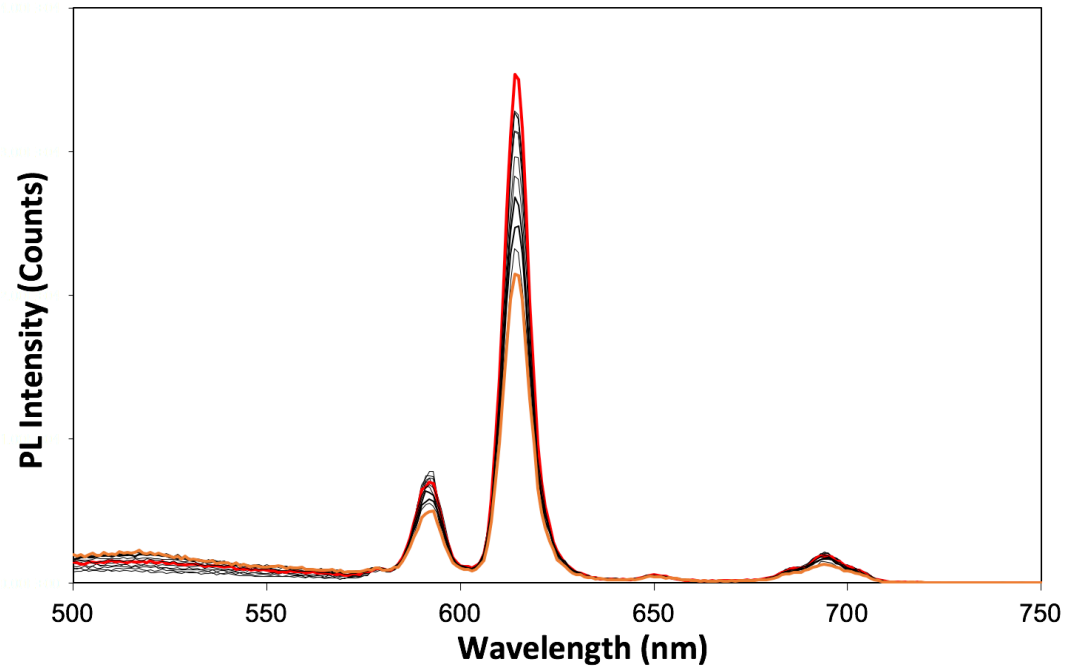

Figure S9. Eu(Tta)$_3$Phen **1** (1x10^{-8} M; THF; 298 K) titrated with successive aliquots of DPA (2.0x10^{-7}M), up to 5.0 molar equivalents at 298 K (λ_{ex} = 340 nm).

Table S1. Emission intensities (at 609 nm) of **1** (1 x 10^{-5} M) titrated with aliquots of each analyte. DPA: dipicolinic acid; Pic: 2-picolinic acid; Nic: nicotinic acid; Cat: catechol; BenzA: benzoic acid; Gly: glycine; Asp: *L*-aspartic acid.

	Emission Intensity						
[Analyte]	DPA	Pic	Nic	Cat	BenzA	Gly	Asp
0	9.08E+04	4.63E+03	4.17E+03	9.427E+04	4.52E+03	4.88E+03	4.47E+03
1.00E+05	7.10E+04	4.52E+03	4.02E+03	9.102E+04	4.30E+03	4.74E+03	4.18E+03
2.00E+05	3.99E+04	4.34E+03	3.96E+03	8.322E+04	4.21E+03	4.22E+03	4.11E+03
3.00E+05	1.55E+04	4.11E+03	3.87E+03	8.181E+04	4.16E+03	4.01E+03	3.96E+03

Table S2. Degree of quenching calculated from Table S1 of **1** (1 x 10^{-5} M) titrated with aliquots of each analyte. DPA: dipicolinic acid; Pic: 2-picolinic acid; Nic: nicotinic acid; Cat: catechol; BenzA: benzoic acid; Gly: glycine; Asp: *L*-aspartic acid.

	$(I_o-I)/I_o$						
Equiv.	DPA	Pic	Nic	Cat	BenzA	Gly	Asp
0	0	0	0	0	0	0	0
1	0.218	0.022	0.035	0.035	0.050	0.029	0.065
2	0.561	0.062	0.049	0.117	0.070	0.136	0.080
3	0.840	0.112	0.071	0.132	0.081	0.179	0.116

1H NMR Studies:

Series of spectra were collected assessing the NMR signals of **1** and the response observed upon addition of dipicolinic acid in small aliquots, as noted. This was then repeated using compound **2**.

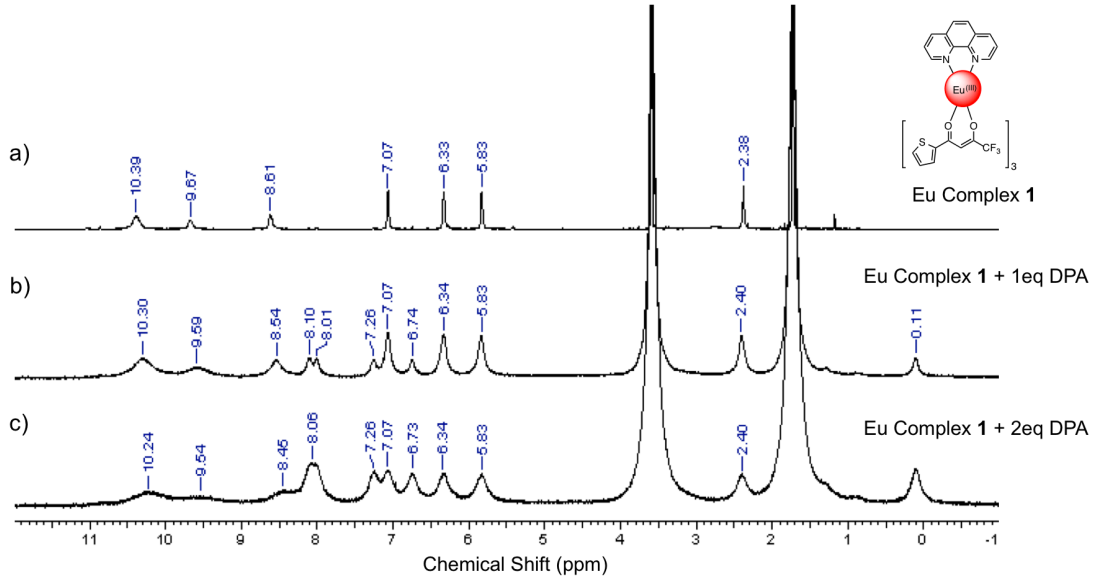

Figure S10. Overlaid NMR Spectra of a) Eu(tta)$_3$Phen **1** (5.0×10^{-3}M), b) Eu(tta)$_3$Phen at a 1:1 ratio with DPA, and c) Eu(tta)$_3$Phen at a 1:2 ratio with DPA in THF-d_8 (298 K). Note: Para-magnetic nature of **1** limits ability to appropriately interpret.

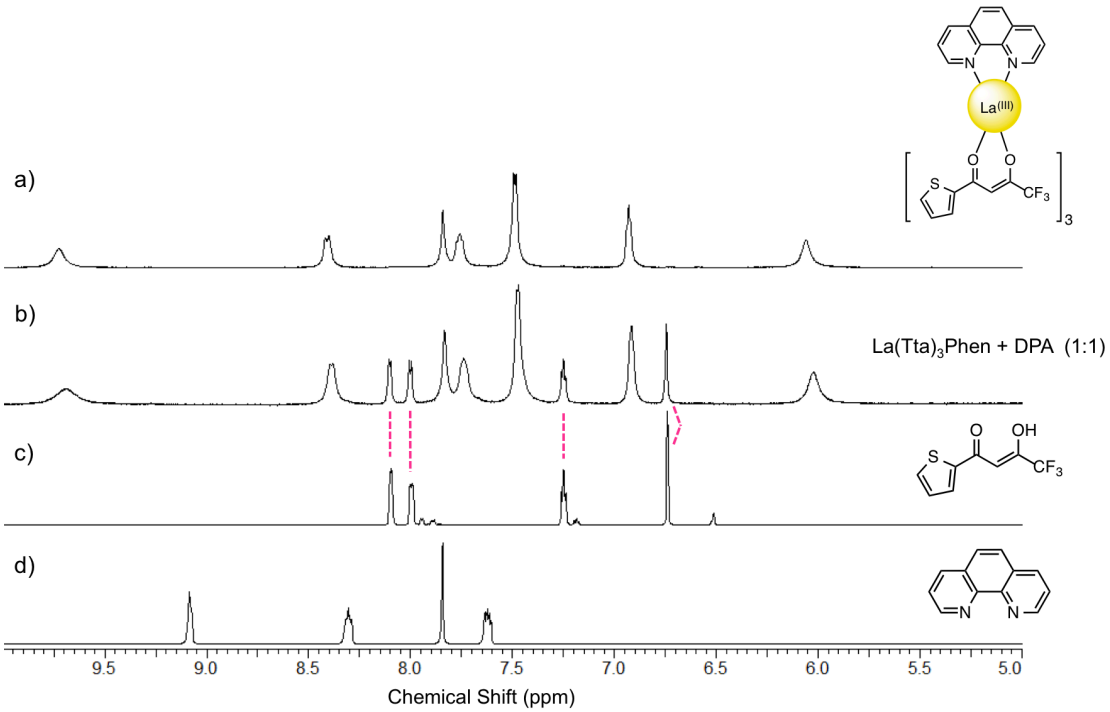

Figure S11. Overlaid ^{1}H-NMR Spectra of (a) La(Tta)$_3$Phen **2** (5.0×10^{-3} M), (b) La(Tta)$_3$Phen at a 1:1 ratio with DPA, (c) TtaH, and (d) Phen in THF-d_8 (298 K). Note: upon addition of DPA, La-DPA complex precipitates leaving unreacted **2** and no-longer ligated TtaH visible in NMR spectrum (b).

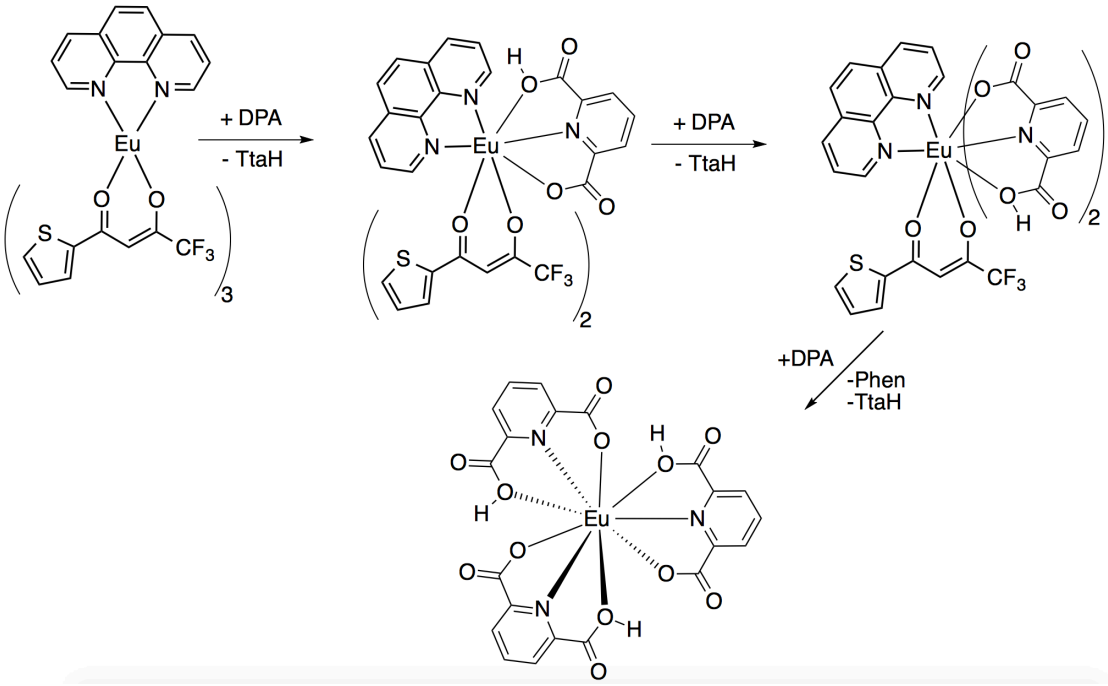

Figure S11. Illustrated is a proposed ligand exchange pathway for the mode of action in sensing **1**. This is supported by the stepwise reduction in emission intensity and in the appearance of free TtaH (thienoyltrifluoroacetone) as **2** is titrated with DPA and visualised by ^{1}H NMR.

References:

1. C. Freund, W. Porzio, L. Giovanella, F. Vignali, M. Pasini and S. Destri, *Inorg. Chem.* 2011, **50**, 5417.