Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Highly luminescent charge-neutral europium (III) and terbium (III) complexes with tridentate nitrogen ligands

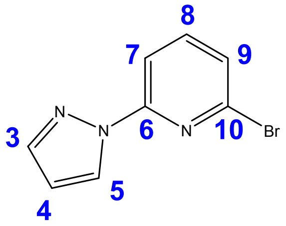
Kuppusamy Senthil Kumar, [a] Bernhard Schäfer, [b] Sergei Lebedkin, [b] Lydia Karmazin, [c] Manfred M. Kappes[b,d] and Mario Ruben[a,b]*

[a]Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS-Université de Strasbourg, 23, rue du Loess, BP 43, 67034 Strasbourg cedex 2, France
[b]Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany
[c]Service de Radiocristallographie, Institut de Chimie de Strasbourg UMR7177 CNRS-Université de Strasbourg, 1 rue Blaise Pascal, BP 296/R8, 67008 Strasbourg cedex, France
[d]Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany
*Email: mario.ruben@kit.edu

Table of contents p. 2

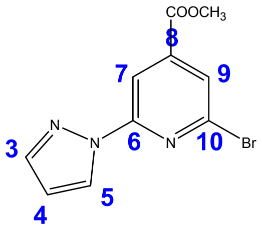
1. Synthesis

1.1. Synthesis of 2-bromo-6-pyrazol-1-yl-pyridine (1): In a clean and dry 100 mL two-neck flask, NaH (65% in mineral oil, 0.786 g, 18mmol, 1.2 eq) was dispersed completely in dry DMF (20 mL) by stirring the mixture under Ar atmosphere. To this solution pyrazole (1.2 g, 18 mmol, 1.2 eq) was added slowly to minimize the violent reaction that occurred due to the formation of sodium salt of pyrazole. The mixture was stirred for about 45 min at 100℃. 2, 6-Dibromo-pyridine **1** (3.55g, 15 mmol, 1.0 eq) was added into this reaction mixture and heated at 130◦C for 2hrs under Ar atmosphere. The mixture was cooled and DMF was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (150 ml), successively washed water and brine and dried over Na_2SO_4. Crude product was purified by silica gel column chromatography using CH_2Cl_2 as eluent to yield title compound as pure white solid. **Yield:** 1.95g (58%).



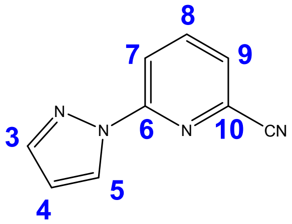
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ= 8.48 (d, ^{3}J=3.2 Hz, 1H; H5), 7.88 (d, ^{3}J=7.9 Hz, 1H; H9), 7.69 (s, 1H; H3), 7.60 (t, ^{3}J=7.9 Hz, 1H; H8), 7.29 (d, ^{3}J=7.8 Hz, 1H; H7) 6.42 (t, ^{3}J=2 Hz; 1H; H4). **^{13}C NMR (75 MHz, $CDCl_3$, 300 K):** 108.1, 110.7, 125.1, 127.456, 139.8, 140.4, 142.6, 152.3, ppm. **GC-MS** in Acetone (Da): Time, m/z, (rel. intensity, assigned structure) = 7.651min, 223 (100%, $C_8H_6BrN_3$, calc. = 222.97). **Elemental Analysis:** Calc. for: $C_8H_6BrN_3$ C, 42.88; H, 2.71; N, 18.75; Found: C, 42.86; H, 2.67; N, 18.86.

1.2. Synthesis of 2-bromo-6-pyrazol-1-yl-isonicotinic acid methyl ester (2): In a dry 250 mL three-neck flask, NaH (65% in mineral oil, 0.441, 10.08 mmol, 1.2 eq) was dispersed in dry DMF (20 mL) by stirring the mixture for 1 h under Ar atmosphere. To this solution pyrazole (0.71 g, 10.08 mmol, 1. 2 eq) was added slowly to minimize the violent reaction that occurred due to the formation of sodium salt of pyrazole. The mixture was stirred for about 30 min at 100°C. Methyl-2, 6-dibromoisonicotinate **1** (2.6 g, 8.4 mmol, 1.0 eq) was added into this reaction mixture and heated at 130 ◦C for 2hrs under Ar atmosphere. The mixture was cooled and poured into water. The mixture was acidified with conc. HCl until completion of precipitation and the formed precipitate was filtered, washed with water and dried under vacuum. MeOH (75 ml) and H_2SO_4 (2 ml) were added to the crude carboxylic acid (1.82g) and heated to 80°C overnight. After being cooled to room temperature, MeOH was evaporated and the resulting residue was dissolved in CH_2Cl_2 (150 ml), washed with saturated $NaHCO_3$ solution and water and dried over $MgSO_4$. Crude ester was purified by silica gel column chromatography using CH_2Cl_2 as eluent. **Yield:** 1.01 g (43%).



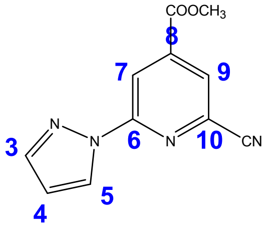
^{1}H NMR (300 MHz, CDCl$_3$, 300 K): δ= 8.46(d, ^3J=2.7 Hz, 1H; H5), 8.36 (d, ^4J=0.6 Hz, 1H; H9), 7.81 (s, 1H; H3), 7.71 (d, ^4J=0.9 Hz, 1H; H7), 6.44 (dd, ^3J=2.6 Hz, 1.5 Hz; 1H; H4), 3.93(s, 3H; CH_3). **^{13}C NMR (75 MHz, CDCl$_3$, 300 K):** 53.3 (CH_3), 108.8, 110.9, 124.7, 127.8, 140.6, 142.3, 143.3, 152.1, 163.8 (C=O), ppm. **GC-MS** in acetone (Da): Time, m/z, (rel. intensity, assigned structure) = 8.638 min, 280.9 (100%, $C_{10}H_8BrN_3O_2$, calc. = 280.98). **Elemental Analysis:** Calc. for: $C_{10}H_8BrN_3O_2$ C, 42.58; H, 2.86; N, 14.9; Found: C, 42.63; H, 2.9; N, 14.91.

1.3. Synthesis of 6-pyrazol-1-yl-pyridine-2-carbonitrile (3): To 5 ml of dry and Ar bubbled DMF, 2-bromo-6-pyrazol-1-yl-pyridine (0.448 g, 2 mmol) and copper(I)cyanide (0.214 g, 3 mmol) were added and the mixture heated to 150°C under Ar for 4 hrs. DMF was evaporated under reduced pressure. A green solid was obtained, to this 1g of potassium cyanide in 5 ml of water was added leading to the formation of white precipitate. This was extracted with dichloromethane, washed with distilled water and dried over Na_2SO_4. Purification of the crude product by silica gel chromatography using dichloromethane as eluent yielded the title compound as white solid. **Yield:** 0.281 g (83 %).



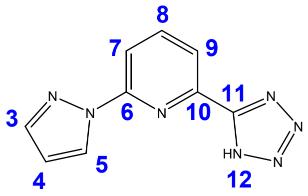
^{1}H NMR (300 MHz, CDCl$_3$, 300 K, TMS): δ= 8.55 (d, ^3J=2.7 Hz, 1H; H5), 8.23 (d, ^3J=8.5 Hz, 1H; H9), 7.95 (t, ^3J=8.5 Hz, 1H; H8), 7.75 (s, 1H; H3), 7.57 (d, ^3J=7.5 Hz, 1H; H7), 6.506 (t, ^3J=2.9 Hz, 1.7 Hz; 1H; H4). **^{13}C NMR (75 MHz, CDCl$_3$, 300 K):** 108.7, 116.2, 116.6, 125.7, 127.5, 131.6, 139.6, 143, 152, ppm. **GC-MS** in acetone (Da): Time, m/z, (rel. intensity, assigned structure) = 7.75 min, 170 (100%, $C_9H_6N_4$, calc. = 170.06). **Elemental Analysis:** Calc. for: $C_9H_6N_4 \cdot 0.4H_2O$ C, 60.94; H, 3.86; N, 31.59; Found: C, 60.84; H, 3.42; N, 30.56.

1.4. Synthesis of 2-cyano-6-pyrazol-1-yl-isonicotinic acid methyl ester (4): To 5 ml of dry and Ar bubbled DMF, 2-bromo-6-pyrazol-1-yl-isonicotinic acid methyl ester (0.843g, 3 mmol) and copper(I)cyanide (0.358g, 4 mmol) were added and the mixture heated to 150°C under Ar for 2 hrs. DMF was evaporated under reduced pressure, solids were extracted with EtOAc and washed with distilled water and dried over $MgSO_4$. Purification of the crude mixture by silica gel chromatography using dichloromethane as eluent yielded compound 4 as white solid. **Yield:** 0.336g (49%).



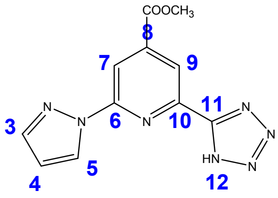
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): ^{1}H NMR (300 MHz, $CDCl_3$, 300 K, TMS): δ= 8.76 (d, ^{4}J=1.2 Hz, 1H; H9), 8.57 (d, ^{3}J=2.7 Hz, 1H; H5), 8.08 (d, ^{4}J=1.2 Hz, 1H; H7), 7.80 (d, ^{3}J=1.5 Hz, 1H; H3), 6.54 (dd, J=2.7 Hz; 1H; H4), 3.93 (s, 3H; CH_3). **^{13}C NMR (300 MHz, $CDCl_3$, 300 K):** 55.5 (CH_3), 109.4, 116.3, 124.9, 127.9, 132.5, 141.7, 143.7, 153.1, 163.3 (C=O), ppm. **GC-MS** in acetone (Da): Time, m/z, (rel. intensity, assigned structure) = 8.556 min, 228.0 (100%, $C_{11}H_8N_4O2$, calc. = 228.06). **Elemental Analysis:** Calc. for: $C_{11}H_{8.8}N_4 \cdot 0.4H_2O$ C, 56.12; H, 3.77; N, 23.8; Found: C, 56.17; H, 3.45; N, 23.58.

1.5. Synthesis of 2-pyrazol-1-yl-6-(1H-tetrazol-5-yl)-pyridine (L^{1}H): To 6 ml of dry DMF, 6-pyrazol-1-yl-pyridine-2-carbonitrile (0.272 g, 1.6 mmol), sodium azide (0.256g, 4 mmol) and ammonium chloride (0.211g, 4 mmol) were added and the mixture heated to 130°C for 20 hrs. Reaction mixture was poured into ice cold water and pH adjusted to 2 using 1N HCl. The precipitate was filtered and washed with water and dried under reduced pressure. The white solid was washed with dichloromethane and dried under vacuum to yield the title compound. **Yield:** 0.318g (93%).



^{1}H NMR (300 MHz, DMSO, 300 K): δ= 9.02 (d, ^{3}J=2.1 Hz, 1H; H5), 8.25 (m, 1H, H9), 8.12 (m, 2H), 7.89 (s, 1H), 6.68 (d, ^{3}J=1.2 Hz, 1H; H4) ppm. **^{13}C NMR (75 MHz, DMSO, 300 K):** 109, 114.1, 120.2, 128.4, 142, 143.3, 151.2, 154.6 ppm. **ESI-MS** in DMSO (Da): m/z, (rel. intensity, assigned structure) = 236.05 (100%, $C_9H_7N_7Na$, calc. = 236.05). **Elemental Analysis:** Calc. for: $C_9H_7N_7$ C, 50.7; H, 3.31; N, 45.99; Found: C, 50.63; H, 3.31; N, 45.73.

1.6. Synthesis of 2-pyrazol-1-yl-6-(1H-tetrazol-5-yl)-isonicotinic acid methyl ester (L^{1}H-COOMe) To 6 ml of dry DMF, 2-cyano-6-pyrazol-1-yl-isonicotinic acid methyl ester (0.228g, 1 mmol), sodium azide (0.192 g, 3 mmol) and ammonium chloride (0.158g, 3 mmol) were added and the mixture heated to 130°C for 20 hrs. Reaction mixture was poured into ice cold water and pH adjusted to 3 using 1N HCl. The precipitate was filtered and washed with water and dried under reduced pressure. The white solid was further washed with dichloromethane and dried under vacuum. **Yield:** 0.181g (67%).



^{1}H NMR (300 MHz, C_2D_6SO, 300 K): δ= 9.02 (d, ^{3}J=2.7 Hz, 1H; H5), 8.38 (s, 2H), 7.93 (d, ^{4}J=1.2 Hz, 1H; H7), 6.72 (dd, ^{3}J=2.7 Hz, 2.4 Hz; 1H; H4), 3.98 (s, 3H; CH_3) ppm. **^{13}C NMR (300 MHz, $CDCl_3$, 300 K):** 53.2 (CH_3), 109.1, 112.5, 118, 128.2, 141.8, 143.3, 143.4, 151.6, 154, 163.7 (C=O) ppm. **ESI-MS** in DMSO (Da): m/z, (rel. intensity, assigned structure) = 294.09 (100%, $C_{11}H_9N_7NaO_2$, calc. = 294.07). **Elemental Analysis:** Calc. for: $C_{11}H_9N_7O_2{\cdot}0.55H_2O$ C, 46.99; H, 3.62; N, 34.87; Found: C, 47.08; H, 3.53; N, 34.87.

1.7. General procedure for the synthesis of lanthanide complexes: Ligand L^{1}H or L^{1}H-COOMe (0.38 mmol) was dissolved in 14 ml of CH_2Cl_2 and 6 ml of MeOH solvent mixture followed by addition of Et_3N (55 µl, 0.4 mmol) and the mixture was stirred at RT for 15 mins. To this, $LnCl_3{\cdot}6H_2O$ (0.1 mmol) was added and stirred at RT for 2 hours. The reaction mixture was filtered and allowed to stand at RT. After 1 to 2 weeks time colorless crystalline solids were deposited in the case of L^{1}H based complexes, the complexes were separated by filtration and dried under vacuum to yield the expected complexes in analytically pure form.

In the case of L^1H-COOMe series gradual precipitation occurred over a period of 1 hour after the addition of $LnCl_3·6H_2O$ to the ligand solution, the mixture was further stirred for 1 more hour. The colorless microcrystalline precipitates were separated by filtration, washed with methanol and dichloromethane and dried under vacuum to yield the expected complexes in analytically pure form.

1.7.1. Eu* $(L^1)_3·3H_2O$: Yield: 28 mg, 36%. **ESI-MS (CH_2Cl_2/CH_3OH):** m/z = 790.13 ([M+H]$^+$, *for ^{153}Eu). **Elemental Analysis:** Calc. for: Eu$(L)_3·3H_2O$ ($C_{27}H_{24}EuN_{21}O_3$) C, 38.49; H, 2.87; N, 34.91; Found: C, 38.49; H, 2.49; N, 34.57.

1.7.2. Gd$(L^1)_3·3H_2O$: Yield: 43 mg, 54%. **ESI-MS (CH_2Cl_2/CH_3OH):** m/z = 795.13 [M+H]$^+$. **Elemental Analysis:** Calc. for: Gd$(L)_3·3H_2O$ ($C_{27}H_{24}GdN_{21}O_3$) C, 38.25; H, 2.85; N, 34.69; Found: C, 38.68; H, 2.67; N, 34.75.

1.7.3. Tb$(L^1)_3·3H_2O$: Yield: 45 mg 57%. **ESI-MS (CH_2Cl_2/CH_3OH):** m/z = 796.14 [M+H]$^+$. **Elemental Analysis:** Calc. for: Tb$(L)_3·3H_2O$ ($C_{27}H_{24}TbN_{21}O_3$) C, 38.17; H, 2.85; N, 34.62; Found: C, 38.49; H, 2.49; N, 34.57.

1.7.4. Eu*$(L^1\text{-COOMe})_3·6H_2O$:Yield: 86mg 89%. **ESI-MS (CH_2Cl_2/CH_3OH):** m/z = 964.15 ([M+H]$^+$, *for ^{153}Eu). **Elemental Analysis:** Calc. for: Eu(EW-L)$_3·6H_2O$ ($C_{33}H_{36}EuN_{21}O_{12}$) C, 37.02; H, 3.39; N, 27.47; Found: C, 37.34; H, 3.30; N, 27.16.

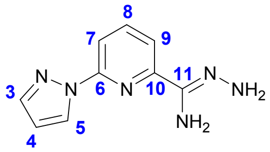
1.7.5. Gd$(L^1\text{-COOMe})_3·6H_2O$: Yield: 81 mg, 84%, **ESI-MS (CH_2Cl_2/CH_3OH):** m/z = 969.15 [M+H]$^+$. **Elemental Analysis:** Gd(EW-L)$_3·6H_2O$ ($C_{33}H_{36}GdN_{21}O_{12}$), Calc. for: C, 36.84; H, 3.37; N, 27.34; Found: C, 35.03; H, 3.14; N, 24.02.

1.7.6. Tb$(L^1\text{-COOMe})_3·5.5H_2O$: Yield: 43 mg, 54 %. **ESI-MS (CH_2Cl_2/CH_3OH):** m/z = 970.16 [M+H]$^+$. **Elemental Analysis:** Calc. for: Tb(EW-L)$_3·5.5H_2O$ ($C_{33}H_{35}TbN_{21}O_{11.5}$) C, 37.09; H, 3.30; N, 27.52; Found: C, 37.14; H, 2.90; N, 27.27.

1.8. Synthesis triazole-pyridine-pyrazole ligand (L^2H) and its lanthanide complexes

1.8.1. Synthesis of 6-(1H-pyrazol-1-yl)picolinohydrazonamide

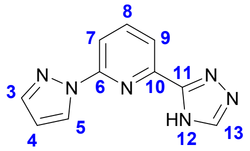
6-(1H-pyrazol-1-yl)picolinonitrile (1.286 g, 7.56 mmol) was suspended in EtOH (25 cm^3) and hydrazine hydrate (98%, 6 cm^3) was added. The reaction mixture was stirred at room temperature for about 36 h. A fine white powdered precipitate was formed that was different to the also white starting material. The EtOH was removed using a rotary evaporator (water bath, T=36 °C, 10 mbar). The precipitate was filtered off, washed with water (2 x 3 cm^3) and dried under a stream of air of a membrane pump. Yield: m=1.446 g (7.15 mmol, 94 %). The compound was used without further purification.



^{1}H NMR (500 MHz, CDCl$_3$): δ=8.59 (dd, J = 2.72, 0.42 Hz, 1H, H5), 7.99 (dd, J = 7.94, 0.91 Hz, 1H, H7), 7.94 (dd, J = 7.8 Hz, 0.94 Hz, 1H, H9), 7.86 (t, J = 7.88, 7.9 Hz, 1H, H8), 7.78 (d, J = 1.19 Hz, 1H, H3), 6.52 (dd, J = 2.53, 1.75 Hz, 1H, H4), 5.20 (s, 2H, NH2), 4.67 (s-broad, 2H, NH2) ppm. **^{13}C NMR** (126 MHz, D$_6$-DMSO): δ=150.2 (C11), 149.5 (C6), 147.7 (C10), 142.2 (C3), 139.2 (C8), 126.7 (C5), 117.3 (C9), 112.4 (C7), 107.8 (C4) ppm.

1.8.2. 2-(1H-pyrazol-1-yl)-6-(4H-1,2,4-triazol-3-yl)pyridine (L^{2}H):

6-(1H-pyrazol-1-yl)picolinimidohydrazide (0.905 g, 4.47 mmol) was added in small portions into 25 cm^3 of formic acid (T=9°C). After the addition was finished, the reaction was stirred at room temperature (for 0.5 h) and later it was refluxed (16 h, overnight). The solvent was removed under reduced pressure and the reaction mixture was concentrated to about 3 cm^3. This was cooled with a water-ice bath and a small amount of water was added. The pH was adjusted to a value of about 4-5 using NaOH (aqu. 1 mol/dm^3). It was kept in the ice bath for about 2-3 h. The precipitate was collected by filtration, washed with water (4 cm^3) and was dried at a stream of air over-night using a pump. The crude product was purified by column chromatography (SiO$_2$, eluent CH$_2$Cl$_2$ and MeOH). Yield: 0.448 g (2.1 mmol, 47%).



^{1}H NMR (500 MHz, d6-DMSO): δ=14.73 (s, 1H, H12), 9.06 (s, 1H, H5), 8.29 (s, 1H, H13), 8.14 (t, ^{3}J=7.86, 7.86 Hz, 1H, H8), 7.99 (d, ^{3}J = 7.99 Hz, 1H, H7) 7.98 (d, ^{3}J = 7.38 Hz, 1H, H9), 7.87 (s, 1H, H3), 6.65 (s, 1H, H4) ppm. **^{13}C NMR (126 MHz, D$_6$-DMSO):** δ=154.4 (C11), 150.8 (C6), 150.5 (C13), 145.4 (C10), 142.5 (C3), 141.0 (C8), 127.9 (C5), 118.5 (C7), 112.3 (C9), 108.3 (C4) ppm. **ESI-TOF-MS (in DMSO):** m/z= 235.08 (100%, $[(C_{10}H_8N_6)Na]^+=[M+Na]^+$). **Elemental Analysis:** $[L^2H\cdot(H_2O)_{2/3}$ with $(C_{30}H_{28}N_{18}O_2)$ (672.7)]: calc. C 53.57, H 4.20, N 37.48; found C 53.74, H 4.61, N 37.59.

1.8.3. Eu(L²)₃·1.5(H₂O)

L2H (0.08 g, 0.38 mmol, 3 eq.) was suspended in EtOH (10 mL) and an aqueous solution of NaOH (1.16 mL, 0.33 mol/dm³) was added and stirred at 40°C. $Eu(H_2O)_6Cl_3$ (46 mg, 0.126 mmol, 1 eq.) was added to this solution and the reaction was heated at 70°C for 3 h. After three days the precipitate was collected by filtration and washed three times with 0.7 mL H_2O/EtOH (V, 1:1). The product was dried at 80 °C and 1 mbar. Yield: 54 mg (0.068 mmol, 55%). **Elemental Analysis:** [M·1.5(H_2O) with $(C_{60}H_{48}Eu_2N_{36}O_3)_{0.5}$ (812.6)]: calc. C 44.34, H 2.98, N 31.03; found C 44.19, H 2.85, N 30.84. **ESI-TOF-MS (in CH_3CN):** m/z= 787.145 (100%, $[((C_{10}H_7N_6)_3Eu^*)H]^+=$ ($[M+H]^+$, *for ^{153}Eu), calc.=787.148), 809.127 (70%, $[((C_{10}H_7N_6)_3Eu^*)Na]^+=[M+Na]^+$, calc.=809.130).

1.8.4. Tb(L²)₃·H₂O

L2H (0.0733 g, 0.345mmol, 3 eq), aqueous NaOH (0.25M, 1.5 cm³, 0.384 mmol), water (1mL), EtOH (2 cm³), and $Tb(H_2O)_6Cl_3$ (42.9 mg, 0.115 mmol, 1 eq) was heated in a sealed tube in a microwave oven (T=120°C, 10 min). Afterwards the EtOH was removed under reduced pressure. Some water (2 cm³) was added and allowed to stand overnight. The precipitate was filtered, washed with water (3 x 1 cm³) and dried at vacuum. Yield 0.078 g (98µmol, 85%). **Elemental Analysis:** [M·H_2O with $(C_{30}H_{23}TbN_{18}O)$ (810.56)]: calc. C 44.45, H 2.86, N 31.10; found C 44.04, H 2.78, N 30.93. **ESI-TOF-MS (in CH_3CN):** m/z=793.13 (85%, $[((C_{10}H_7N_6)_3Tb)H]^+=[M+H]^+$, calc.=793.15), 815.11 (100%, $[((C_{10}H_7N_6)_3Tb)Na]^+=[M+Na]^+$, calc.=815.13).

1.8.5. Gd(L²)₃·2H₂O

A sealed tube was charged with L2H (0.1 g, 0.47 mmol, 3 eq.), MeOH (2 cm³), aqueous NaOH (1.5 cm³, 0.33 mol/dm³), and $Gd(H_2O)_6Cl_3$ (58.3 mg, 0.157 mmol, 1 eq.). It was heated and stirred in a microwave oven (80°C, 10 min). Afterwards 3 cm³ of water was added and the MeOH was removed by rotary evaporation. It was allowed to stand overnight in the fridge. The precipitate was collected by filtration and washed three times with 1 cm³ H_2O. The product was dried at vacuo. Yield: 63 mg (79.6 µmol, 50%). **Elemental Analysis:** [M·$2H_2O$ with $(C_{30}H_{25}GdN_{18}O_2)$ (826.9)]: calc. C 43.58, H 3.05, N 30.49; found C 43.87, H

3.31, N 30.68. **ESI-TOF-MS** (in CH$_3$CN): m/z= 792.150 (100%, [((C$_{10}$H$_7$N$_6$)$_3$Gd)H]$^+$=[M+H]$^+$, calc.=792.151), 814.133 (13%, [((C$_{10}$H$_7$N$_6$)$_3$Gd)Na]$^+$=[M+Na]$^+$, calc.=814.134).

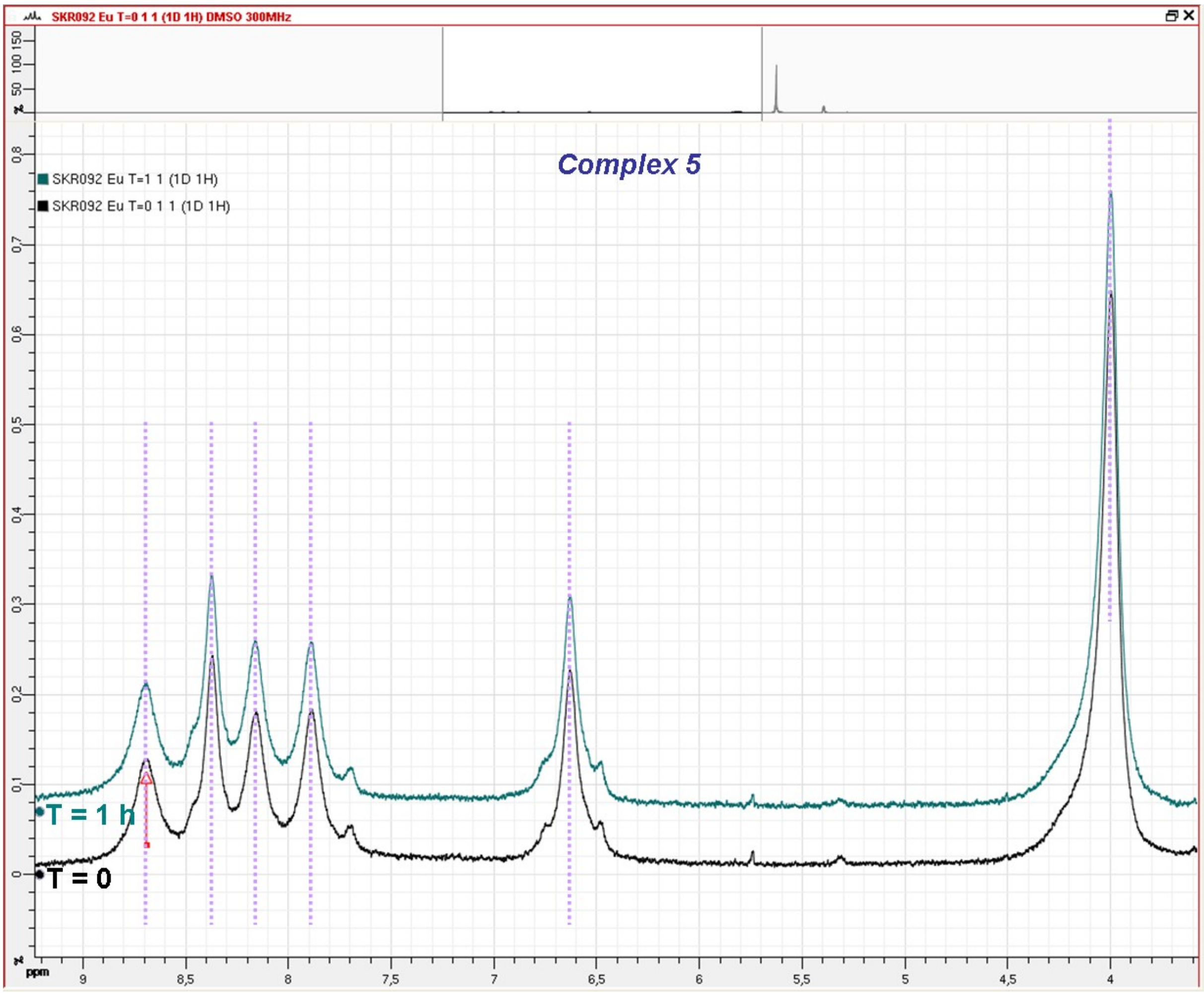


Figure S1. Time dependant NMR Spectra of Complex 5 in d^6-DMSO

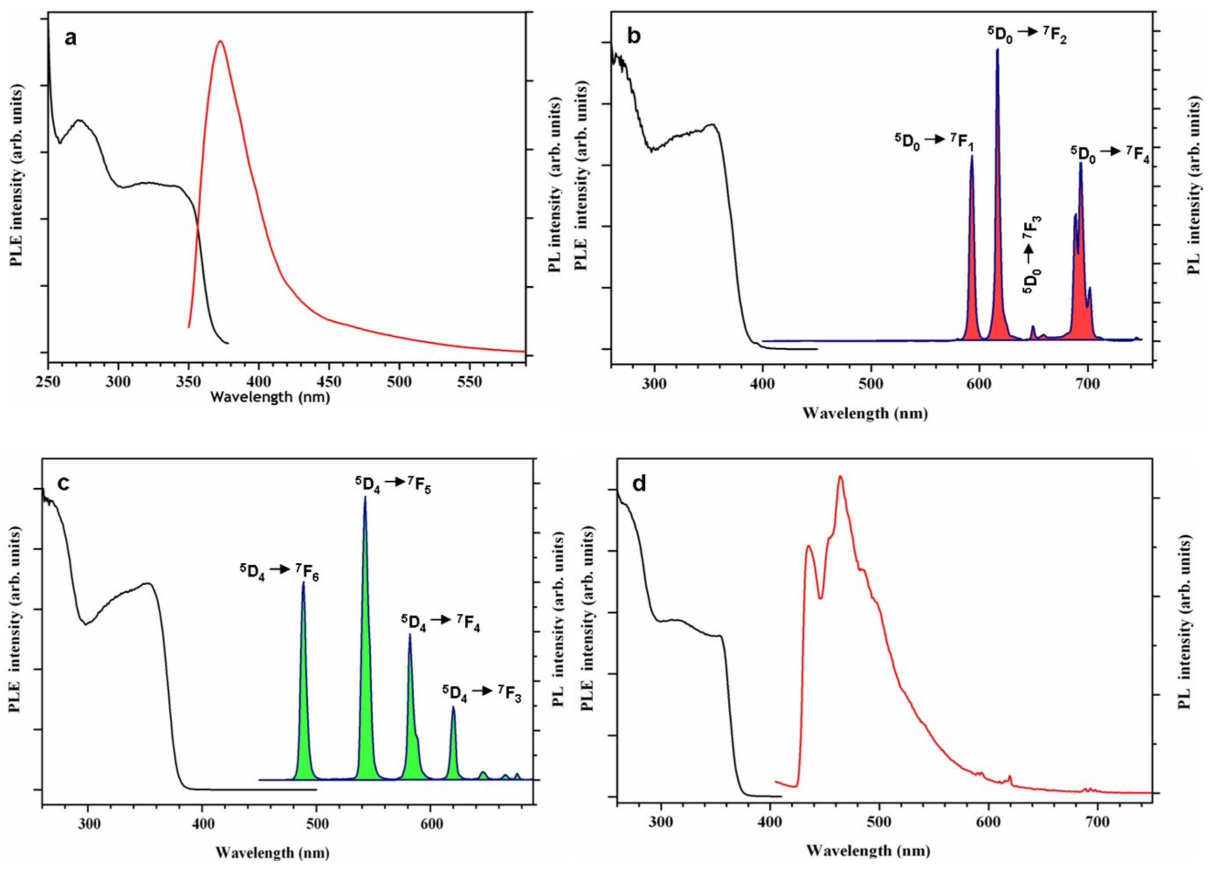


Figure S2. a. Photoluminescence excitation (PLE) and emission (PL) spectra of ligand L^{1}H-COOMe at 295 K, the PL and PLE spectra were excited and recorded at 300 and 370 nm respectively. b and c. Excitation and emission spectra of Eu(L^1-COOMe)$_3$ and Tb(L^1-COOMe)$_3$ at 295 K, the PL and PLE spectra were excited and recorded at 360 and 616 nm for europium complex and at 360 and 490 nm for terbium complex. d. PLE and phosphorescence emission spectrum of Gd(L^1-COOMe)$_3$ PL and PLE spectra were excited and recorded at 350 and 464 nm respectively at the temperature of 20 K. All measurements were carried out in solid state.

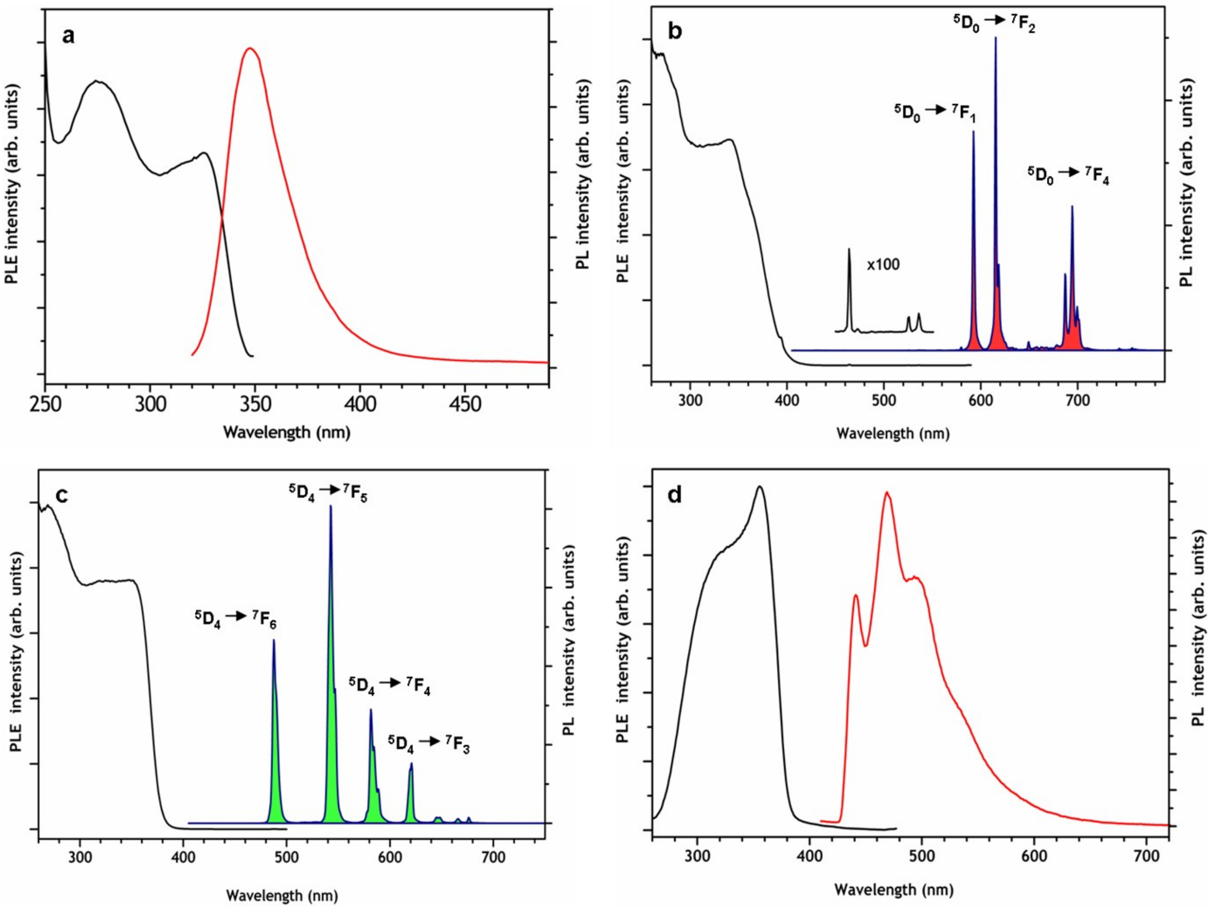


Figure S3. a) Photoluminescence excitation (PLE) and emission (PL) spectra of ligand L^{2}H at 295 K, the PL and PLE spectra were excited and recorded at 300 and 360 nm, respectively. b) and c) Excitation and emission spectra of Eu(L^2)$_3$ and Tb(L^2)$_3$ at 20 and 295 K, the PL and PLE spectra were excited and recorded at 330 and 617 nm for europium complex and at 300 and 490 nm for terbium complex. d) Phosphorescence emission spectrum of Gd(L^2)$_3$ excited at 330 nm at the temperature of 20 K. All measurements were carried out in solid state.

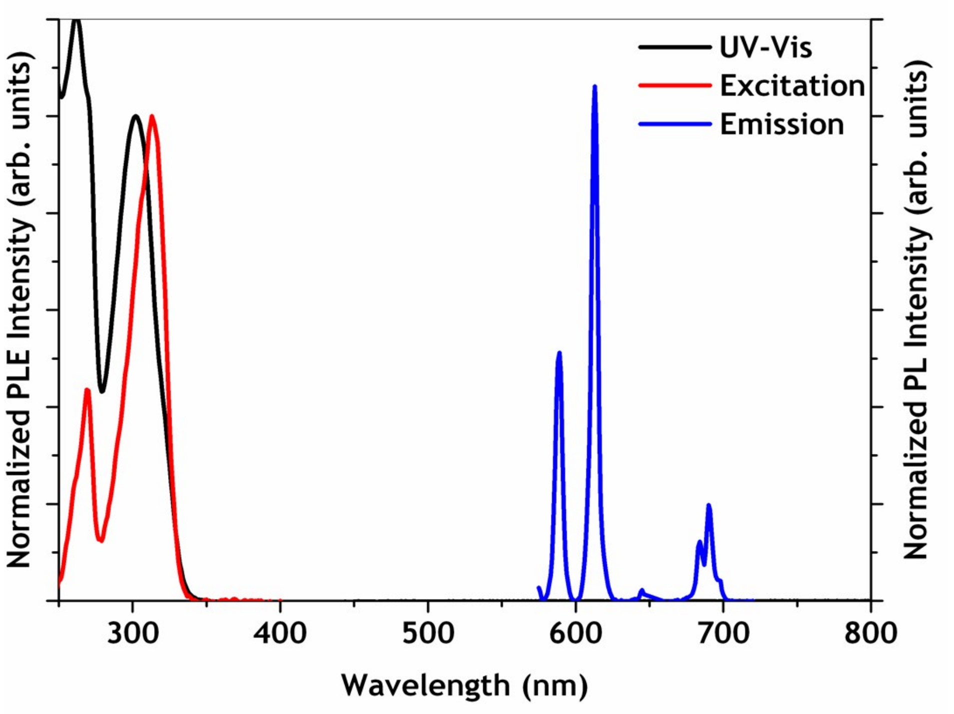


Figure S4. The UV-vis, excitation and luminescence spectrum of Eu(L^1)$_3$ at 295 K in ethanol, the PL and PLE spectra were excited and recorded at 302 and 617 nm.

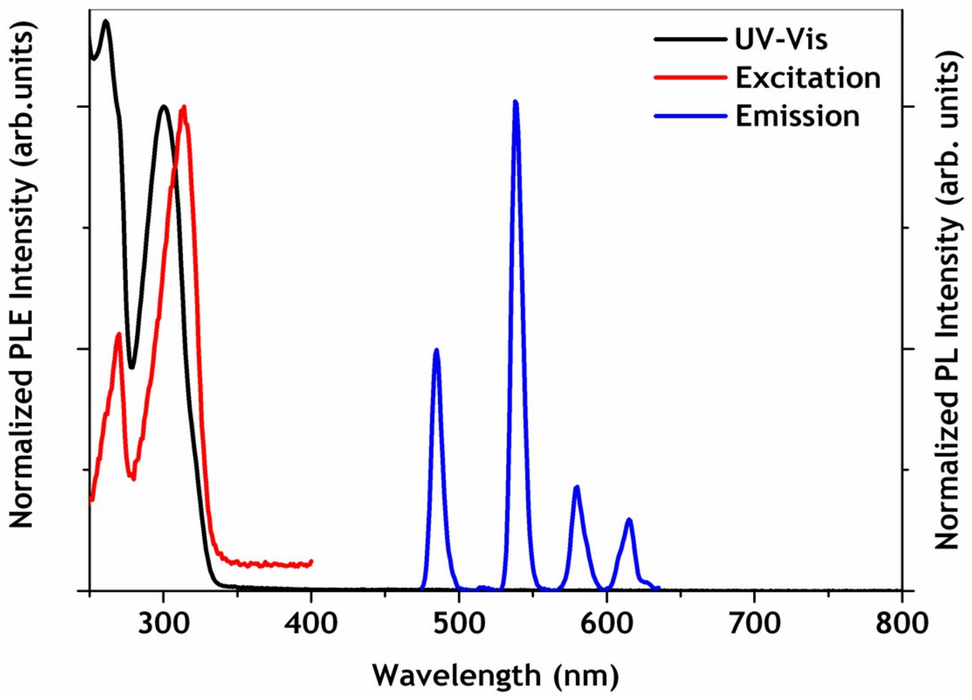


Figure S5. The UV-vis, excitation and luminescence spectrum of Tb(L^1)$_3$ at 295 K in ethanol, the PL and PLE spectra were excited and recorded at 302 and 490 nm.

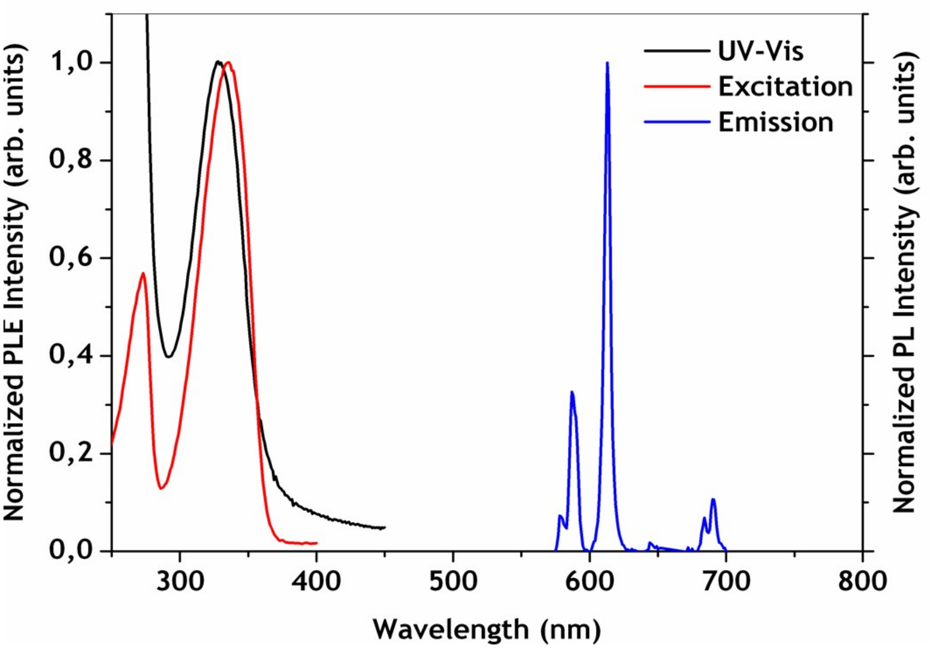


Figure S6. The UV-vis, excitation and luminescence spectrum of Eu(L^2-COOMe)$_3$ at 295 K in ethanol, the PL and PLE spectra were excited and recorded at 323 and 617 nm.

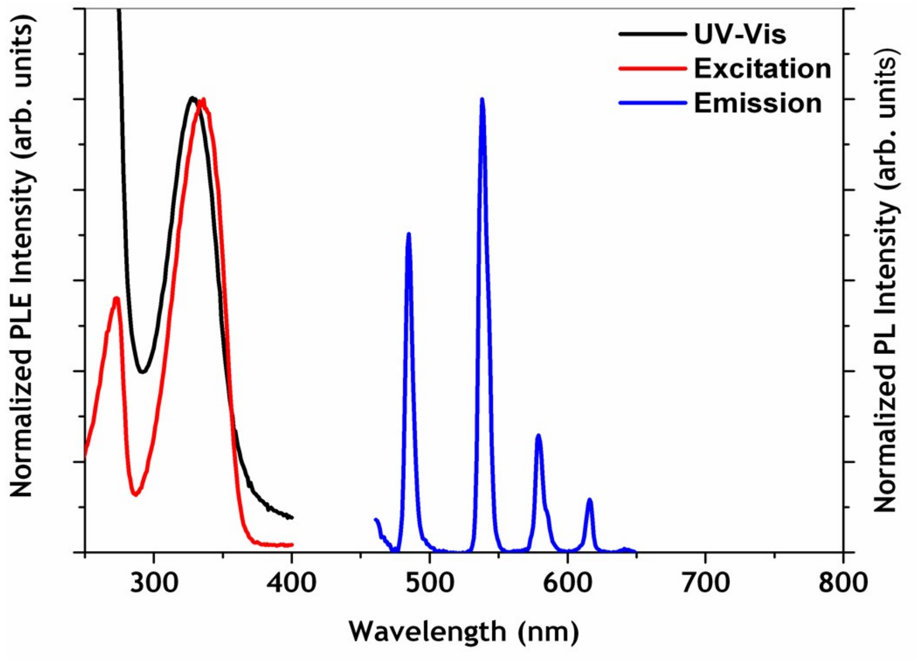


Figure S7. The UV-vis, excitation and luminescence spectrum of Tb(L^2-COOMe)$_3$ at 295 K in ethanol, the PL and PLE spectra were excited and recorded at 323 and 490 nm.

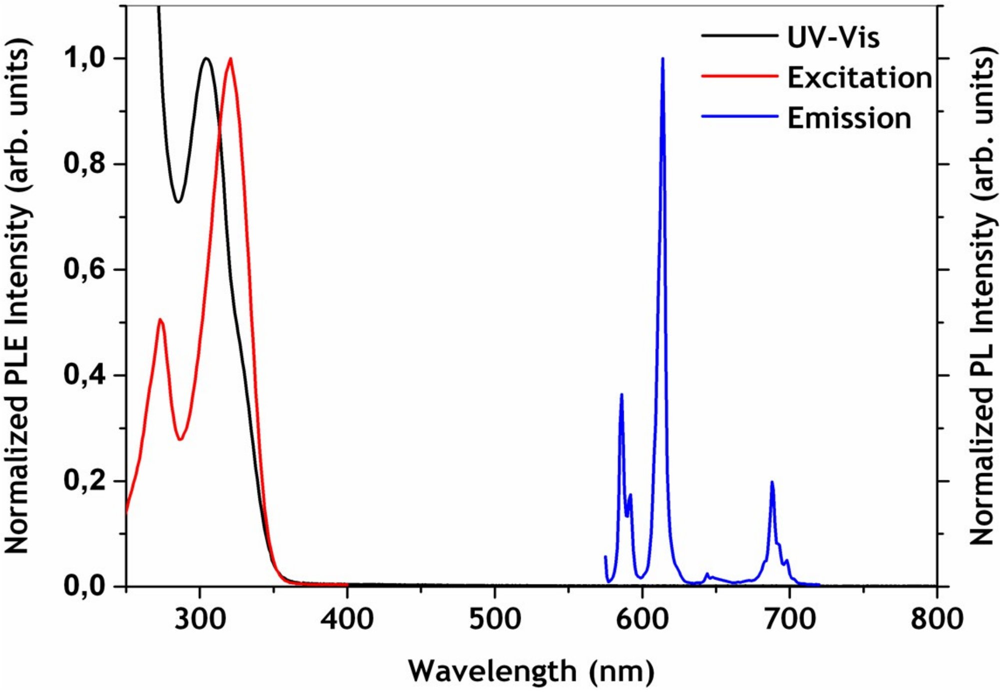


Figure S8. UV-vis, excitation and emission spectra of Eu(L^2)$_3$ at 295 K in ethanol, the PL and PLE spectra were excited and recorded at 302 and 617 nm.

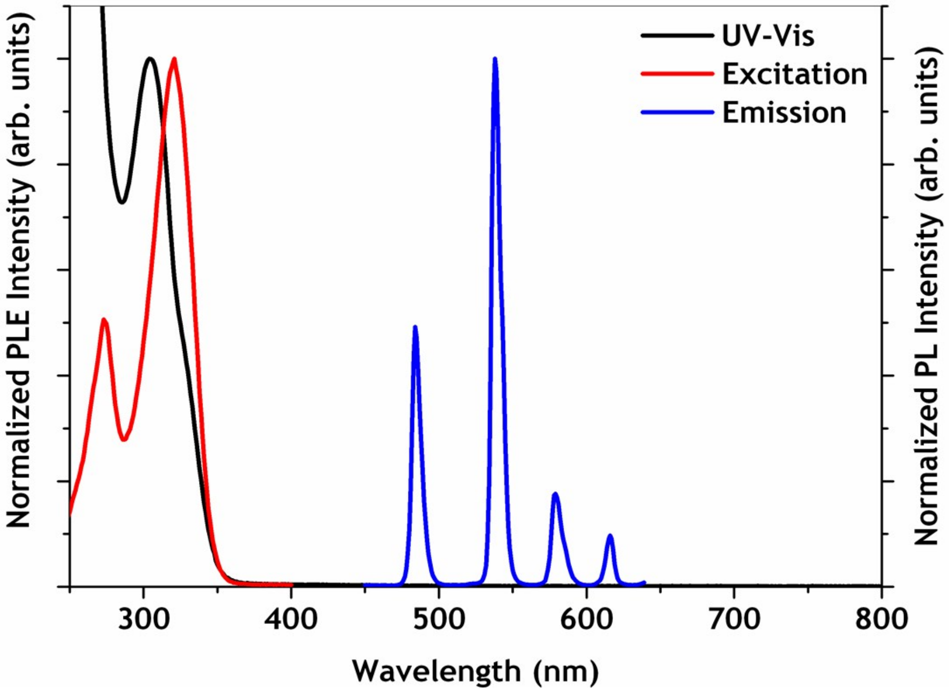


Figure S9. UV-vis, excitation and emission spectra of Tb(L^2)$_3$ at 295 K in ethanol, the PL and PLE spectra were excited and recorded at 302 and 490 nm.