Supporting Information for

Chromo-fluorogenic BODIPY-complexes for selective detection of V-type nerve agent surrogates.

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Experimental section

General remarks: CH_3CN was distilled from P_2O_5 under Ar prior to use. $NaAuCl_4$ was prepared by neutralization of an aqueous solution of $HAuCl_4$ with $NaHCO_3$. All the other solvents and starting materials were purchased from commercial sources where available, and were used without purification.^{1}H-NMR (300 MHz), ^{13}C NMR spectra were determined in a Bruker AV 300 spectrometer. Chemical shifts are reported in parts per million (ppm), calibrated to the solvent peak set.

Synthesis of 1: Synthesis of *(E)-4,4-difluoro-5-(4-((2-hydroxyethyl)(methyl)amino)styryl)-1,3,7-trimethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene* has been reported previously.[1]

Synthesis of 1-Eu^{3+}: To a solution of **1** (243 mg; 0.5 mmol) in 30 mL of MeOH an aqueous solution of $Eu(NO_3)_2 \cdot 5H_2O$ (214 mg; 0.5 mmol) was added dropwise and the mixture was stirred for 3 h. at rt. The resulting bright pink reaction mixture was evaporated under reduced pressure. The solid was recrystallized from EtOH-water (1:1) to give **1**-Eu^{3+} (285 mg; 61 %).^{1}H-MNR (300 MHz; $CDCl_3$) δ 7.64(dd, J=17.4, 9.0 Hz,4 H) , 7.43(m, 3H) , 7.23(m, 3H) , 7.10(d, J=16.4Hz, 1H), 6.54(s, 1H) ,5.99 (s, 1H), 3.86(s,2H), 3.57(s,2H), 3.20(s,3H), 2.54(s,3H), 1.34 (d, J=8.6 Hz, 6H). UV/vis (CH_3CN) λ_{max} = 553.0; λ_{em} = 572.8 nm.

Synthesis of 1-Au^{3+}: To a solution of $NaAuCl_4$ (150 mg; 0.40mmol) in H_2O (20 mL), $NaHCO_3$ (35 mg; 0.40 mmol) and KPF_6 (150 mg; 0.82 mmol) was added. To this solution a solution of **1** (200 mg; 0.41 mmol) in MeOH (5 mL) was added dropwise. The product precipitated as a pink solid, which was separated by filtration and recrystallized from EtOH-water (1:1) to give **1**-Au^{3+} (170 mg; 47 %).^{1}H-MNR (300 MHz; $CDCl_3$) δ 7.71(dd, J=17.4, 9.0 Hz,4 H) , 7.49(m, 3H) , 7.30(m, 3H) , 7.17(d, J=16.4Hz, 1H), 6.61(s, 1H) ,6.06 (s, 1H), 3.93(s,2H), 3.64(s,2H), 3.27(s,3H), 2.58(s,3H), 1.38 (m,6H). UV/vis (CH_3CN) λ_{max} = 552.5; λ_{em} = 573.2nm.

Spectroscopic studies: Acetonitrile was purchased at spectroscopic grade from Aldrich Chemicals Co., used as received, and was found to be free of fluorescent impurities. Absorption and fluorescence spectra were recorded using a Shimadzu UV-2600 spectrophotometer and a Varian Cary Eclipse spectrofluorimeter, respectively. Fluorescence quantum yields were measured at room temperature in the N_2-purgued solution using rhodamine B ($\Phi_{EtOH} = 0.49$)[2] at 525 nm as standard. The fluorescence quantum yields were calculated from Eq. (1).[3] Here, F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the medium.

$$\phi_{exp} = \phi_{ref} \frac{F\{1 - exp(-A_{ref} ln10)\}n^2}{F_{ref}\{1 - exp(-A\, ln10)\}n_{ref}^2} \tag{1}$$

Limits of detection measurements: Increasing amounts of demeton-S dissolved in acetonitrile were progressively added to 3.5 mL solutions of **1**-Eu^{3+} and **1**-Au^{3+} (1.0 x 10^{-5} M). The UV-visible and fluorescence spectra were recorded in 1-cm path length cells at 25ºC. Representation of Δ of absorbance or fluorescence at the appropriate wavelength vs. concentration of simulant allowed the limit of detection to be calculated by using the equation (2) where K=3; Sb_1 is the standard deviation of the blank solution and S is the slope of the calibration curve.[4]

$$LOD = K\frac{Sb_1}{S} \tag{2}$$

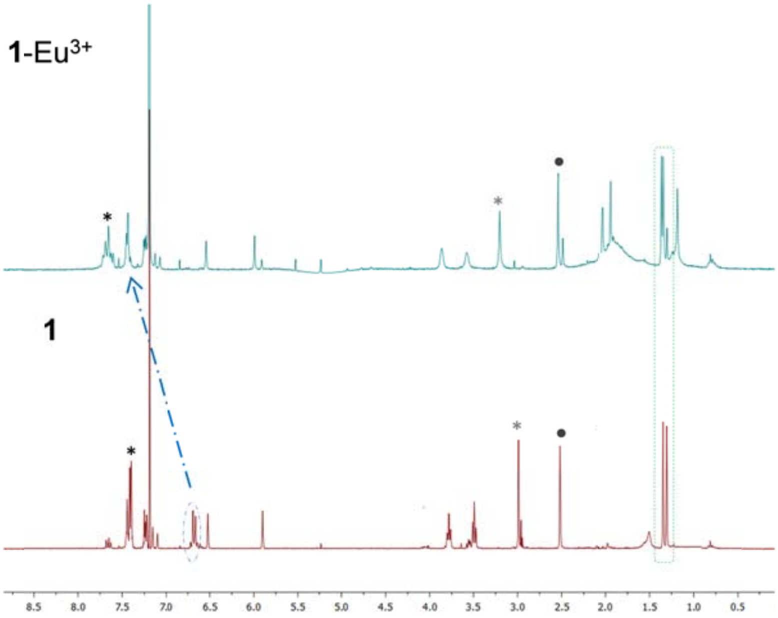

Figure 1. ^{1}H-NMR spectra of **1** (in $CDCl_3$) before and after complexation with Eu^{3+}.

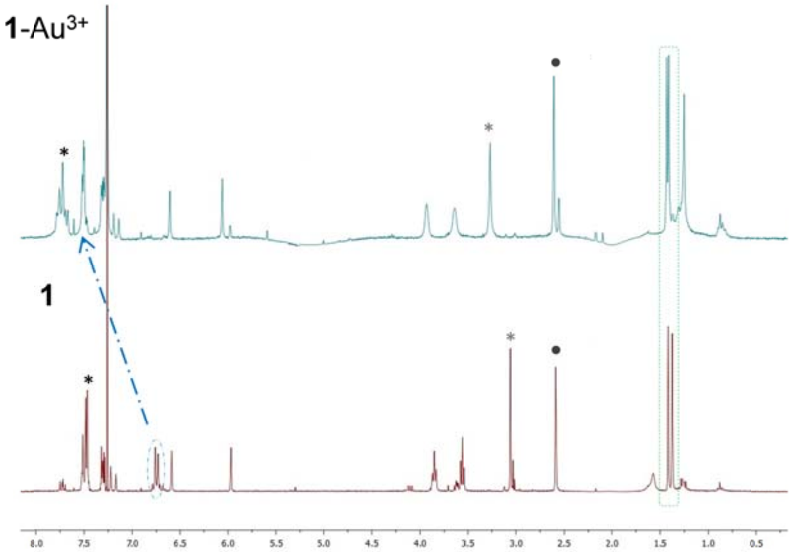

Figure 2. ^{1}H-NMR spectra of **1** (**i**n $CDCl_3$) before and after complexation with Au^{3+}.

Structural proposal 1-Eu^{3+} and 1-Au^{3+}: ^{1}H NMR spectra of ligand **1** free and the presence of Eu^{3+} and Au^{3+} were recorded in $CDCl_3$. The most important modifications of the signals of **1** after complexation with Au^{3+} were observed in the phenyl moiety (7.48 and 6.74 ppm) which underwent a significant downfield shift upon the addition of Eu^{3+} and Au^{3} (0.23 and 0.75 ppm respectively). The change is especially important in the *ortho*-protons to the amino group. On the other hand the methylene groups show a downfield shift around 0.1 ppm . A displacement of downfield of 0.20 ppm in the methyl on the amino group is observed .Finally, there were no changes in the protons of the pyrrole units .These data strongly suggest the direct involvement of the amino group in the M^{3+} coordination. Similar behavior was observed for Eu^{3+}.

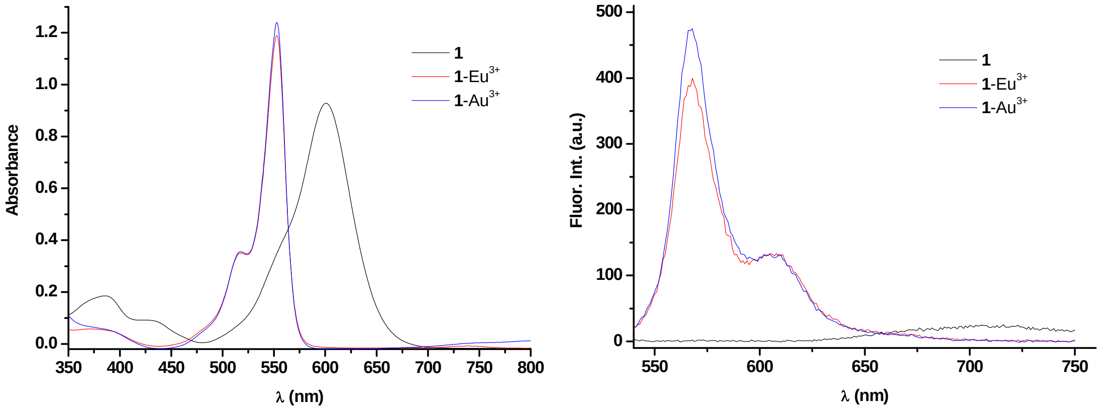

Figure 3. Absorption (left) and fluorescence (right) spectra (λ_{ex} = 530nm) recorded for **1**, **1**-Eu^{3+} and **1**-Au^{3+} (1.0 x 10^{-5} M in CH$_3$CN).

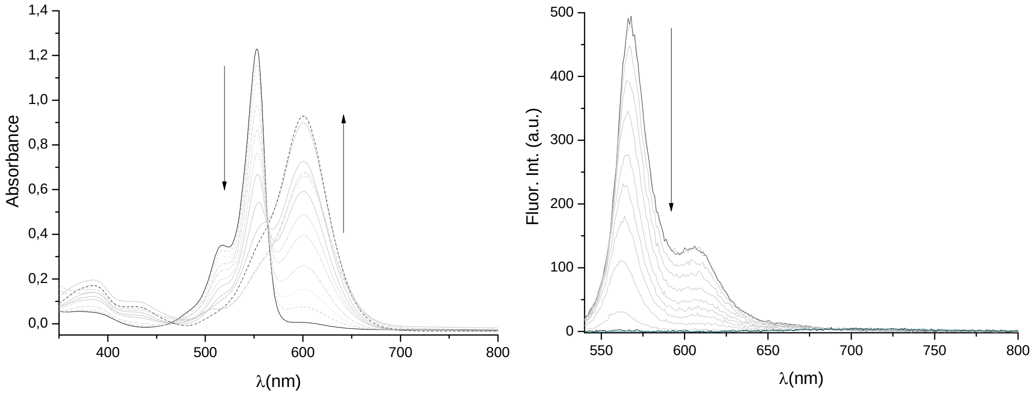

Figure 4. Absorption (left) and fluorescence (right) titration (λ_{ex} = 530nm) of **1**-Au^{3+} (1.0 x 10^{-5} M in CH$_3$CN) upon addition of incremental amounts of demeton-S (1.0 x 10^{-4} M in CH$_3$CN).

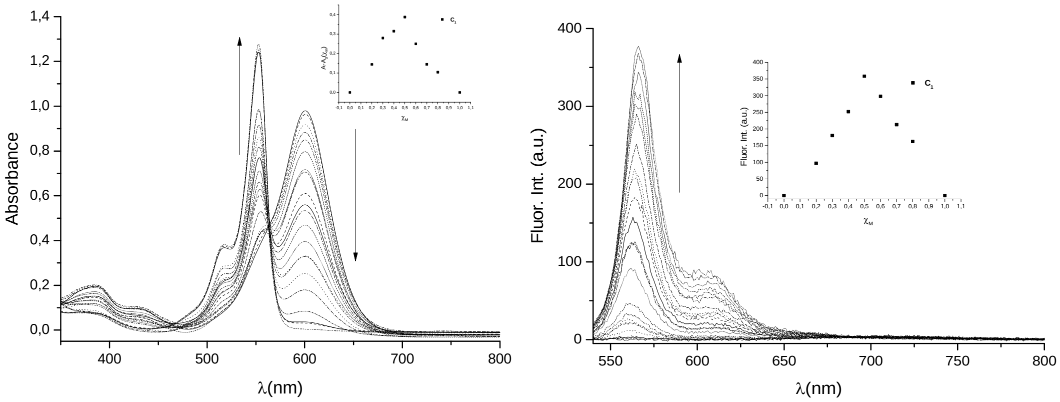

Figure 5. Absorption (left) and fluorescence (right) titration (λ_{ex} = 530nm) of **1** (1.0 x 10^{-5} M in CH$_3$CN) upon addition of incremental amounts of Eu^{3+} used for association constants calculations. The inset shows the corresponding Job plot´s.

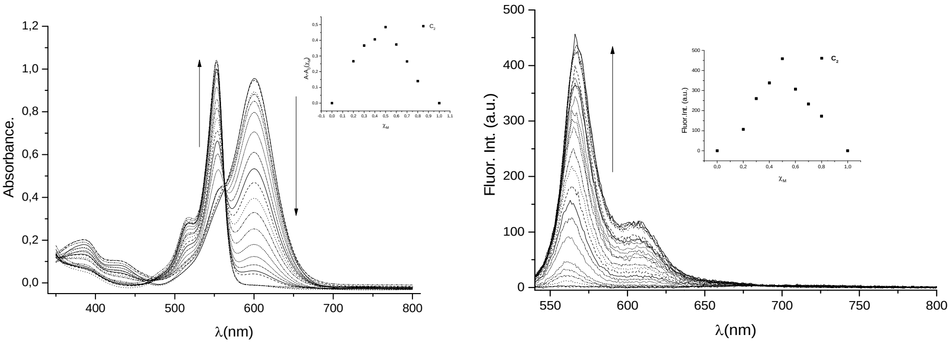

Figure 6. Absorption (left) and fluorescence (right) titration (λ_{ex} = 530nm) of **1** (1.0 x 10 $^{-5}$ M in CH_3CN) upon addition of incremental amounts of Au^{3+}, used for association constants calculations. The inset shows the corresponding Job plot´s.

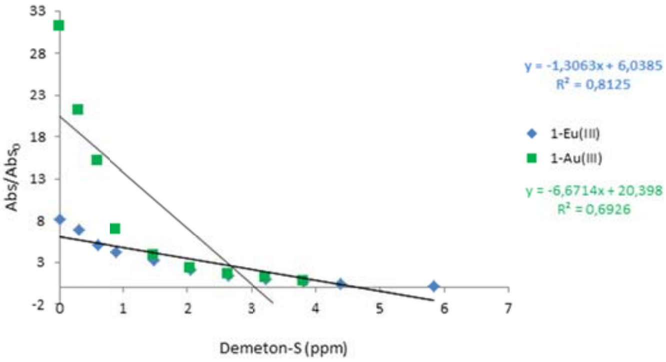

Figure 7. Abs/ Abs_0 of **1**-Eu^{3+} and **1**-Au^{3+} (1.0 x 1$0^{-5}$M) versus increasing amounts of Demeton-S at room temperature .

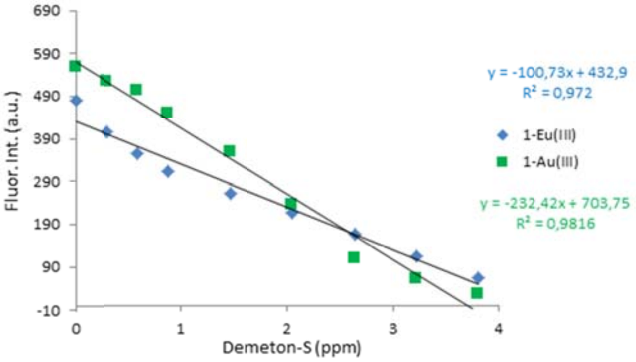

Figure 8. Fluorescence Intensity of **1**-Eu^{3+} and **1**-Au^{3+} (1.0 x 10^{-5}M) versus increasing amounts of Demeton-S at room temperature.

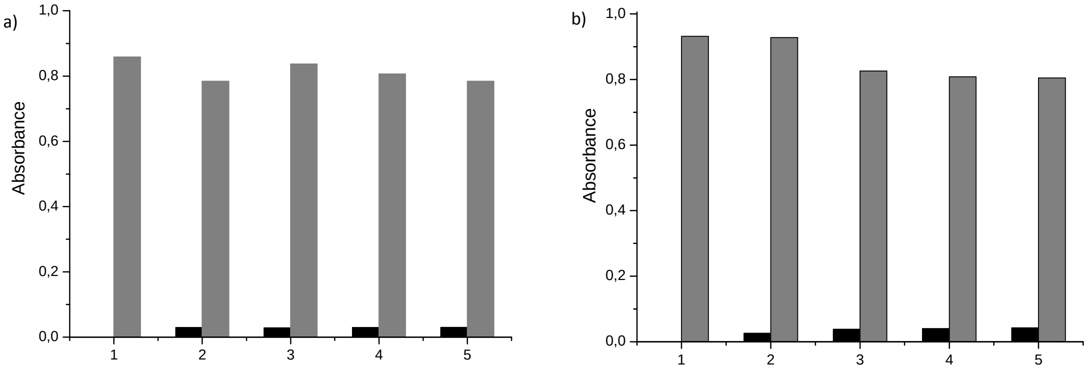

Figure 9: Absorbance (measured at 600.5 nm) of a) **1**-Eu^{3+} and b) **1**-Au^{3+} in the presence of Demeton-S and G-type derivatives. The black bars represent the addition of G-type derivatives (200 ppm) to the solution of **1**-M^{3+}. The grey bars represent the subsequent addition of Demeton-S (100ppm) to the above solution. 1-5 represent **1**-M^{3+}, DCNP, DFP, DMMP and DCNP + DFP + DMMP, respectively.

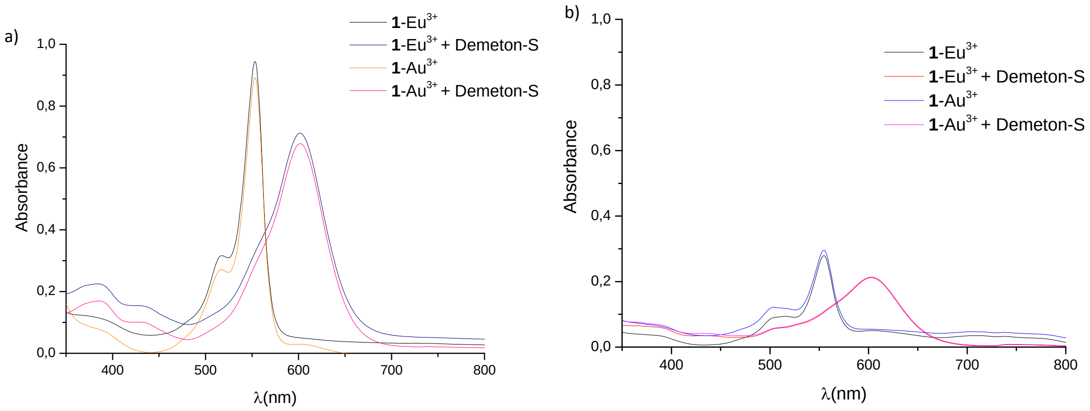

Figure 10: Visible spectra of **1**-Eu^{3+} and **1**-Au^{3+} (10^{-5} M) in aqueous mixtures a) H_2O:CH_3CN (10:90 v/v), b) H_2O:CH_3CN (50:50 v/v) alone and in the presence of Demeton-S (100 ppm).

References

1. A. Barba-Bon, L. Calabuig, A. M. Costero, S. Gil, R. Martinez-Mañez and F. Sancenon, *RSC Adv*., 2014, **4**, 8962-8965.
2. K. G. Casey and E. L. Quitevis, *J. Phys. Chem.*, 1988, **92**, 6590-6594.
3. P. Didier, G. Ulrich, Y. Mely and R. Ziessel, *Org. Biomol. Chem*., 2009, **7**, 3639-3642.
4. M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang and D. Zhu, *Org. Lett*., 2008, **10**, 1481-1484.