

**Supplementary Information for:**

**Selective Activation of Lanthanide luminescence with Triarylboron-  
functionalized Ligands and Visual Fluoride Indicators**

Maria Varlan, Barry A. Blight and Suning Wang\*

Department of Chemistry, Queen's University  
90 Bader Lane, Kingston, Ontario, Canada K7L 3N6  
\*suning.wang@chem.queensu.ca

## **General Information and Materials:**

Ligand synthesis procedures were performed under N<sub>2</sub> using standard Schlenk line techniques. Complex synthesis was undergone under air at room temperature. Starting materials were purchased from Aldrich Chemical Co. and were utilized without further purification. Solvents were acquired from Fisher Sci. and purified using the solvent purification system (Innovation Technologies Co.). Deuterated solvents CDCl<sub>3</sub> and MeOD were purchased from Cambridge Isotopes and used as acquired without additional purification or drying. NMR spectra were acquired on a Bruker Advance 400 Spectrometer. UV-Vis data was recorded on a Varian Cary 50 Bio spectrometer. Fluorescence emission spectra were acquired using a PTI Time Master Pro spectrometer. Solid-state emission data was detected using a PTI LabSphere integration sphere simultaneously with the fluorescence spectrometer. Elemental analyses were performed at the Elemental Analysis Laboratory at the University of Montreal, Montreal, Quebec.

## **Synthesis:**

### **4-(dimesitylboryl)-2,3,5,6-tetramethylbenzoic acid (1)**

Intermediate (4-bromo-2,3,5,6-tetramethylphenyl)dimesitylborane was synthesized as previously reported<sup>1</sup> by lithiating 1.2 g (4.11 mmol) of precursor 1,4-dibromo-2,3,5,6-tetramethylbenzene<sup>2</sup> at -78 °C with n-BuLi (4.8 mmol) in dry nitrogenated THF and subsequently reacting it with dimesitylboron fluoride (1.1 g, 4.11 mmol) by using air and water sensitive schlenk line methods. The reaction was stirred overnight, worked up using water and CH<sub>2</sub>Cl<sub>2</sub> and the product was purified using column chromatography and eluted with hexanes. The final product was created by stirring (4-bromo-2,3,5,6-tetramethylphenyl)dimesitylborane (1.5 g, 3.26 mmol) in dry degassed THF at -78 °C under air and water sensitive schlenk line conditions and adding n-BuLi (3.6 mmol) drop wise to the reaction flask. The mixture was stirred at -78 °C for 60 min after which CO<sub>2</sub> gas was bubbled into the reaction for an additional hour. Aqueous 1 M HCl solution was added to the reaction mixture to acidify the compound and the mixture was subsequently worked up using CH<sub>3</sub>Cl and water. Column chromatography was used to purify the components of the reaction with the final product (**1**) being eluted with (5: 95) MeOH: CH<sub>2</sub>Cl<sub>2</sub> as a white solid in 67% yield. <sup>1</sup>H NMR (400MHz, 2% CD<sub>3</sub>OD in CDCl<sub>3</sub>): δ 6.66(4H, s), 2.14(12H, d, J=40Hz), 1.92(6H, s), 1.88(12H, s) ppm; <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ 175.4, 143.1, 139.9, 139.7, 138.5, 134.8, 133.5, 128.0, 127.8, 22.0, 20.2, 18.7, 16.0 ppm; <sup>11</sup>B NMR (400MHz, 2% CD<sub>3</sub>OD in CDCl<sub>3</sub>): δ 77.95 ppm; IR (cm<sup>-1</sup>): <sub>asy</sub>(CO<sub>2</sub><sup>-</sup>)1696, <sub>sy</sub>(CO<sub>2</sub><sup>-</sup>)1416 ; LRMS, m/z: [M<sup>+</sup>] = 426.27; [M<sup>+</sup>-mesityl] = 306.15. Anal Calcd for C<sub>29</sub>H<sub>35</sub>BO<sub>2</sub>: C, 81.69; H, 8.27. Found: C, 81.17; H, 8.33.

### **4'-(dimesitylboryl)biphenyl-4-carboxylic acid (2)**

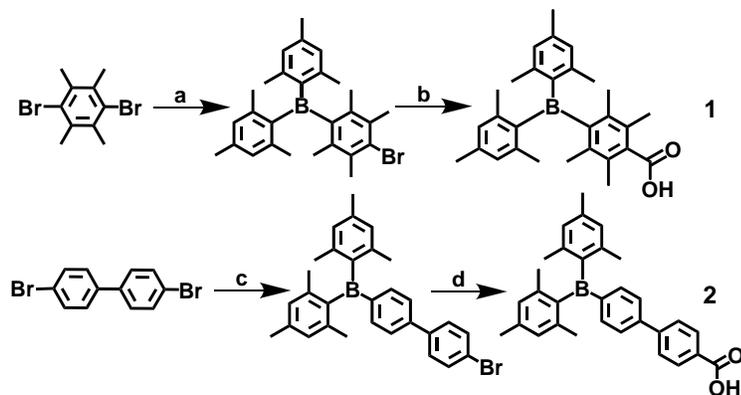
Product was synthesized, using a previously reported method<sup>3</sup>, by dissolving (4'-bromobiphenyl-4-yl)dimesitylborane (1.1 g, 2.3 mmol) in dry degassed THF and cooled to -78 °C under N<sub>2</sub>. Once cooled, n-BuLi (2.5 mmol) was slowly added dropwise to the flask and the mixture was left to stir for 60 min. CO<sub>2</sub> gas was bubbled into the reaction flask for an additional hour followed by the addition of 1 M aqueous HCl to acidify the mixture. The reaction was worked up

<sup>1</sup> Yamaguchi, S.; Shirasaka, T.; Tamao, k. *Org. Lett.* **2000**, 2(26), 4129-4132.

<sup>2</sup> Liu, Y.; Xu, X.; Zheng, F.; Cui, Y. *Angew. Chem. Int. Ed.* **2008**, 47, 4538-4541.

<sup>3</sup> Blight, B. A.; Stewart, A. F.; Wang, N.; Lu, J-S.; Wang, S. *Inorg. Chem.* **2012**, 51, 778-780.

using water and  $\text{CH}_3\text{Cl}$  and purified using column chromatography with (0.5: 99.5)  $\text{MeOH}:\text{CH}_2\text{Cl}_2$  as the eluent. Final product (**2**) is a white powder in 54% yield.



**Scheme S1.** Reagents and conditions: a) (i)  $n\text{-BuLi}$ ,  $-78\text{ }^\circ\text{C}$ , THF, 1 h; (ii)  $(\text{Mes})_2\text{BF}$ , RT, 12 h; b) (i)  $n\text{-BuLi}$ ,  $-78\text{ }^\circ\text{C}$ , THF, 1 h; (ii)  $\text{CO}_2$ , RT, 12 h; (iii)  $\text{HCl aq.}$  c) (i)  $n\text{-BuLi}$ ,  $-78\text{ }^\circ\text{C}$ , THF, 1 h; (ii)  $(\text{Mes})_2\text{BF}$ , RT, 12 h; d) (i)  $n\text{-BuLi}$ ,  $-78\text{ }^\circ\text{C}$ , THF, 1 h; (ii)  $\text{CO}_2$ , RT, 12 h; (iii)  $\text{HCl aq.}$

#### Potassium salt synthesis (1-OK & 2-OK)

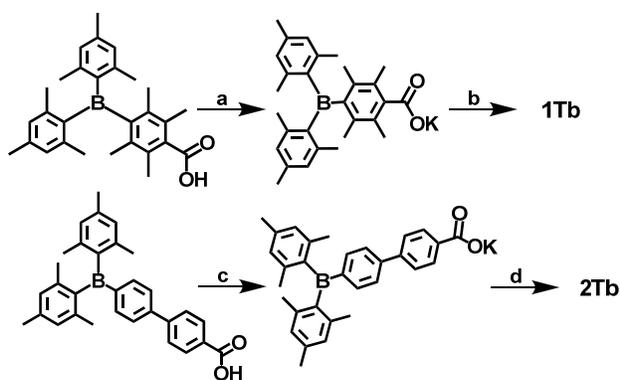
4-(dimesitylboryl)-2,3,5,6-tetramethylbenzoic acid and 4'-(dimesitylboryl)biphenyl-4-carboxylic acid were modified into their respective potassium salts by individually dissolving the compounds in dry nitrogenated THF at  $0\text{ }^\circ\text{C}$  and stirring them for 10 min under schlenk line conditions. A molar equivalent amount of potassium *t*-butoxide was added then to the reaction flasks and the reaction mixtures were left to stir at  $0\text{ }^\circ\text{C}$  for 60 min. Solvent was removed by vacuum, and their individual potassium salts were produced in quantitative yields.

#### 1Tb Synthesis

To a solution of potassium 4-(dimesitylboryl)-2,3,5,6-tetramethylbenzoate (45 mg, 0.096 mmol) in 10 mL of MeOH, a mixture of  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (14 mg, 0.033 mmol) in 5 mL MeOH was added dropwise and left to stir at room temperature for 1 h. The product was rinsed with MeOH 4 times and was collected as a white solid in 78% yield. IR ( $\text{cm}^{-1}$ ):  $\text{asy}(\text{CO}_2^-)$ 1543,  $\text{sy}(\text{CO}_2^-)$ 1419; LRMS-MALDI,  $\text{M}^+$   $m/z$  (amu) = 1435.12. Anal Calcd for  $\text{C}_{87}\text{H}_{102}\text{B}_3\text{O}_6\text{Tb} \cdot 2\text{MeOH}$ : C, 71.35; H, 7.33. Found: C, 71.24; H, 7.28. Vacuum-dried sample, anal. Calcd for  $\text{C}_{87}\text{H}_{102}\text{B}_3\text{O}_6\text{Tb}$ : C, 72.81; H, 7.16. Found: C, 72.75; H, 7.11.

#### 2Tb Synthesis

This compound was prepared as a white solid using the same procedure as described for  $(\text{B1})_3\text{Tb}$  except by using potassium 4'-(dimesitylboryl)biphenyl-4-carboxylate (28 mg, 0.058 mmol) and  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (8.3 mg, 0.019 mmol). The product was rinsed with MeOH 4 times and was collected in 60% yield. IR ( $\text{cm}^{-1}$ ):  $\text{asy}(\text{CO}_2^-)$ 1549,  $\text{sy}(\text{CO}_2^-)$ 1420; Anal Calcd for  $\text{C}_{64}\text{H}_{66}\text{B}_2\text{O}_4\text{Tb} \cdot 2\text{MeOH}$ : C, 69.08; H, 6.07. Found: C, 68.15; H, 5.74.



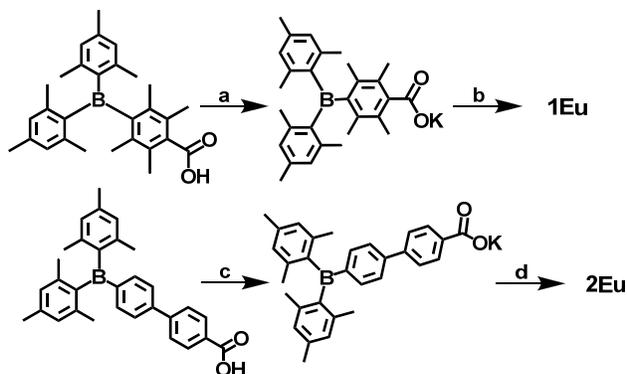
**Scheme S2.** Reagents and conditions: a) (i)  $t\text{BuOK.}$ ,  $0\text{ }^\circ\text{C}$ , 60 min,  $\text{N}_2$  b) (i)  $\text{Tb}(\text{NO}_3)_3$ , MeOH, RT, 1 h; c) (i)  $t\text{BuOK.}$ ,  $0\text{ }^\circ\text{C}$ , 60 min,  $\text{N}_2$  d) (i)  $\text{Tb}(\text{NO}_3)_3$ , MeOH, RT, 1 h.

### 1Eu Synthesis

4-(dimesitylboryl)-2,3,5,6-tetramethylbenzoate (45 mg, 0.096 mmol) was dissolved in 10 mL of MeOH and a solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (14 mg, 0.033 mmol) in 5 mL MeOH was added dropwise and left to stir at room temperature for 1 h. The product was rinsed with MeOH 4 times and was collected as a white solid in 89% yield. IR ( $\text{cm}^{-1}$ ):  $\text{asy}(\text{CO}_2^-)$ 1541,  $\text{sy}(\text{CO}_2^-)$ 1420; LRMS-MALDI,  $\text{M}^+$   $m/z$  (amu) = 1478.03. Anal Calcd for  $\text{C}_{87}\text{H}_{102}\text{B}_3\text{O}_6\text{Eu} \cdot \text{MeOH} \cdot 2\text{H}_2\text{O}$ : C, 70.69; H, 7.35. Found: C, 69.24; H, 7.02.

### 2Eu Synthesis

This compound was prepared as a white solid using the same procedure as described for  $(\text{B}1)_3\text{Eu}$  except by using potassium 4'-(dimesitylboryl)biphenyl-4-carboxylate (50 mg, 0.103 mmol) and  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (15.3 mg, 0.034 mmol). The product was rinsed with MeOH 4 times and was collected in 84% yield. IR ( $\text{cm}^{-1}$ ):  $\text{asy}(\text{CO}_2^-)$ 1550,  $\text{sy}(\text{CO}_2^-)$ 1420; LRMS-MALDI,  $\text{M}^+$   $m/z$  (amu) = 1078.98. Anal Calcd for  $\text{C}_{64}\text{H}_{66}\text{B}_2\text{O}_4\text{Eu} \cdot 2\text{MeOH}$ : C, 69.51; H, 6.11. Found: C, 70.02; H, 5.99.



**Scheme S3.** Reagents and conditions: a) (i)  $t\text{BuOK.}$ ,  $0\text{ }^\circ\text{C}$ , 60 min,  $\text{N}_2$  b) (i)  $\text{Eu}(\text{NO}_3)_3$ , MeOH, RT, 1 h; c) (i)  $t\text{BuOK.}$ ,  $0\text{ }^\circ\text{C}$ , 60 min,  $\text{N}_2$  d) (i)  $\text{Eu}(\text{NO}_3)_3$ , MeOH, RT, 1 h.

## $^1\text{H}$ NMR, $^{11}\text{B}$ NMR and $^{13}\text{C}$ NMR of Ligands

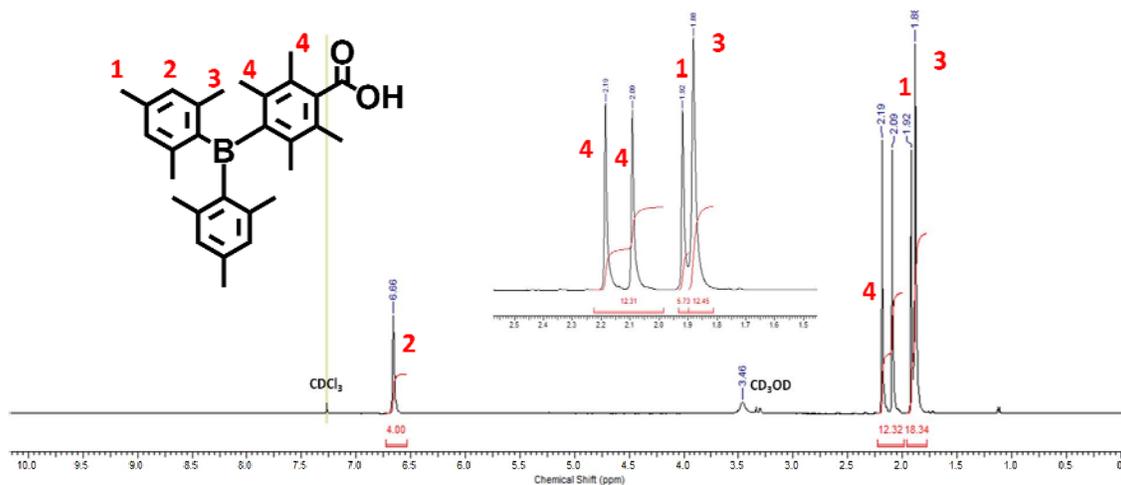


Figure S1:  $^1\text{H}$  NMR spectrum of ligand **1** in  $\text{CDCl}_3$  with a drop of  $\text{MeOD}$ .

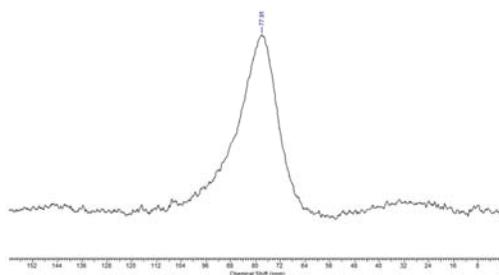


Figure S2:  $^{11}\text{B}$  NMR spectrum of ligand **1** in  $\text{CDCl}_3$ .

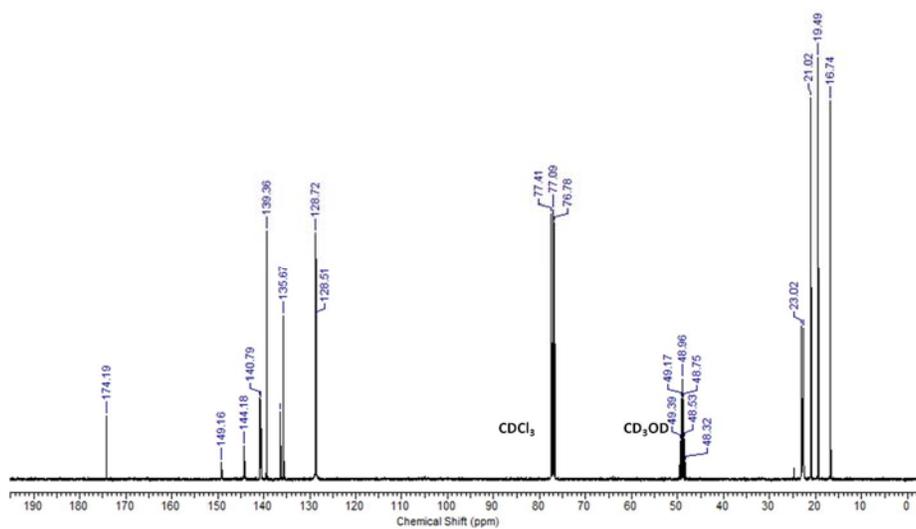


Figure S3:  $^{13}\text{C}$  NMR spectrum of ligand **1** in  $\text{CDCl}_3$  with a drop of  $\text{MeOD}$ .

Table S4: IR spectroscopic data for the two ligands, their respective lanthanide complexes and the reference compounds. Stretching frequencies of C=O and CO<sub>2</sub><sup>-</sup> vibrations in cm<sup>-1</sup>.

Compounds	$\nu_s$ (COO <sup>-</sup> )	$\nu_{as}$ (COO <sup>-</sup> )	$\Delta(\nu_s$ (COO <sup>-</sup> ) - $\nu_{as}$ (COO <sup>-</sup> ))
Tb(Bz) <sub>3</sub>	1424 s	1541 s	117
Eu(Bz) <sub>3</sub>	1415 s	1532 s	117
<b>1</b>	1416 s	1696 s	280
<b>2</b>	1423 s	1694 s	271
<b>1Tb</b>	1419 s	1543 s	124
<b>2Tb</b>	1420 s	1549 s	129
<b>1Eu</b>	1420 s	1541 s	121
<b>2Eu</b>	1420 s	1550 s	130

### Photophysical Properties:

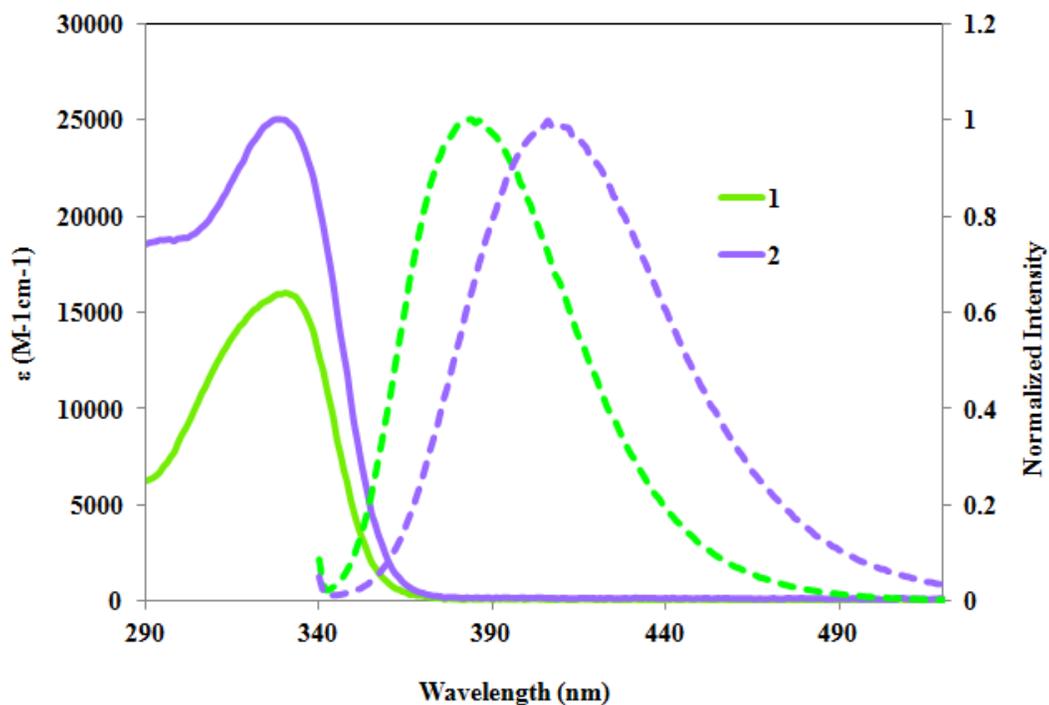


Figure S5: UV-Vis absorption and normalized fluorescence emission spectra of ligands **1** and **2** in THF at RT.

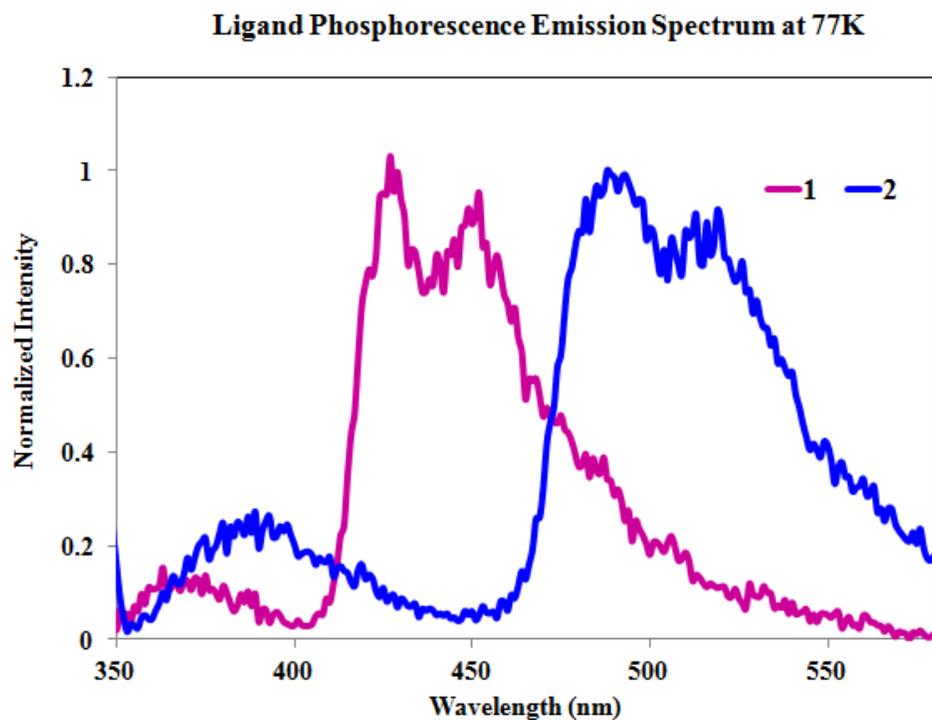


Figure S6: Normalized intensity phosphorescence spectra of ligands **1** and **2** at 77K in THF.

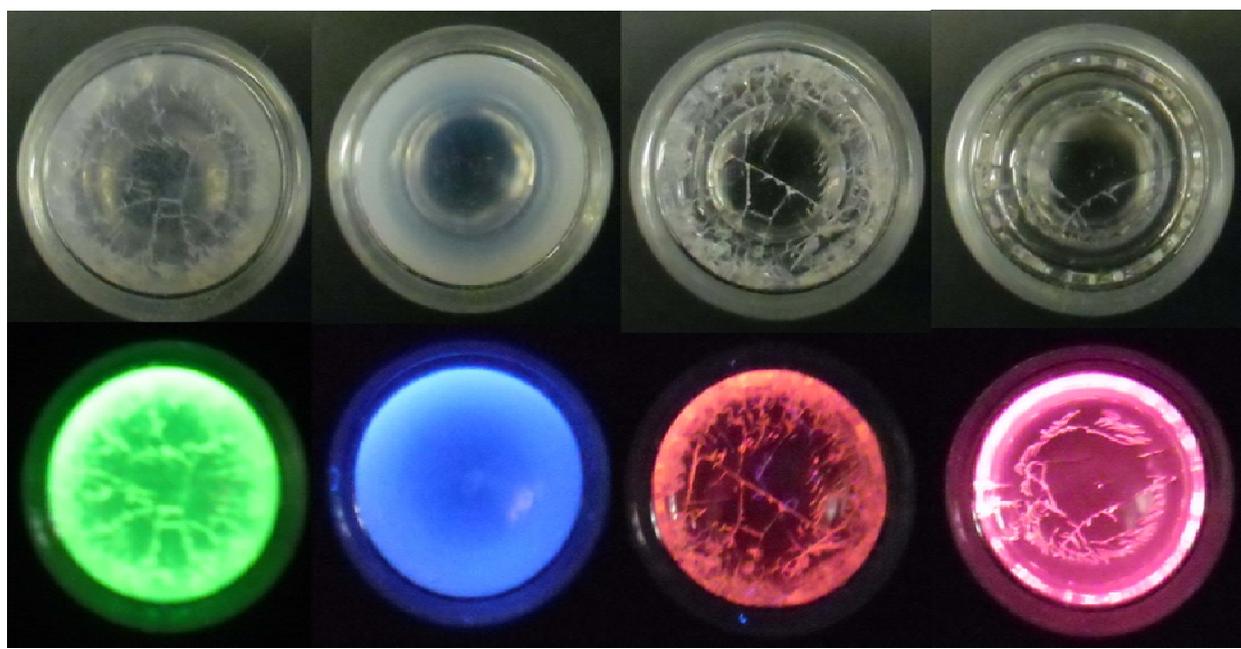


Figure S8: Picture of the 4 complexes **1Tb**, **2Tb**, **1Eu** and **2Eu**, respectively, doped in PMMA (10wt%) at room temperature under ambient light (top) and under 365 nm irradiation (bottom).

## Luminescence Sensor Testing:

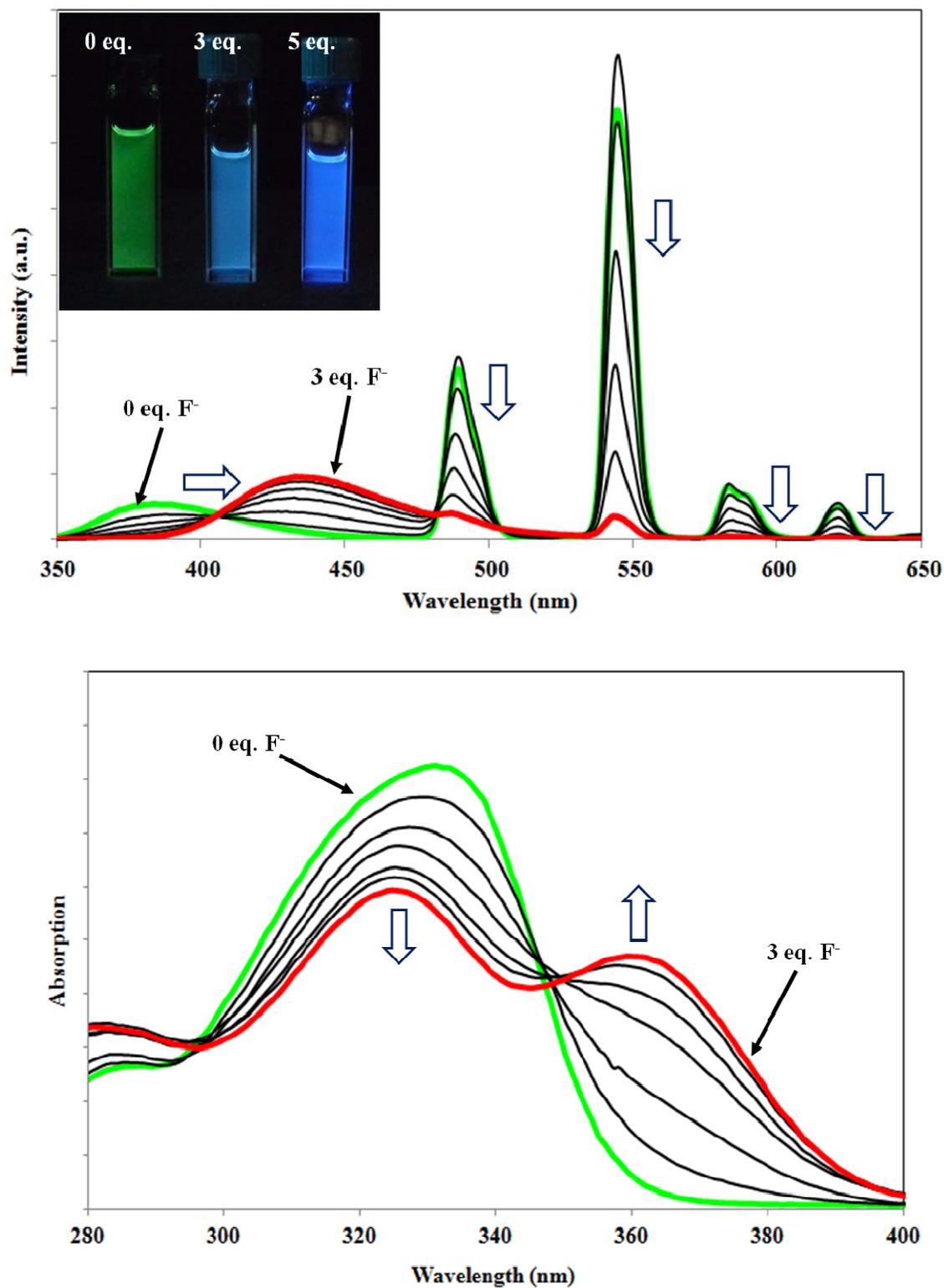


Figure S11: The fluorescence (top) and UV-Vis absorption (bottom) titration spectra of **1Tb** ( $1 \times 10^{-5}$  M) by TBAF in THF at 298 K.

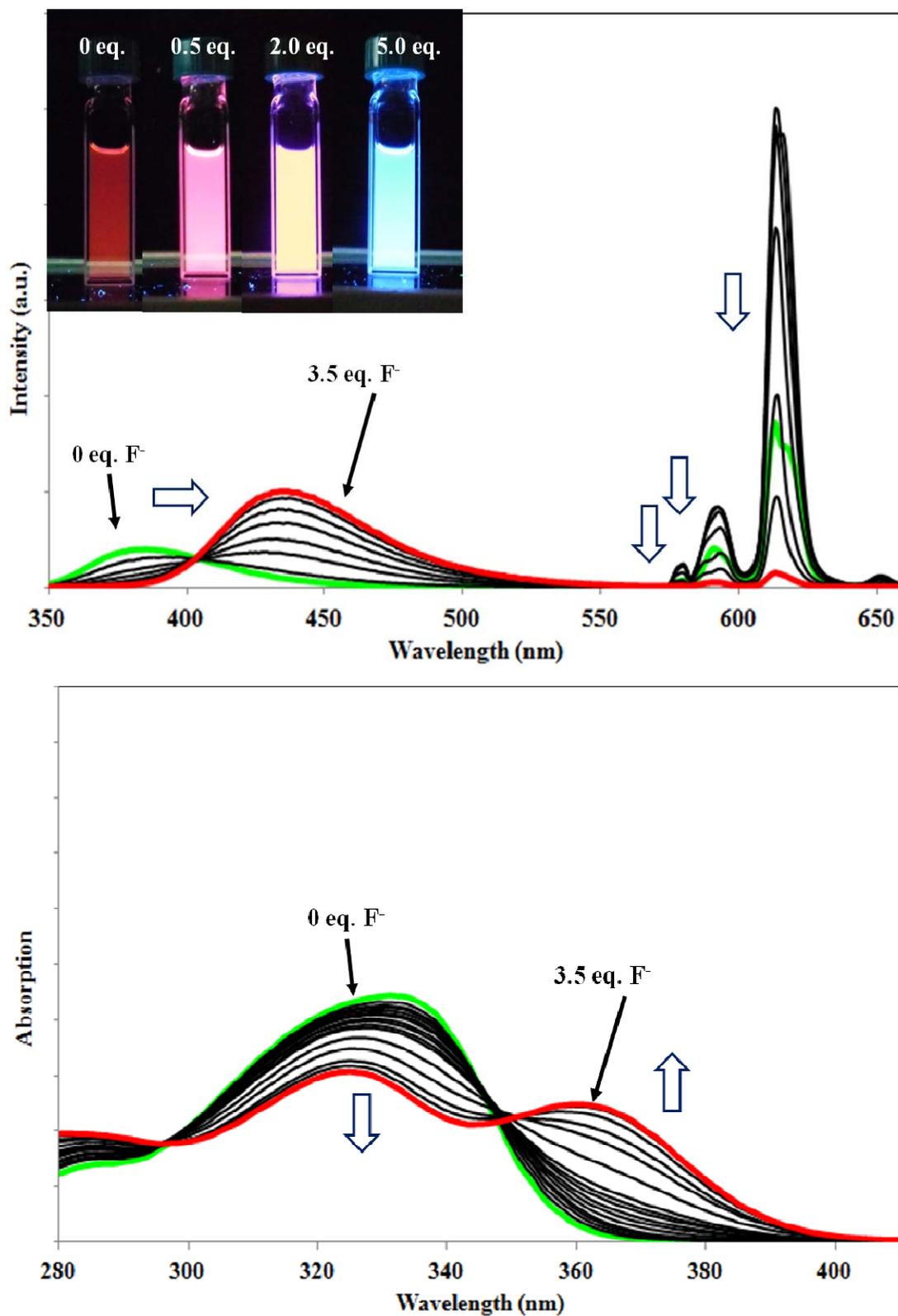


Figure S13: The fluorescence (top) and UV-Vis absorption (bottom) titration spectra of **1Eu** ( $1 \times 10^{-5}$  M) by TBAF in THF at 298 K.

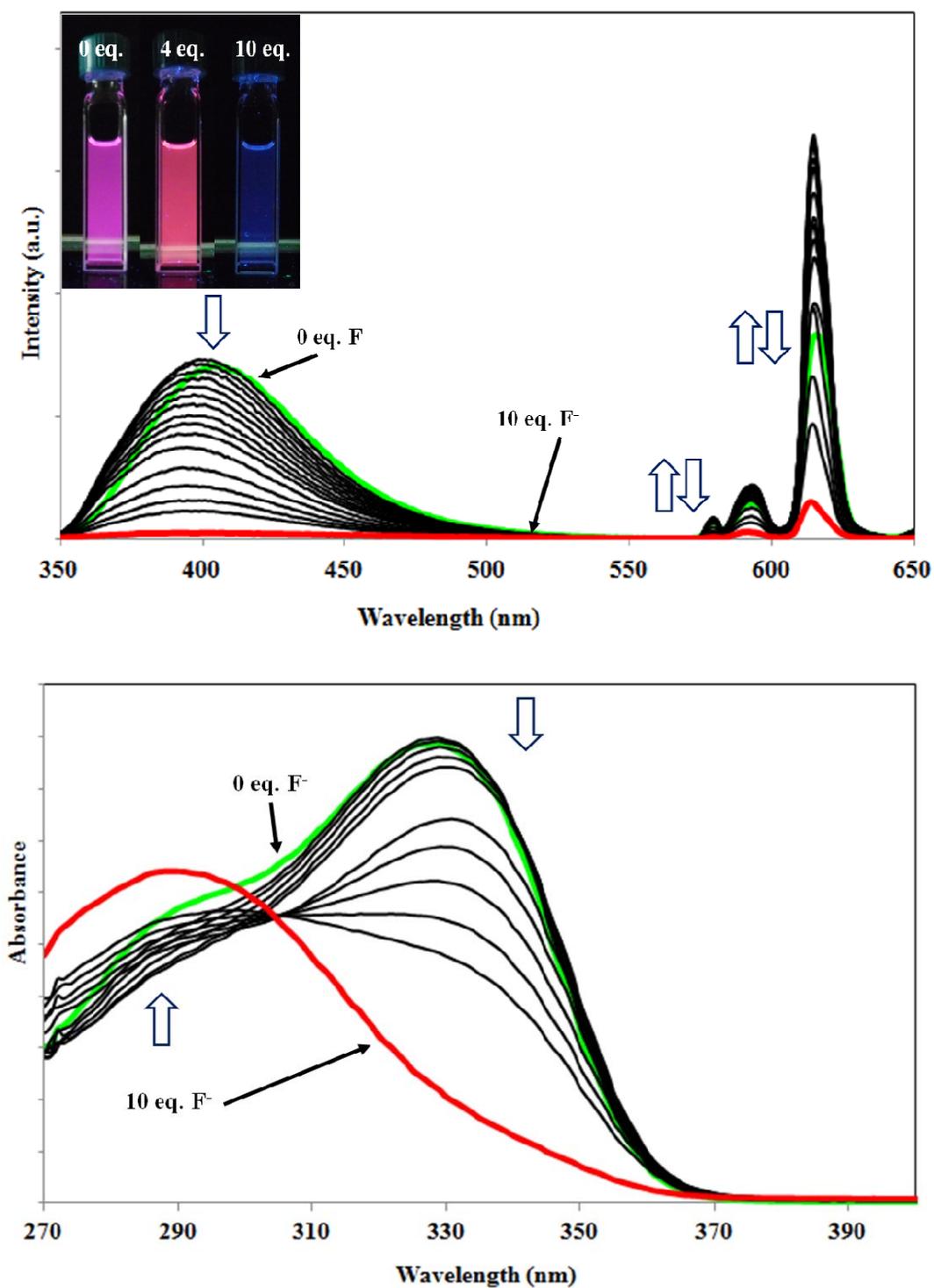


Figure S14: The fluorescence (top) and UV-Vis absorption (bottom) titration spectra of **2Eu** ( $1 \times 10^{-5}$  M) by TBAF in THF at 298 K.

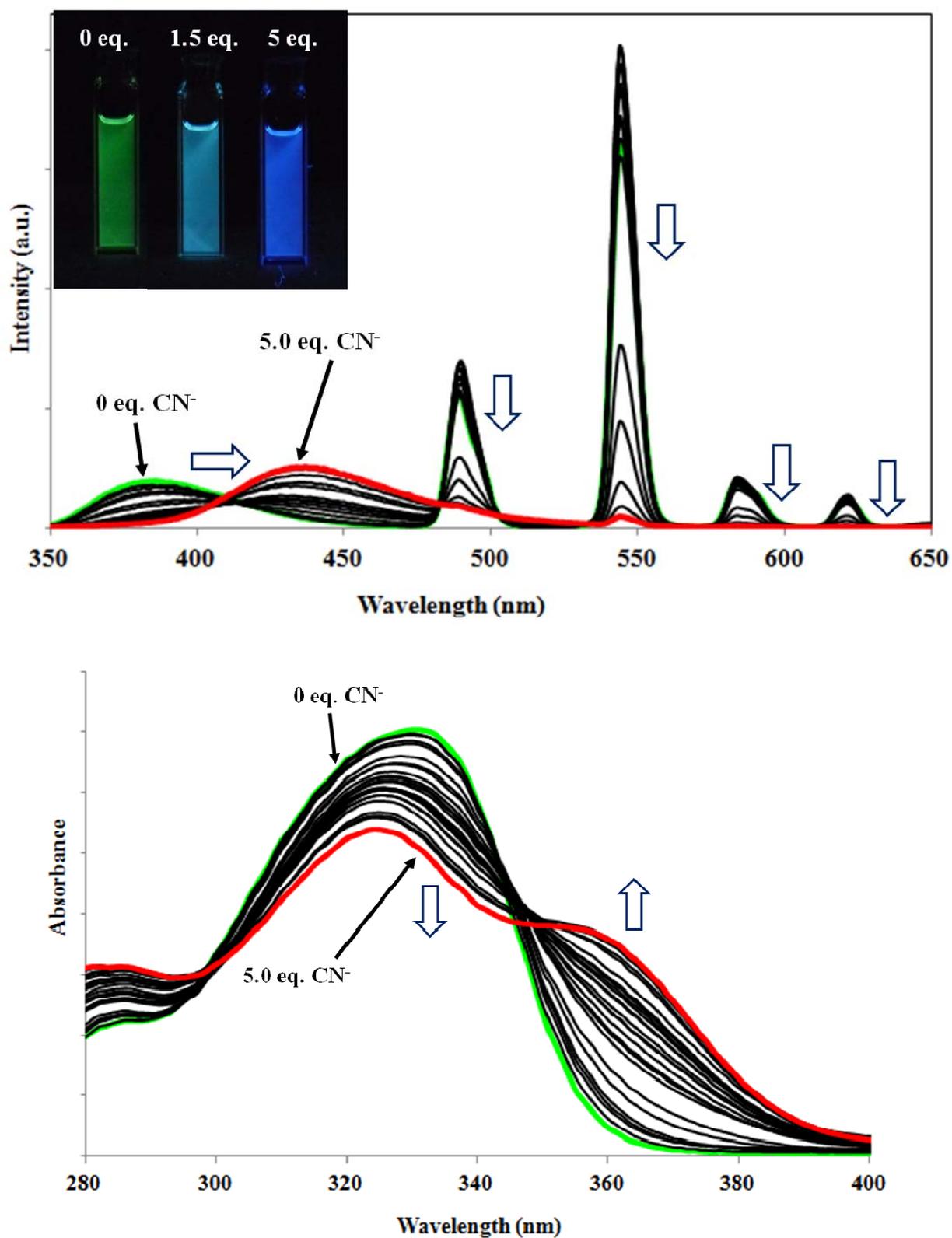


Figure S15: The fluorescence (top) and UV-Vis absorption (bottom) titration spectra of **1Tb** ( $1 \times 10^{-5}$  M) by TBACN in THF at 298 K.

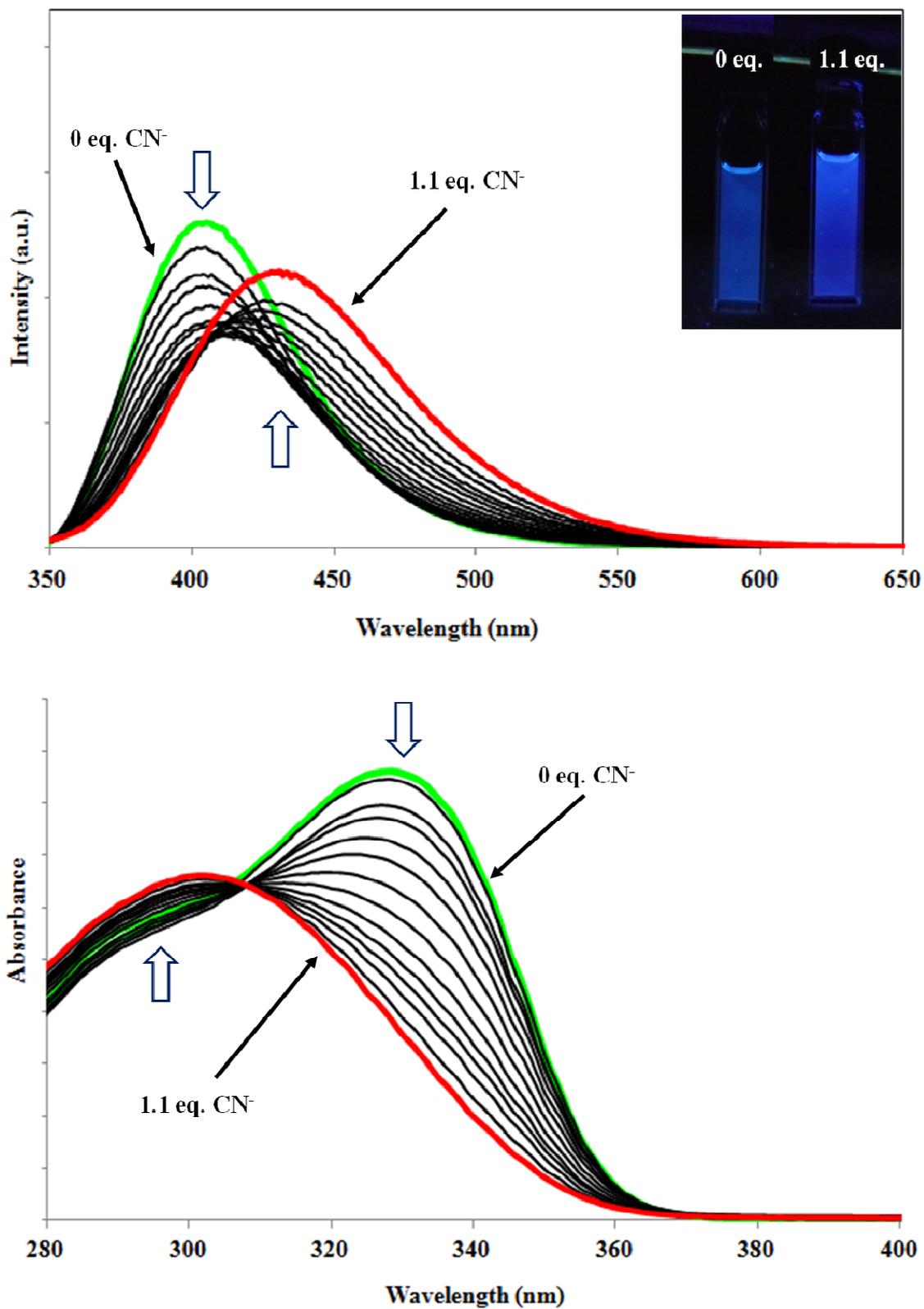


Figure S16: The fluorescence (top) and UV-Vis absorption (bottom) titration spectra of **2Tb** ( $1 \times 10^{-5}$  M) by TBACN in THF at 298 K.

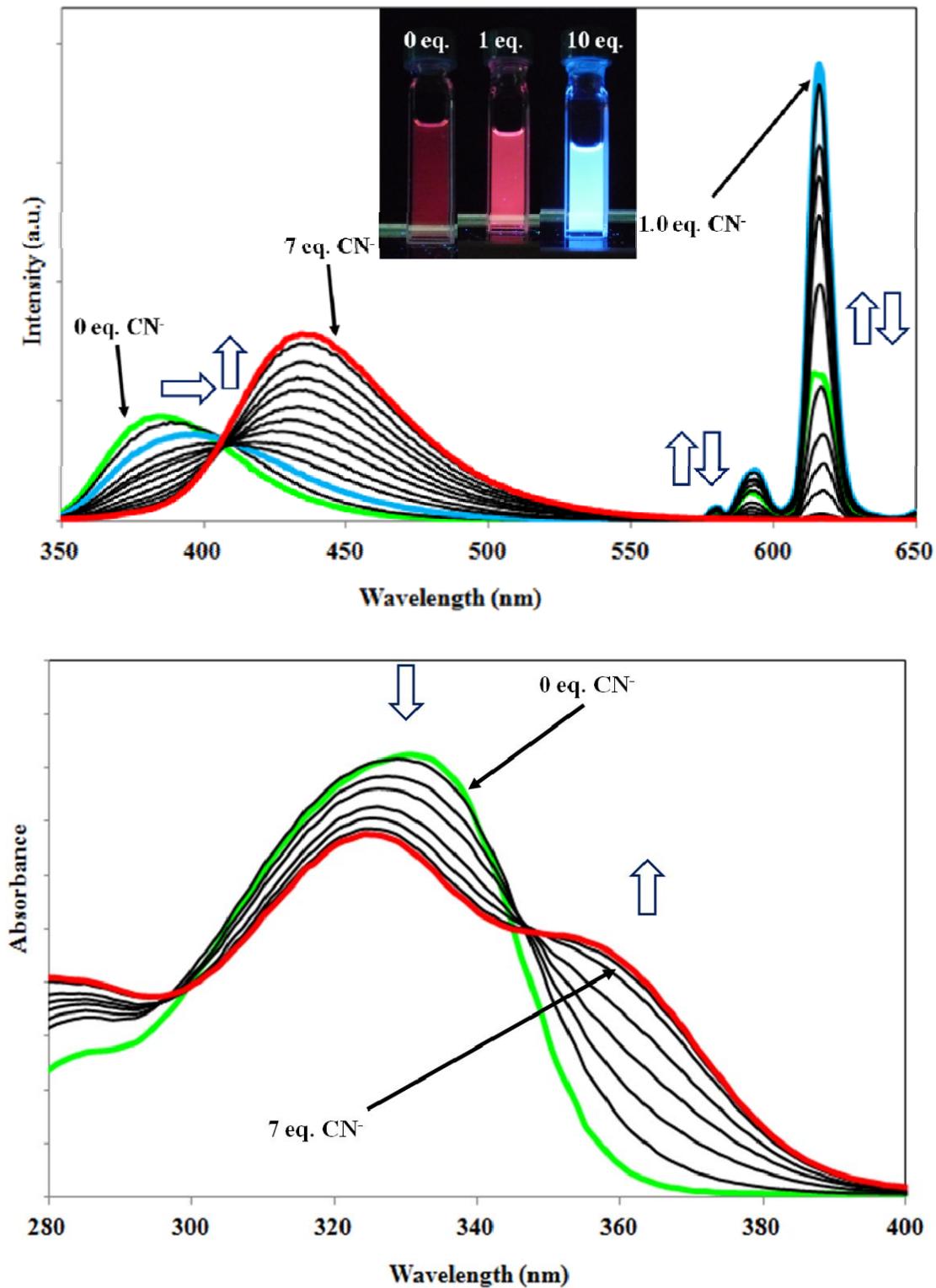


Figure S17: The fluorescence (top) and UV-Vis absorption (bottom) titration spectra of **1Eu** ( $1 \times 10^{-5}$  M) by TBCN in THF at 298 K.

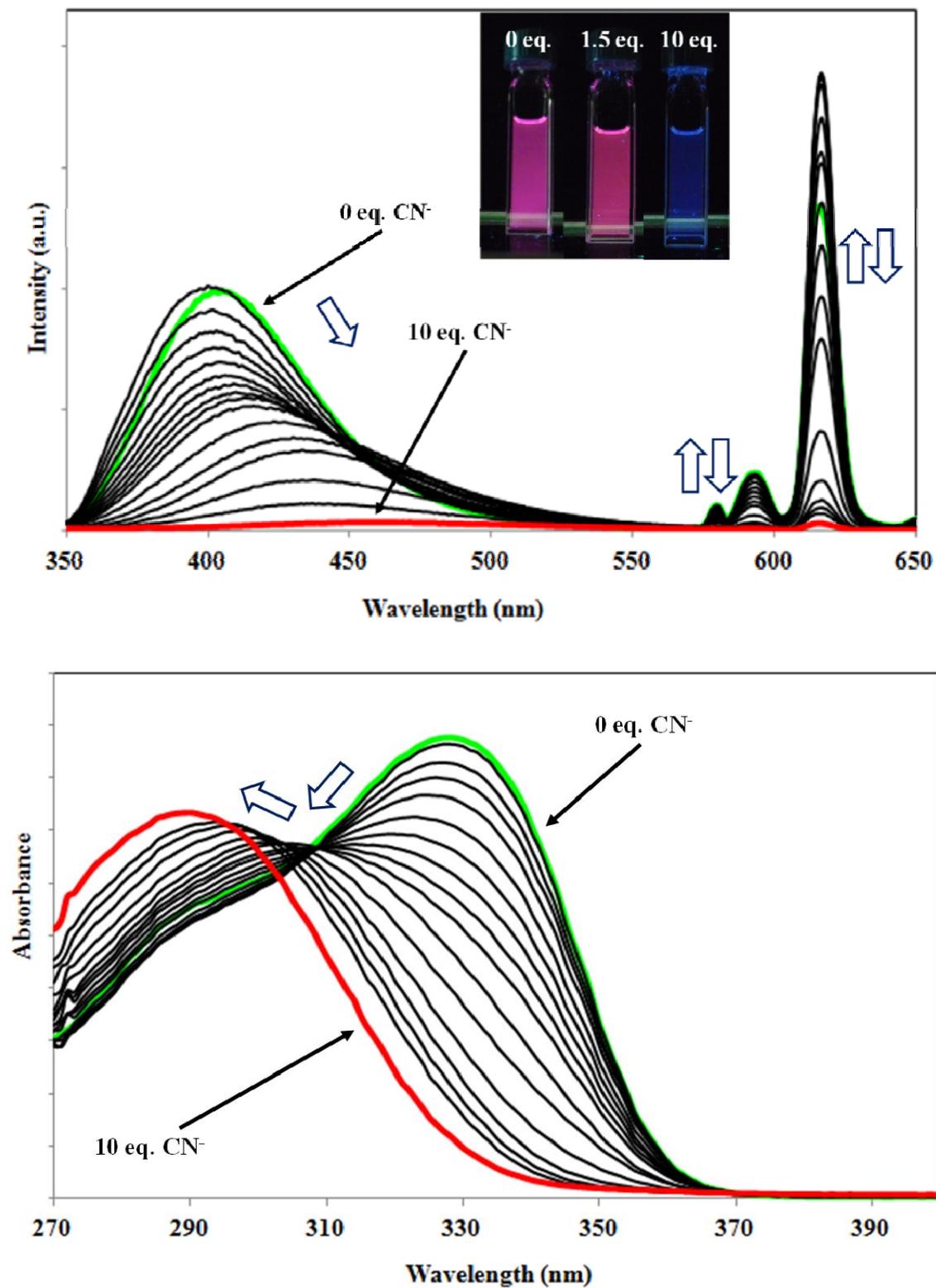


Figure S18: The fluorescence (top) and UV-Vis absorption (bottom) titration spectra of **2Eu** ( $1 \times 10^{-5}$  M) by TBACN in THF at 298 K.

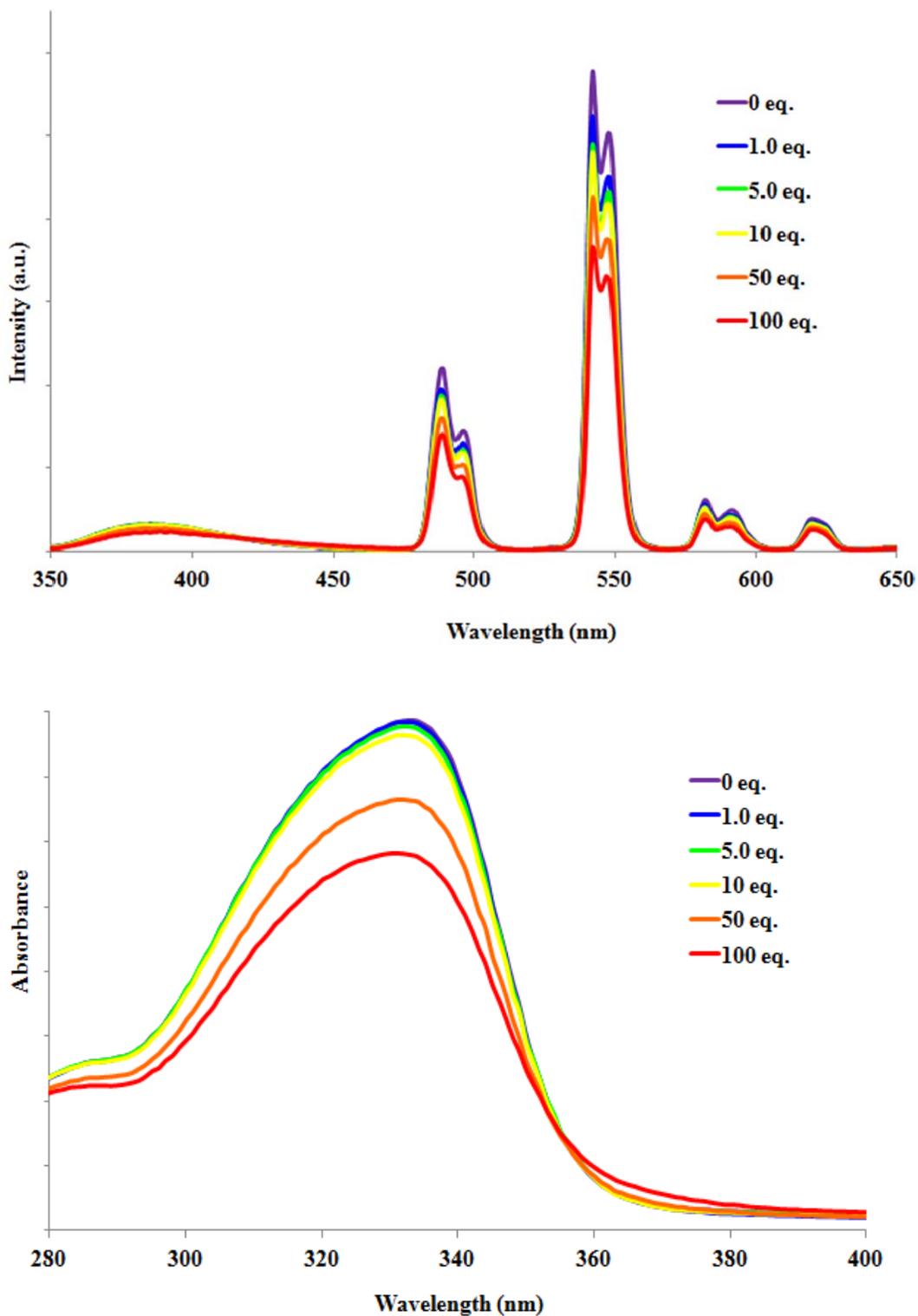


Figure S19: The fluorescence (top) and UV-Vis absorption (bottom) titration spectra of **1Tb** ( $1 \times 10^{-5}$  M) by TBACl in THF at 298 K. Upon addition of  $\text{Cl}^-$  ions to the lanthanide complex, no significant changes are observed to either the fluorescence or absorption spectra.

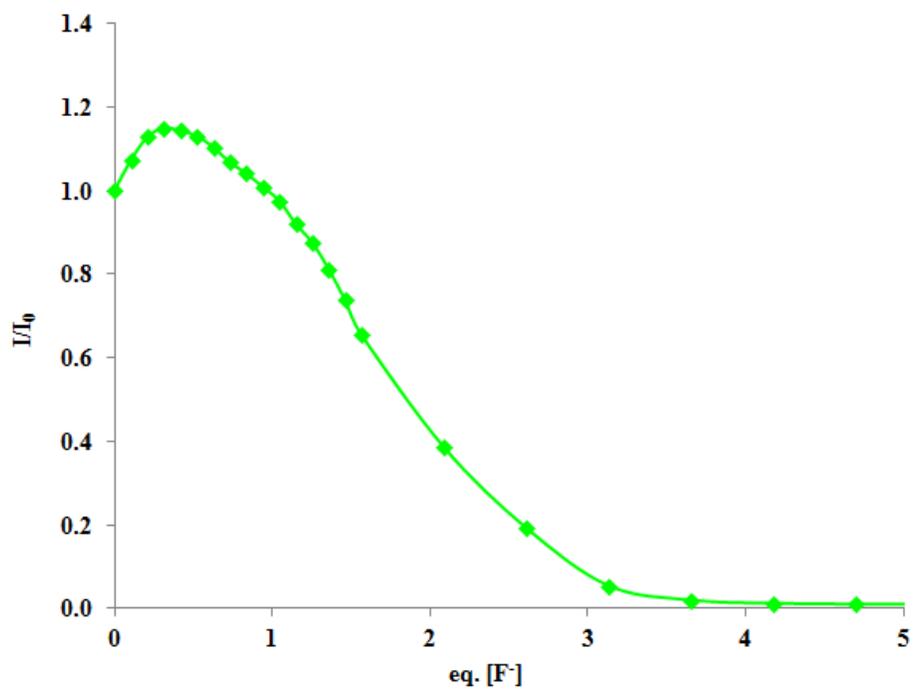


Figure S20: Stern-Volmer Plots of **1Tb** ( $\lambda_{\max}$  = 545 nm) ( $1 \times 10^{-5}$  M) in THF THF at rt when titrated with TBAF.

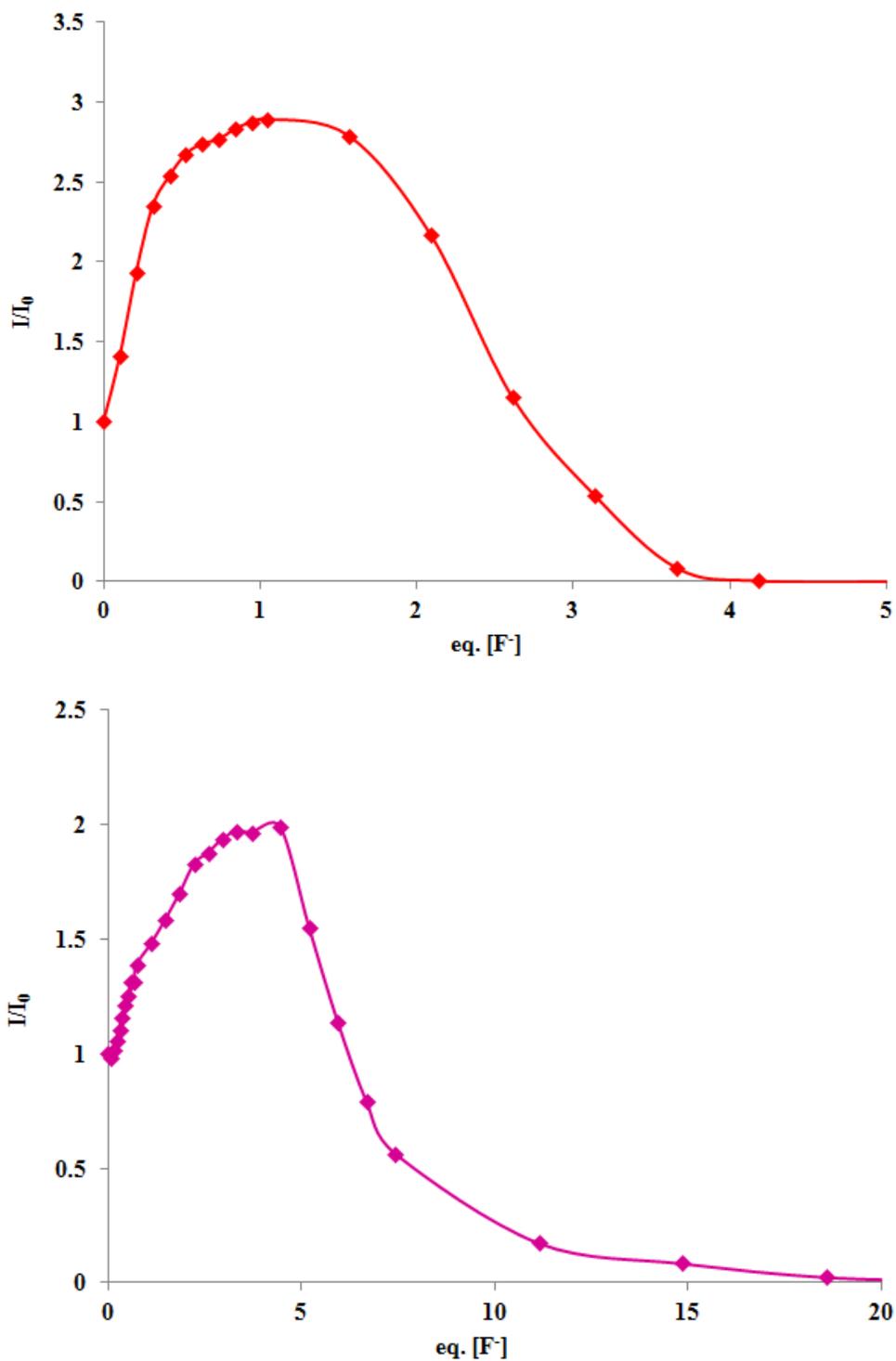


Figure S21: Stern-Volmer Plots of (top) **1Eu** ( $\lambda_{\text{max}} = 615 \text{ nm}$ ) and (bottom) **2Eu** ( $\lambda_{\text{max}} = 615 \text{ nm}$ ) in THF ( $1 \times 10^{-5} \text{ M}$ ) at rt when titrated with TBAF.

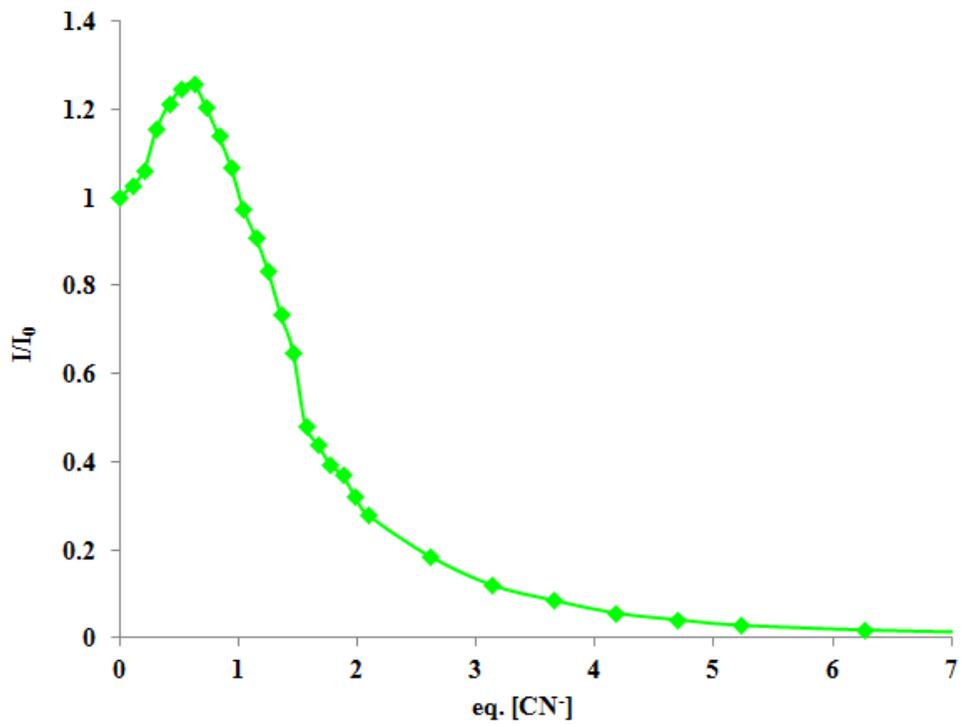


Figure S22: Stern-Volmer Plots of **1Tb** ( $\lambda_{max}= 545$  nm) in THF ( $1 \times 10^{-5}$  M) at rt when titrated with TBA-CN.

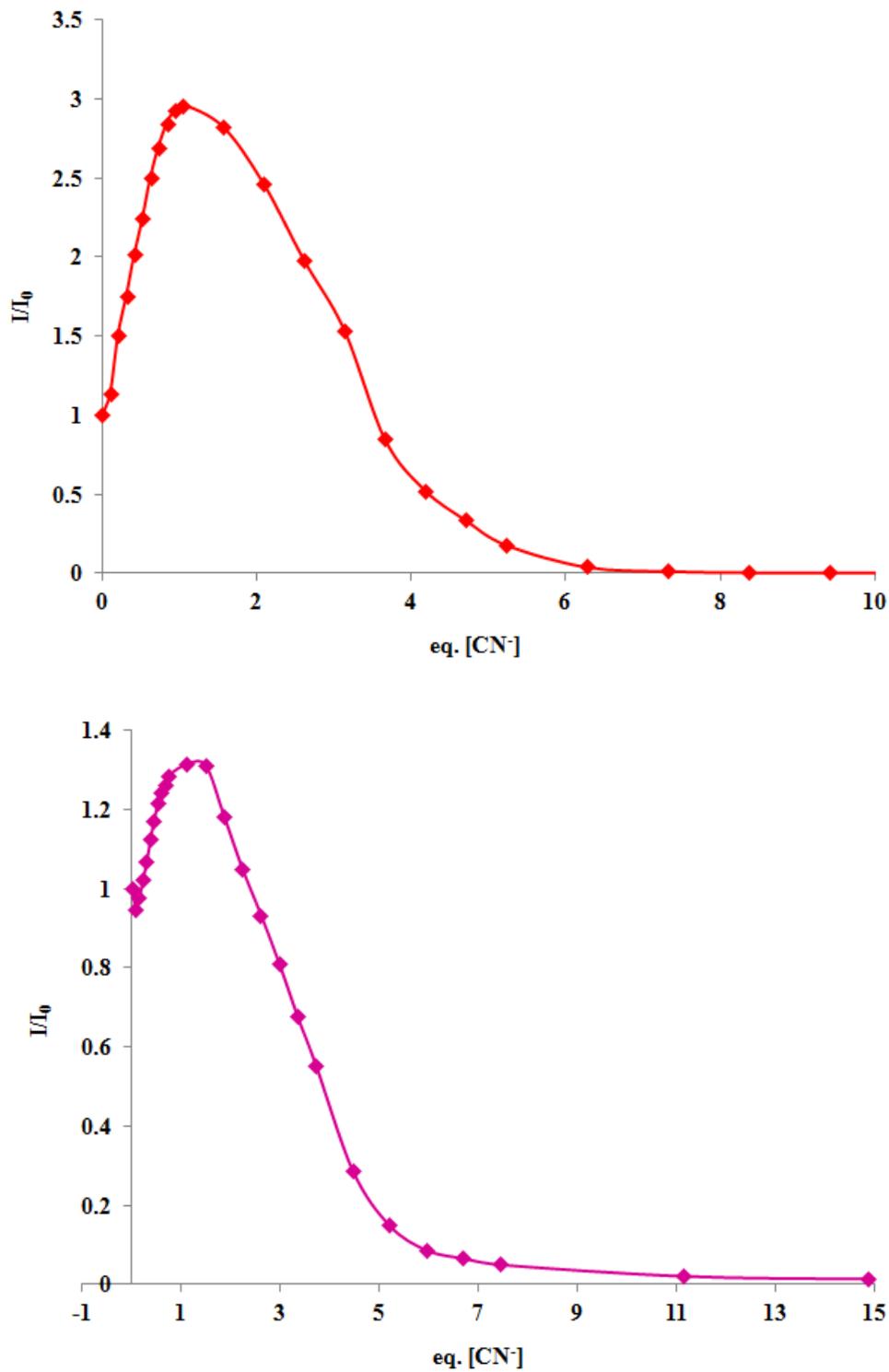


Figure S23: Stern-Volmer Plots of (top) **1Eu** ( $\lambda_{\text{max}} = 615 \text{ nm}$ ) and (bottom) **2Eu** ( $\lambda_{\text{max}} = 615 \text{ nm}$ ) in THF ( $1 \times 10^{-5} \text{ M}$ ) at when titrated with TBACN.

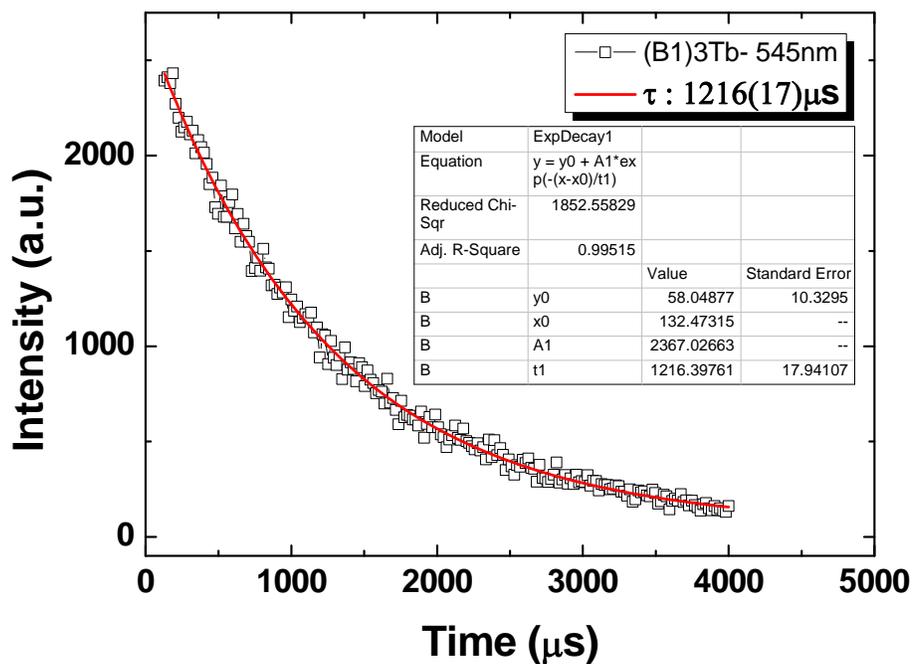


Figure S24: Lifetime fluorescence spectrum for **1Tb** ( $1 \times 10^{-5}$  M) in THF at 298 K ( $\lambda_{em}=545$  nm).

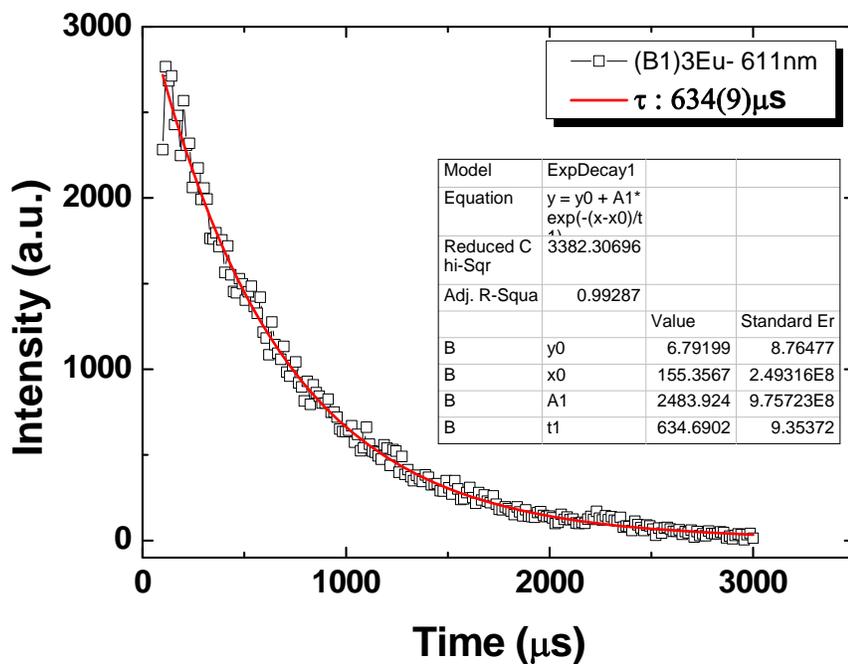


Figure S25: Lifetime fluorescence spectrum for **1Eu** ( $1 \times 10^{-5}$  M) in THF at 298 K ( $\lambda_{em}=611$  nm).

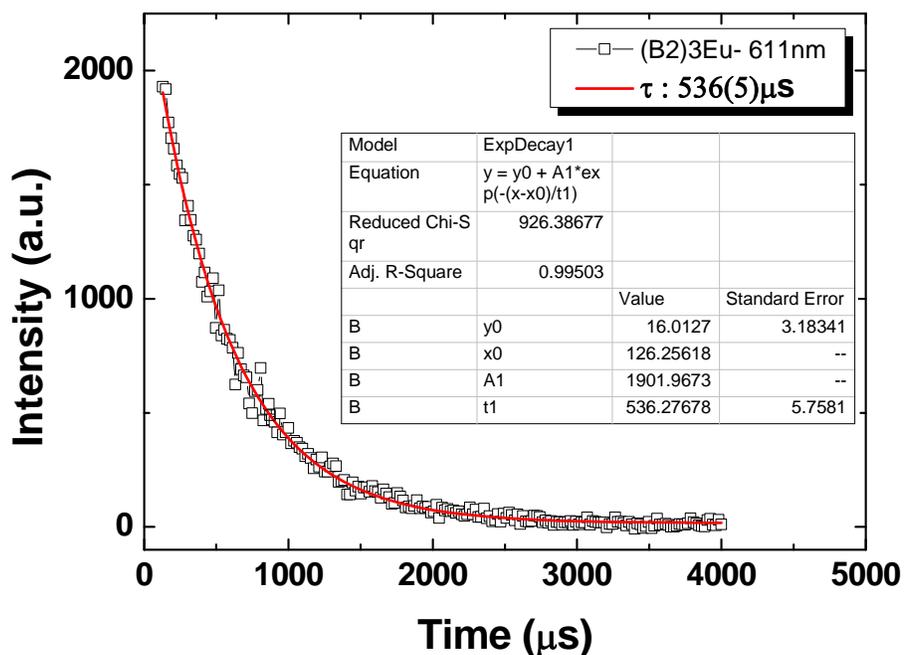


Figure S26: Lifetime fluorescence spectrum for **2Eu** ( $1 \times 10^{-5}$  M) in THF at 298 K ( $\lambda_{em}=611$  nm).

#### Procedure for fluoride and cyanide sensing using filter papers as the substrate:

The lanthanide compounds were loaded onto Whatman qualitative filter papers with  $11 \mu\text{m}$  size pores and a diameter of 7.0 cm. The filter papers were soaked in a THF solution containing about  $10^{-3}$  M of the lanthanide compound. After removal from the solution, the filter papers were left to dry under air for an hour. The substrate was then tested by spotting it with  $10 \mu\text{L}$  of analyte solution in either water or MeOH.

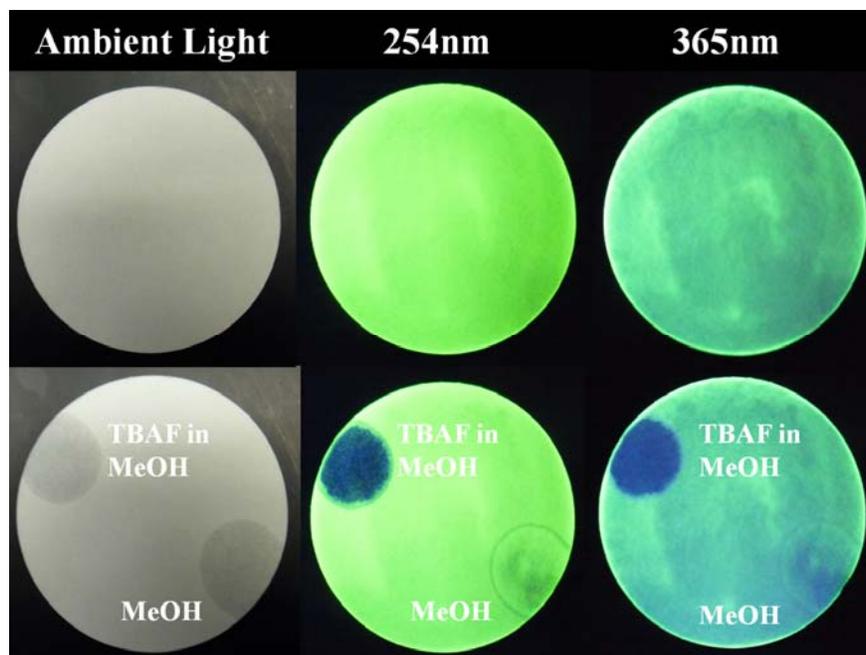


Figure S27: Photographs taken under irradiation wavelength stated above of **1Tb**-loaded filter paper (top) before and (bottom) after spotting with TBAF solution in MeOH.

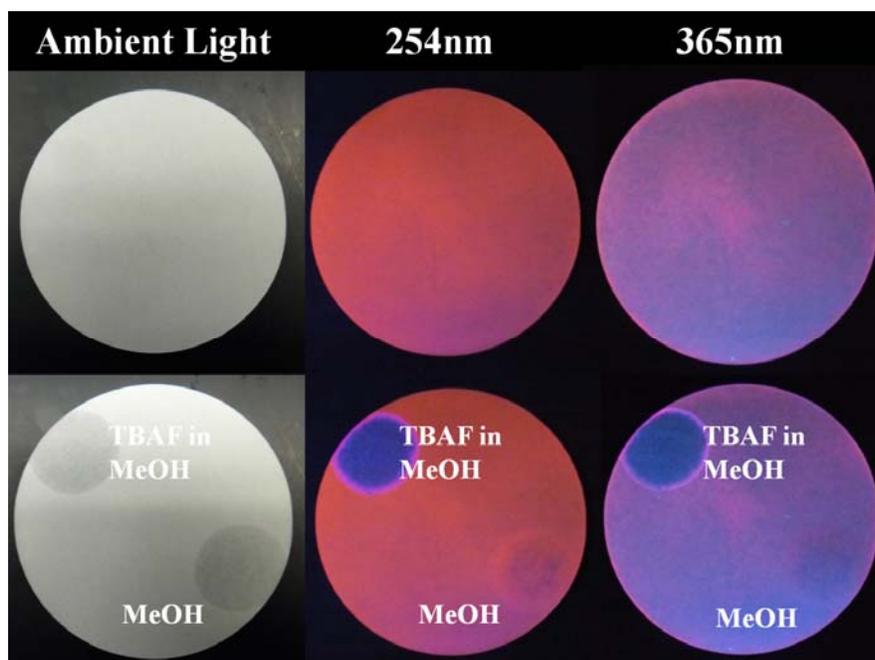


Figure S28: Photographs taken under irradiation wavelength stated above of **1Eu**-loaded filter paper (top) before and (bottom) after spotting with TBAF solution in MeOH.

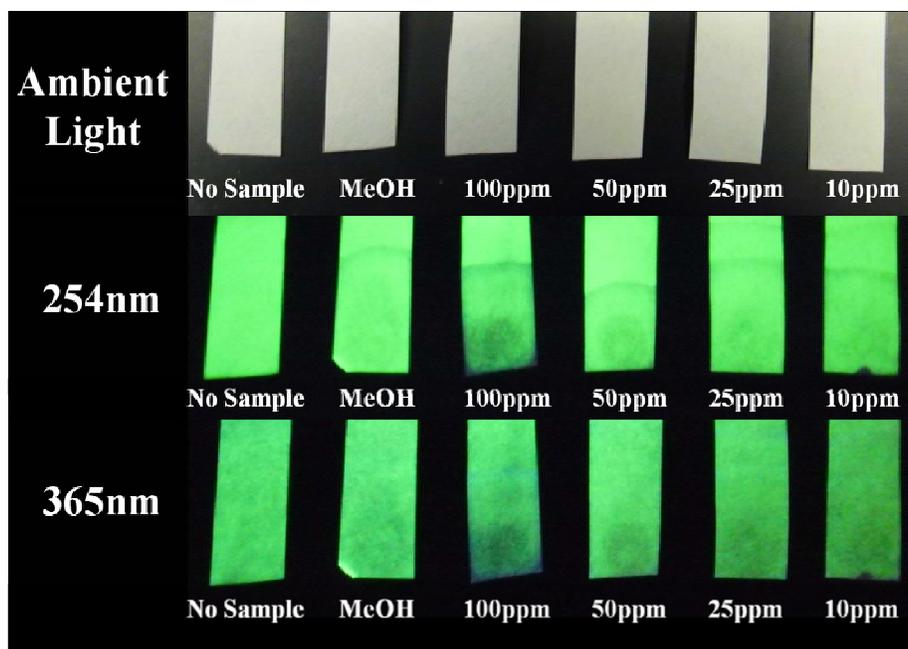


Figure S29: Photographs taken under irradiation described above to deduce the detection limit of **1Tb** doped filter paper for F<sup>-</sup> anions in MeOH.

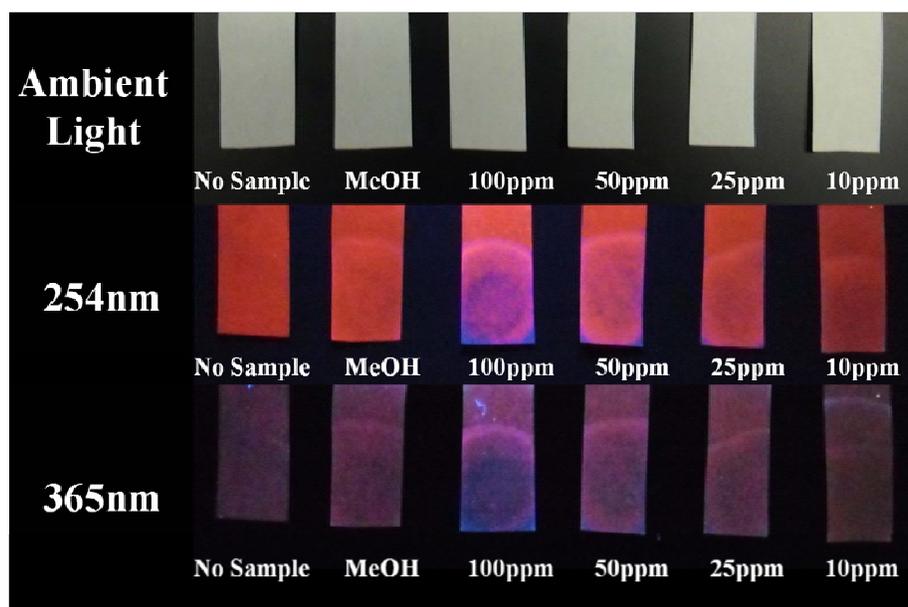


Figure S30: Photographs taken under irradiation described above to deduce the detection limit of **1Eu** doped filter paper for F<sup>-</sup> anions in MeOH.

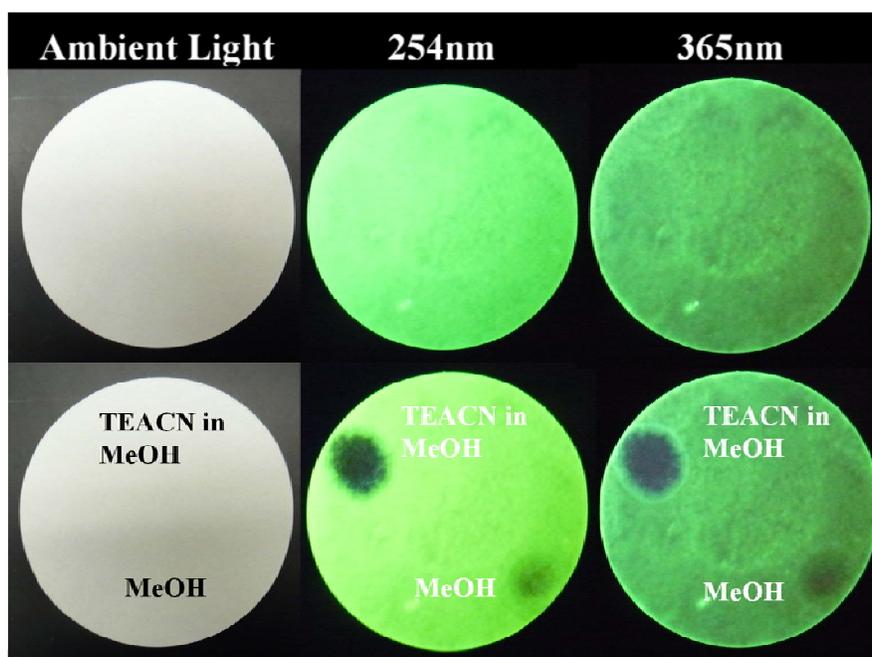


Figure S31: Photographs taken under irradiation wavelength stated above of **1Tb**-loaded filter paper (top) before and (bottom) after spotting with TEACN solution in MeOH.

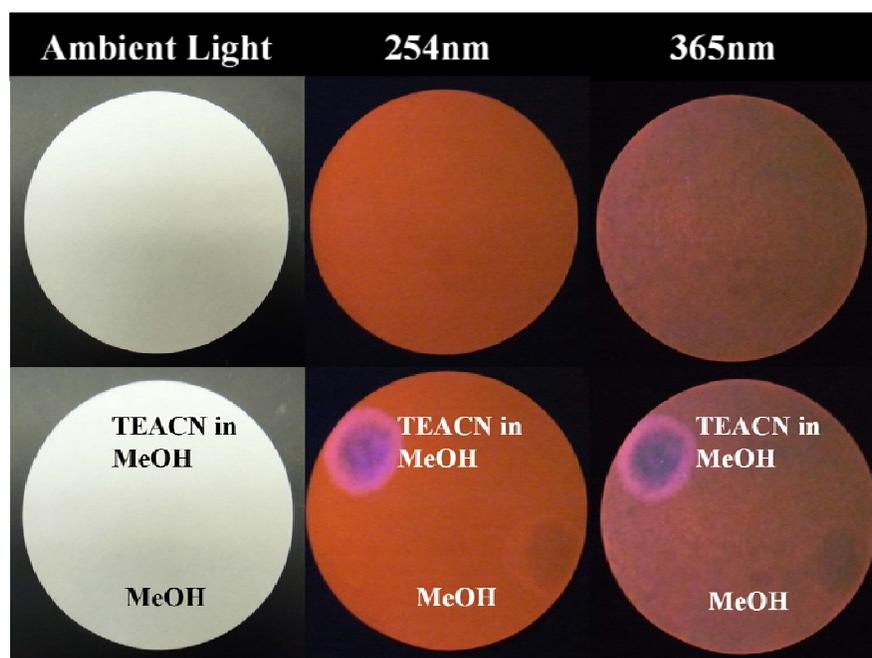


Figure S32: Photographs taken under irradiation wavelength stated above of **1Eu**-loaded filter paper (top) before and (bottom) after spotting with TEACN solution in MeOH.

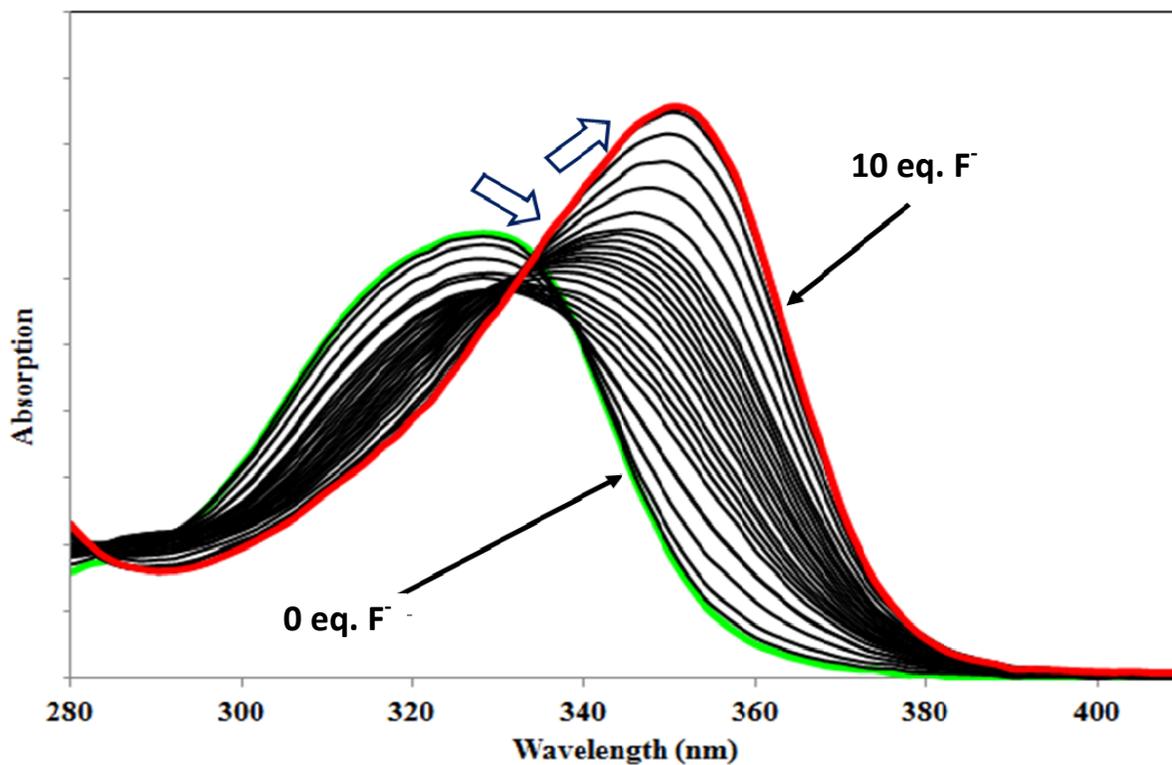


Figure S33. The fluorescence titration spectra of ligand **1** ( $1 \times 10^{-5}$  M) by TBAF in THF at 298 K, showing the behavior of ligand **1** toward fluorides. The complex response toward TBAF is caused by the proton of the carboxylic acid group. Nonetheless the general red-shift trend is characteristic of ligand **1**.

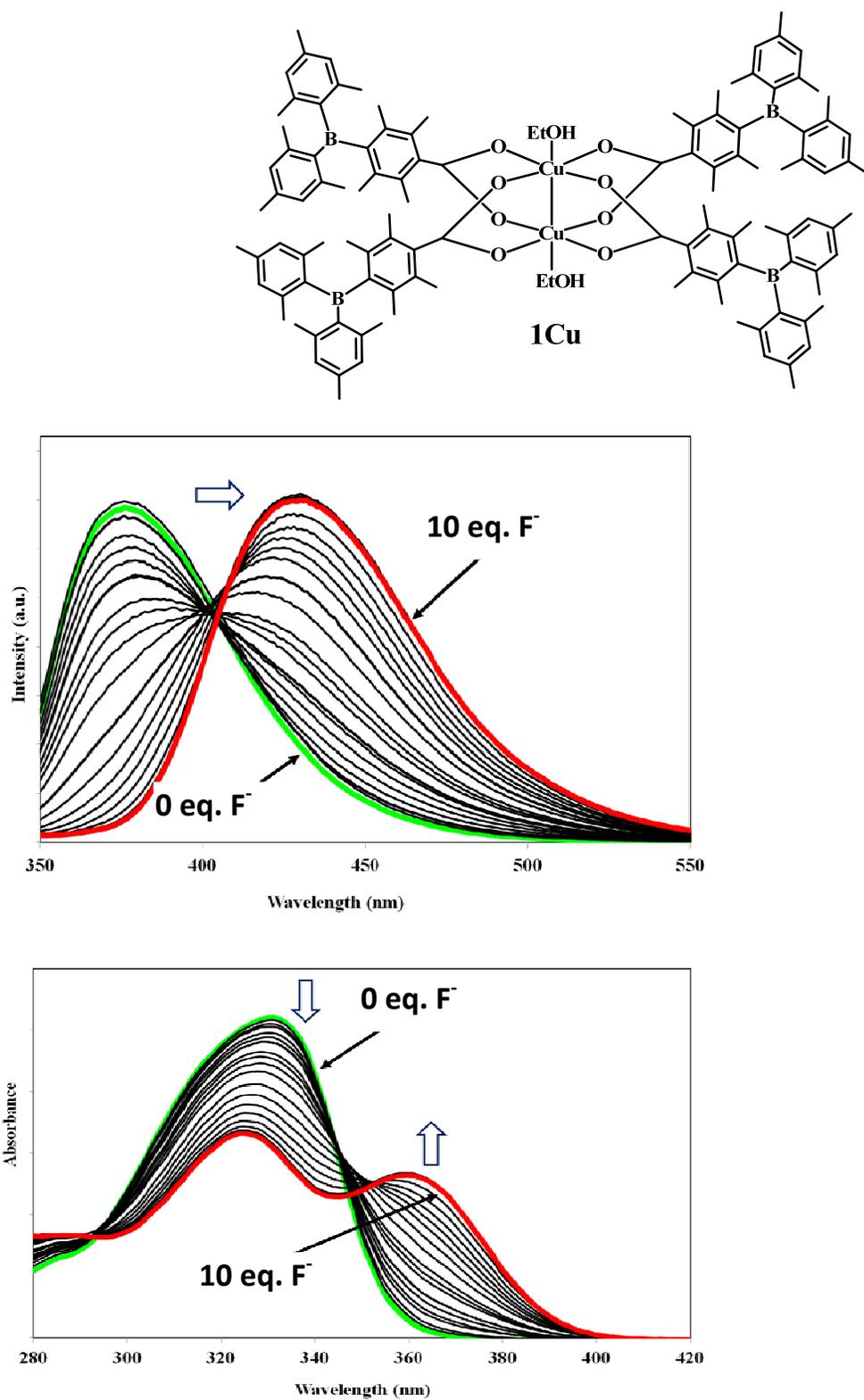


Figure S34. The fluorescence (top) and UV-Vis absorption (bottom) titration spectra of **1Cu** ( $1 \times 10^{-5}$  M) by TBACN in THF at 298 K, showing the behavior of ligand **1** toward anions. Compound **1Cu** is unpublished work from our group.