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Electronic Supplementary Information

Monodisperse silica nanoparticles doped with dipicolinic acids-based luminescent lanthanide (III) complexes for bio-labelling.

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S1. Materials and methods.

NMR

NMR spectra were recorded in Fourier Transform mode with a Bruker AVANCE 400 spectrometer (^{1}H at 400 MHz, ^{13}C at 100 MHz), at 298 K. Residual solvent signals were used as internal references (^{1}H and ^{13}C). Data are reported as chemical shifts (δ) in ppm.

Photoluminescence studies

Emission and excitation spectra were measured using an Agilent Cary Eclipse Fluorescence Spectrometer. The luminescence was excited by unpolarized light and detected at an angle of 90° (10 mm quartz cell), at a concentration of 10^{-5} M in Tris .HCl buffer (0.1 M, pH = 7.45) for lanthanide complexes, and in suspension in water (3 mg.mL^{-1}) for nanoparticles.

Phosphorescence lifetimes were obtained by pulsed excitation, at 616 nm in the case of Europium complexes, and at 545 nm in the case of Terbium complexes. Luminescence Luminescence decay curves were fitted by least-squares analysis using the Gnuplot software.

Photoluminescence quantum yield

Photoluminescence quantum yields were measured using a Hamamatsu C9920 Absolute photoluminescence quantum yield measurement system, at a concentration of 10^{-3} M in Tris.HCl buffer (0.1 M, pH = 7.45) for lanthanide complexes, and in suspension in water (3 mg.mL^{-1}) for nanoparticles. The emission spectra were integrated from 576 nm to 728 nm for europium complexes and from 476 nm to 634 nm for terbium complexes.

TEM

Nanoparticles were suspended in water at a concentration of 1.5 mg/mL followed by deposition and air evaporation of a 10 µL droplet on a collodion coated copper grid. The samples were analysed on a Hitachi H-7650 at the CICS - Centre Imagerie Cellulaire Santé - of Clermont-Ferrand.

HRMS

Electrospray (positive mode) high-resolution mass spectra were recorded on a Q-TOF micro spectrometer (Waters), using an internal lock mass (H_3PO_4) and an external lock mass (leucine enkephalin $[M + H]^+$: m/z = 556.2766).

Anal.

Elemental analyses were performed at the SRSMC - Structure et Réactivité des Systèmes Moléculaires Complexes - of Nancy, on a Thermo Finnigan EA 1112 elemental analyzer.

FTIR

IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer FTIR-8400S.

Zeta Potential

The zeta potentials of the nanoparticles were measured using a Malvern Zetasizer Nano Zs. Samples were prepared by suspending 3 mg of nanoparticles in 1mL of Tris.HCl buffer (pH 7.5). Zeta potential values were calculated from measured velocities using Smoluchowski equation, and results are expressed as the mean of 3 runs.

Stability study

Nanoparticles NP-Eu(**5**)$_3$ and NP-Eu(**5**)$_3$-NH$_2$ were suspended (10 mg/mL) into phosphate-citrate buffer at pH 5.0, 6.0, 7.0 and 8.0, and sonicated for 10 min. After 14 days, the suspensions were centrifuged and the supernatants were removed. Nanoparticles were resuspended into Tris.HCl buffer at pH 7.0. The luminescence of the suspensions (10 mg/mL) was recorded and compared with freshly prepared suspensions of NP-Eu(**5**)$_3$ and NP-Eu(**5**)$_3$-NH$_2$, used as references.

S2. Synthesis.

Ligands

Compounds **4** and **7** were prepared according to reference[1].

Compound **8** was prepared according to reference[2].

Compound **9** was prepared according to reference[3].

1. Z. E. A. Chamas, X. Guo, J.-L. Canet, A. Gautier, D. Boyer, and R. Mahiou, *Dalton Trans.*, 2010, **39**, 7091–7097.
2. B. Letribot, R. Akué-Gédu, N. M. Santio, M. El-Ghozzi, D. Avignant, F. Cisnetti, P. J. Koskinen, A. Gautier, F. Anizon, and P. Moreau, *Eur. J. Med. Chem.*, 2012, **50**, 304–310.
3. E.-H. Ryu and Y. Zhao, *Org. Lett.*, 2005, **7**, 1035–1037.

Dimethyl-4-{4-[(*N*–(hydroxyethyl)-*N*,*N*-dimethylammonio)methyl]-1-*H*-1,2,3-triazol-1-yl}-pyridine-2,6-dicarboxylate chloride (10)

Ammonium salt **8** (728 mg, 4.45 mmol, 1.05 eq.) was added to a suspension of azido diester **7** (1.0 g, 4.24 mmol, 1.0 eq.) in 60 mL of methanol. Then, copper complex [Cu(4,7-dichloro-1,10-phenanthroline)(SIMes)] (53 mg, 2 mol %) was added in one portion. After 4 hours of stirring, the reaction mixture was filtered. The resulting solid was washed with cold MeOH. The white powder thus obtained was then dried under vacuum (1.63 g, 4.07 mmol, 96 %).

Mp: 203-207°C decomp. ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 9.60 (1H, s), 8.82 (2H, s), 5.50 (1H, t, J = 5 Hz), 4.88 (2H, s), 3.99 (6H, s), 3.96 (2H, q, J = 5 Hz), 3.45 (2H, t, J = 5 Hz), 3.14 (6H, s). ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm) 163.8, 149.6, 144.7, 137.0, 127.7, 117.6, 64.5, 58.1, 54.9, 53.0, 50.4. HRMS-ESI *m/z* Calcd for $C_{16}H_{22}N_5O_5$ $[M\text{-}Cl]^+$: 364.1621; found 364.1636. IR (KBr) $\tilde{\nu}$ /cm^{-1}: 3426, 3155, 3043, 2955, 2874, 1751, 1597, 1481, 1261, 1049, 995, 786.

N-((1-(2,6-Dicarboxypyridin-4-yl)-1*H*-1,2,3-triazol-4-yl)methyl)-2-hydroxy-*N*,*N*-dimethylethanaminium chloride (5)

To a solution of **10** (800 mg, 2.0 mmol, 1 eq.) in 10 mL of water was added a solution of lithium hydroxide monohydrate (504 mg, 12.0 mmol, 6 eq.) in 10 mL of water. After 24 hours of stirring, the solution was acidified with 6M HCl to pH < 3. Half of the solvent was eliminated under reduced pressure before addition of acetone. The precipitate was recovered by filtration then dried under vacuum to furnish the title compound as a white solid (660 mg, 1.76 mmol, 88 %).

Mp: 230-233°C decomp. ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 9.55 (1H, s), 8.63 (2H, s), 4.86 (2H, s), 4.2-3.9 (br s), 3.96 (2H, t, J = 5 Hz), 3.46 (2H, t, J = 5 Hz), 3.15 (6H, s). ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm) 164.7, 150.6, 144.6, 137.0, 127.6, 117.1, 64.5, 58.2, 54.9, 50.4. Anal. (%) Calcd for $C_{14}H_{18}ClN_5O_5$.½ HCl: C 43.11, H 4.78, N 17.96; found: C 43.26, H 4.86, N 17.94. IR (KBr) $\tilde{\nu}$ /cm^{-1}: 3426, 3093, 1736, 1601, 1481, 1385, 1246, 1087, 1049, 914, 794, 706, 570.

Dimethyl-4-{4-[(*N*,*N*,*N*-trimethylammonio)methyl]-1-*H*-1,2,3-triazol-1-yl}-pyridine-2,6-dicarboxylate chloride (11)

Ammonium salt **9** (174 mg, 1.30 mmol, 1.1 eq.) was added to a suspension of azido diester **7** (280 mg, 1.18 mmol, 1.0 eq.) in 20 mL. Then, copper complex [Cu(4,7-dichloro-1,10-phenanthroline)(SIMes)] (15 mg, 2 mol %) was added in one portion. After one night of stirring, the reaction mixture was filtered. The resulting off-white solid was washed with cold MeOH and dried under vacuum (430 mg, 1.16 mmol, 98%).

Mp: 205-207°C decomp. ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 9.60 (1H, s), 8.82 (2H, s), 4.80 (2H, s), 3.99 (6H, s), 3.13 (9H, s). ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm) 163.8, 149.6, 144.7, 137.1, 127.4, 117.6, 58.8, 53.0, 51.9. HRMS-ESI *m/z* Calcd for $C_{15}H_{20}N_5O_4$ $[M\text{-}Cl]^+$: 334.1515; found: 334.1529. IR (KBr) $\tilde{\nu}$ /cm^{-1}: 3483, 3424, 3041, 1754, 1596, 1260, 997, 908, 785.

1-(1-(2,6-Dicarboxypyridin-4-yl)-1*H*-1,2,3-triazol-4-yl)-*N*,*N*,*N*-trimethylmethanaminium chloride (6)

To a solution of **11** (470 mg, 1.27 mmol, 1.0 eq.) in 5 mL of water was added a solution of lithium hydroxide monohydrate (320 mg, 7.62 mmol, 6.0 eq.) in 5 mL of water. After 24 hours of stirring, the solution was acidified with 6M HCl to pH < 3. Half of the solvent was eliminated under reduced pressure before addition of acetone. The precipitate formed was recovered by filtration then dried under vacuum to furnish the title compound as a white solid (425 mg, 1.24 mmol, 98 %).

Mp: 260-265°C decomp. ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 9.60 (1H, s), 8.78 (2H, s), 4.80 (2H, s), 3.12 (9H, s). ^{13}C NMR (100 MHz, DMSO-d6) *δ* (ppm) 164.7, 150.6, 144.6, 137.1, 127.4, 117.1, 58.8, 51.8. HRMS-ESI *m/z* Calcd for $C_{13}H_{16}N_5O_4$ [M-Cl]$^+$: 306.1202; found: 306.1201. IR (KBr) $\tilde{\nu}$ /cm^{-1}: 3361, 3038, 1730, 1604, 1483, 1375, 1246, 1050, 1008, 689.

Lanthanide complexes

Diacid (100 mg, 3 eq) and Na_2CO_3 (5 eq) were dissolved into the minimum amount of water. A solution of lanthanide chloride hexahydrate (1eq; in solution into 0.5 mL of water) was added. After 1 hour of stirring, the expected complex precipitated by addition of mehanol. The complex was collected by filtration and washed with methanol.

Complex Eu(**3**)$_3$, Na$_3$:

The procedure was slightly modified as follow: the complex precipitated immediately without addition of acetone. After 1 hour of stirring, the complex was collected by filtration and purified by recrystallisation from water, to afford white crystals (103 mg; yield 72%). Mp > 290°C. ^{1}H NMR (400 MHz, D_2O) δ (ppm) 4.81 (2H, br s), 3.70 (1H, br s). IR (ATR) $\tilde{\nu}$ /cm^{-1}: 3356, 3085, 1615, 1427, 1387, 1368, 1277, 1193, 1018, 917, 761, 734, 654, 516.

Complex Tb(**3**)$_3$, Na$_3$:

The procedure was slightly modified as follow: the complex precipitated immediately without addition of acetone. After 1 hour of stirring, the complex was collected by filtration and purified by recrystallisation from water, to afford white crystals (104 mg; yield 72%). Mp > 290°C. ^{1}H NMR (400 MHz, D_2O) δ (ppm) 39.85 (2H, br s), 35.72 (1H, br s). IR (ATR) $\tilde{\nu}$ /cm^{-1}: 3348, 3085, 1619, 1586, 1429, 1385, 1366, 1279, 1022, 822, 763, 727, 519.

Complex Eu(**4**)$_3$, Na$_3$:

Yellow powder (84 mg; yield 73%). ^{1}H NMR (400 MHz, D_2O) δ (ppm) 7.41 (1H, br s), 4.79 (2H, br s), 4.33 (2H, br s). IR (ATR) $\tilde{\nu}$ /cm^{-1}: 3267, 3125, 1728, 1590, 1427, 1354, 1024, 805, 694, 564.

Complex Tb(**4**)$_3$, Na$_3$:

Yellow powder (94 mg; yield 81%). ^{1}H NMR (400 MHz, D_2O) δ (ppm) 40.67 (2H, br s), 24.02 (1H, br s), 10.81 (2H, br s). IR (ATR) $\tilde{\nu}$ /cm^{-1}: 3262, 3129, 1730, 1588, 1419, 1356, 1047, 1024, 805, 769, 738, 564.

Complex Eu(**5**)$_3$:

Light yellow powder (68 mg; yield 72%). Mp > 290°C. ^{1}H NMR (400 MHz, D_2O) δ (ppm) 8.29 (1H, br s), 4.92 (2H, br s), 4.74 (2H, br s), 4.19 (2H, br s), 3.57 (2H, br s), 3.20 (6H, br s). IR (ATR) $\tilde{\nu}$ /cm^{-1}: 3363, 3102, 1617, 1588, 1417, 1375, 1340, 1043, 805, 736, 573.

Complex Tb(**5**)$_3$:

Light yellow powder (87 mg; yield 91%). Mp > 290°C. ^{1}H NMR (400 MHz, D_2O) δ (ppm) 42.06 (2H, br s), 20.78 (1H, br s), 7.26 (2H, s), 5.76 (2H, br s), 4.8-2.3 (8H, br s). IR (ATR) $\tilde{\nu}$ /cm^{-1}: 3367, 3095, 2964, 1615, 1590, 1421, 1375, 1341, 1045, 807, 738, 571, 468.

Complex Eu(**6**)$_3$:

Light yellow powder (85 mg; yield 90%). Mp > 290°C. ^{1}H NMR (400 MHz, D_2O) δ (ppm) 8.51 (1H, br s, H_{triazole}), 5.01 (2H, br s), 4.77 (2H, br s), 3.43 (9H, br s). IR (ATR) $\tilde{\nu}$ /cm^{-1}: 3377, 3096, 1619, 1586, 1415, 1375, 1340, 1248, 1043, 862, 738, 569.

Complex Tb(**6**)$_3$:

Light yellow powder (53 mg; yield 56%). Mp > 290°C. ^{1}H NMR (400 MHz, D_2O) δ (ppm) 43.21 (2H, br s), 19.61 (1H, br s), 5.50 (2H, br s), 1.34 (9H, br s). IR (ATR) $\tilde{\nu}$ /cm^{-1}: 3378, 3096, 1617, 1586, 1417, 1373, 1337, 1248, 1041, 900, 735, 570.

Disuccinimidyl polyethylene glycol $_{600}$ dicarboxylate NHS-PEG$_{600}$-NHS (12)

Polyethylene glycol 600 bis(carboxymethyl) ether (500 mg, 0.83 mmol, 1.0 eq) was dissolved into 10 mL of dichloromethane. *N*-Hydroxysuccinimide (240 mg, 2.08 mmol, 2.5 eq) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride EDCI-HCl (400 mg, 2.08 mmol, 2.5 eq) were added to the solution. The reaction mixture was stirred overnight at room temperature, then filtered through a short column of silica gel (CH_2Cl_2), and the filtrate was concentrated under reduced pressure to obtain the pure product as a colourless oil (509 mg, yield 77%).

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 4.61 (4H, s, OCH_2COO), 3.67 (4H, m, OCH_2CH_2), 3.57 (4H, m, OCH_2CH_2), 3.51 (36H, m, OCH_2CH_2O) 2.83 (8H, s, $CH_{2\ \text{NHS}}$).

Synthesis of nanoparticles

Ammonia solution (350 µL, 19 % w/w in water) and 75 µL of an aqueous solution of the lanthanide complex (concentration range: 2.5.10^{-2} to 1.10^{-1} Mol.L^{-1}, depending on complex solubility) were added to a mixture of NP$_5$ - nonylphenol pentaglycol ether (4.05 g, 9.02 mmol) and cyclohexane (93.3 mL). After 45 min of stirring at room temperature, 2.3 mL of tetraethyl orthosilicate (TEOS, 10.3 mmol) were added. After 24 hours under stirring, a large excess of acetone was added to the solution. The resulting mixture was left without stirring for 24h and centrifuged (14000 rpm, 15min, 4°C). The nanoparticles were washed by centrifugation with acetone (x2), water (x1), and ethanol (x2). Nanoparticles were dried at 85°C in an oven for 24 h. (~100-200 mg).

Synthesis of functionalised nanoparticles

The procedure was slightly modified as follows:

24 hours after the first addition of TEOS, 230 µL of TEOS (1.03 mmol) and 1.03 mmol of functionalised precursor (APTES: 240 µL; PTEPC: 340 µL) were added to the mixture, and let under stirring for 24h before addition of a large excess of acetone to the solution. The resulting mixture was left without stirring for 24h and centrifuged (14000 rpm, 15min, 4°C). The nanoparticles were washed by centrifugation with acetone (x2), water (x1), and ethanol (x2). Nanoparticles were dried at 85°C in an oven for 24 h. (~150-200 mg).

Grafting of PEG chains on nanoparticles

NP-Eu(**5**)$_3$-NH$_2$ (50 mg) were sonicated into 10 mL of dichloromethane until the suspension was homogeneous (about 10min). Then succinimidyl ester **12** (220 mg, 0.28 mmol) was added to the suspension. The resulting mixture was stirred overnight at room temperature. Then nanoparticles were washed by centrifugation with dichloromethane (x4), methanol (x2) and resuspended into dichloromethane. The nanoparticles were dried at 25°C (49 mg).

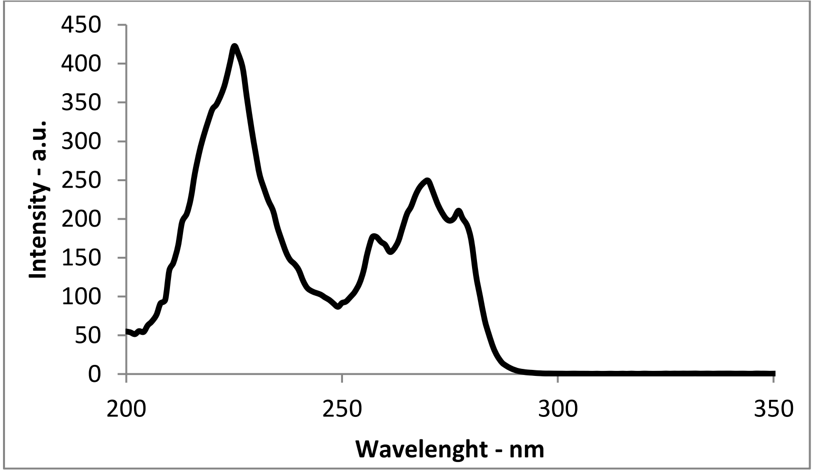
Particles reaction composition / characterisation table

	Concentrations - mMol.L^{-1}									
Particles						Functionalisation			Reaction time - hours	TEM diameter - nm (average 40 measures)
	[TEOS]$_1$	[NP$_5$]	[LnL$_3$]	[H$_2$O]	[NH$_3$]	[TEOS]$_2$	[APTES]	[PTEPC]		
Pure silica	103	92	/	170	42	/	/	/	24	20.9
NP-Eu(**3**)$_3$	103	92	0.075	182	35	/	/	/	24	19.1
NP-Tb(**3**)$_3$	103	92	0.075	182	35	/	/	/	24	21.4
NP-Eu(**4**)$_3$	103	92	0.019	182	35	/	/	/	24	22.0
NP-Tb(**4**)$_3$	103	92	0.019	182	35	/	/	/	24	20.6
NP-Eu(**5**)$_3$	103	92	0.075	182	35	/	/	/	24	19.3
	103	92	0.050	182	35	/	/	/	24	19.7
	103	92	0.025	182	35	/	/	/	24	20.0
NP-Tb(**5**)$_3$	103	92	0.075	182	35	/	/	/	24	20.8
NP-Eu(**6**)$_3$	103	92	0.075	182	35	/	/	/	24	21.3
NP-C≡C	103	92	/	170	42	10.3	/	10.3	48	30.2
NP-NH$_2$	103	92	/	170	42	10.3	10.3	/	48	30.8
NP- Eu(**5**)$_3$-C≡C	103	92	0.075	182	35	10.3	/	10.3	48	30.1
NP- Eu(**5**)$_3$-NH$_2$	103	92	0.075	182	35	10.3	10.3	/	48	32.2

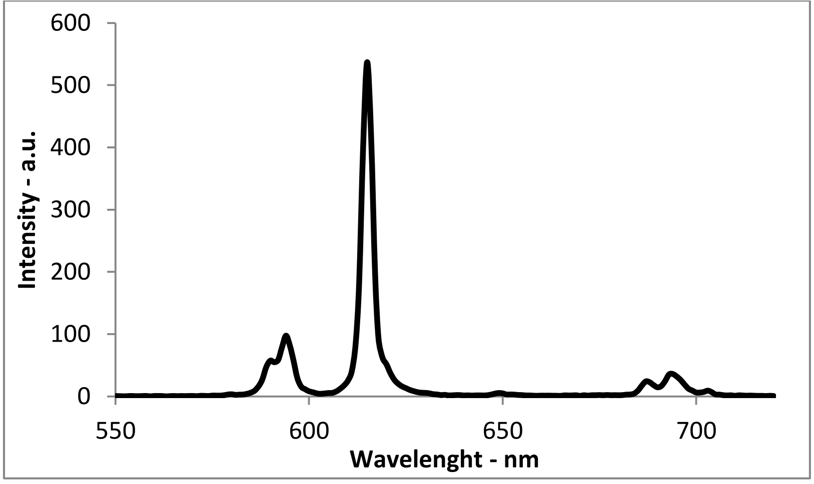
S3. Luminescence properties of complexes

Luminescence properties of tris(pyridine-2,6-dicarboxylate)europiate(III) – Eu(**3**)$_3$, Na$_3$

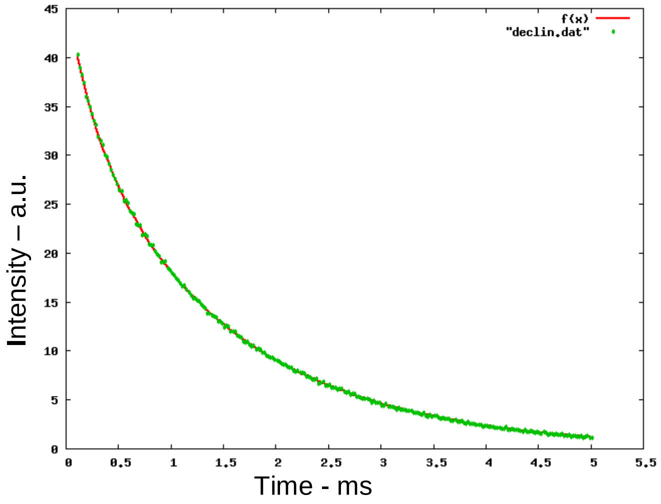
Excitation spectrum at 616 nm



Emission spectrum at 225 nm



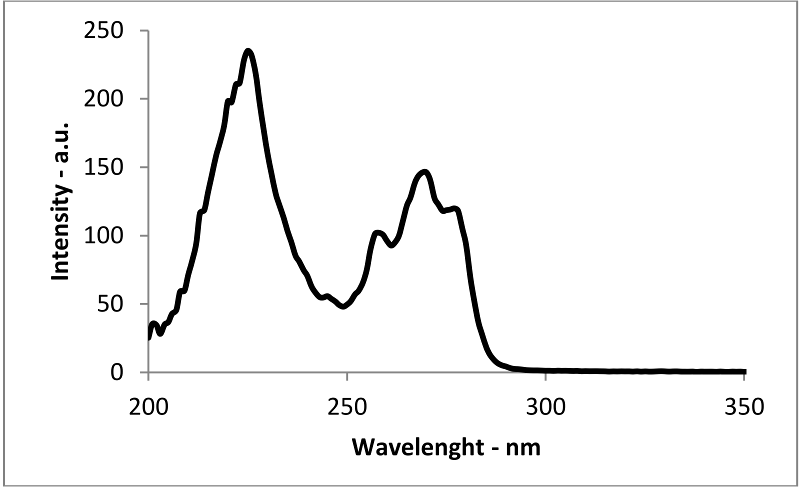
Luminescence decay with λ_{exc} = 226 nm and λ_{em} = 616 nm.



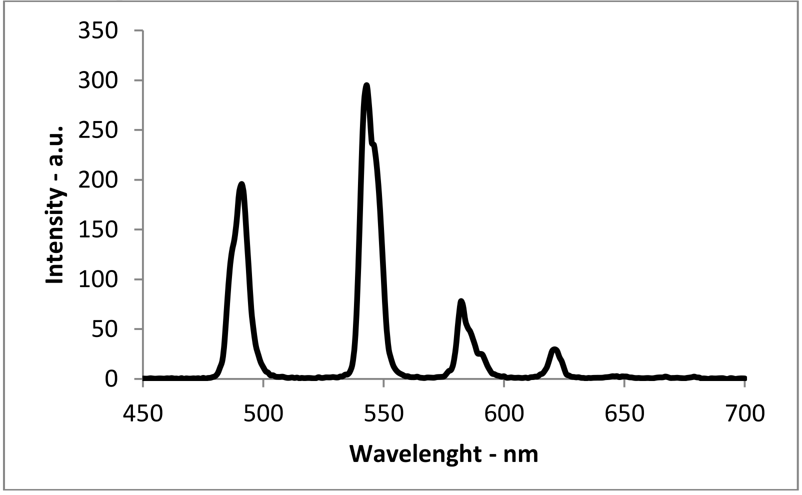
τ_1 = 1.50 ms; τ_2 = 0.30 ms

Luminescence properties of tris(pyridine-2,6-dicarboxylate)terbiate(III) – Tb(**3**)$_3$, Na$_3$

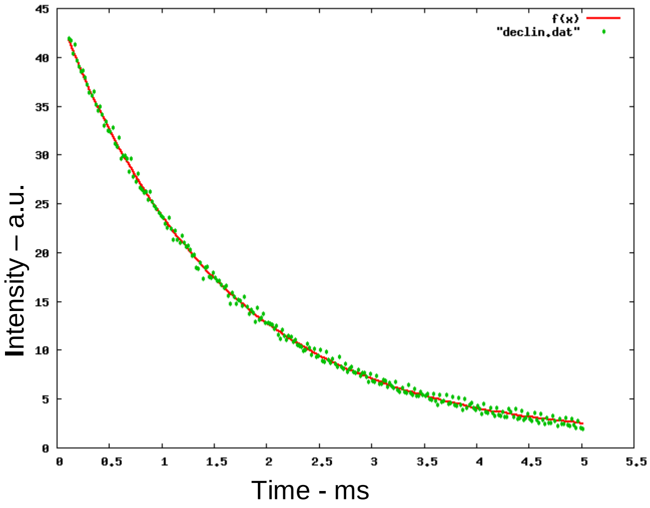
Excitation spectrum at 545 nm



Emission spectrum at 225 nm



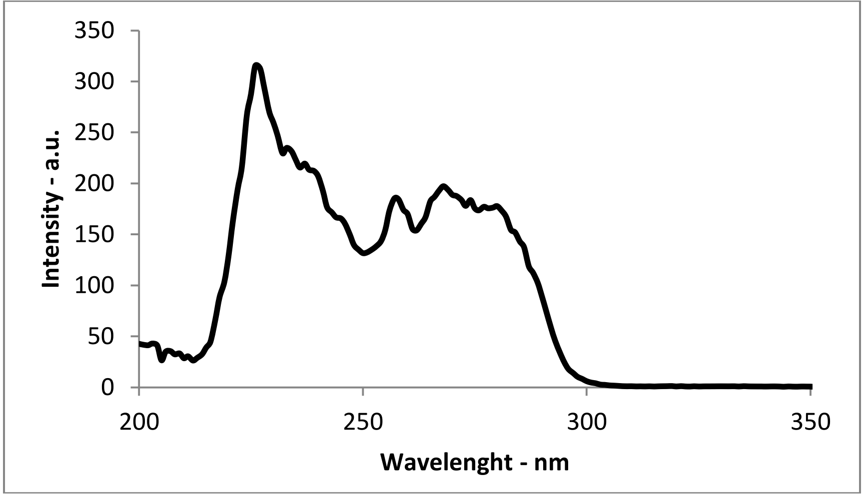
Luminescence decay with λ_{exc} = 225 nm and λ_{em} = 545 nm.



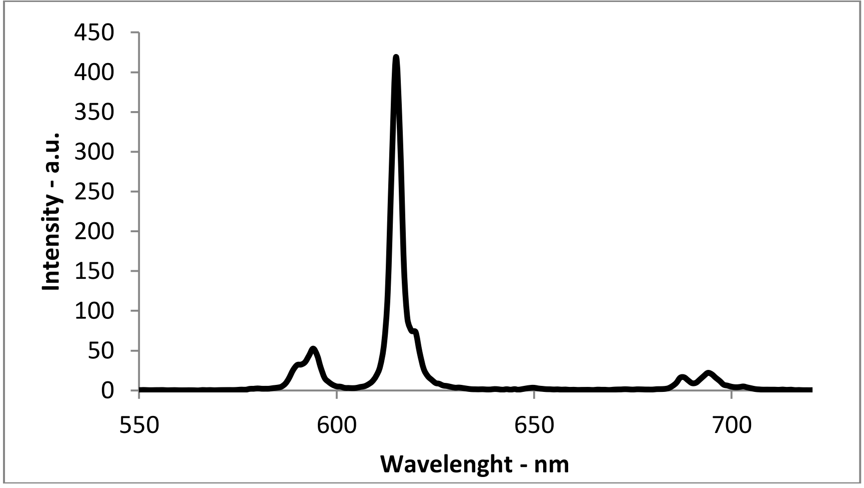
τ_1 = 1.50 ms

Luminescence properties of tris[4-(4-(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylate]europiate(III) – Eu(**4**)$_3$, Na$_3$

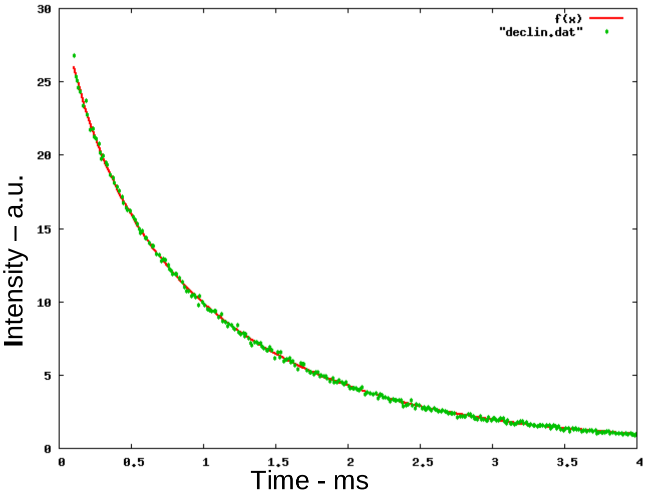
Excitation spectrum at 616 nm



Emission spectrum at 226 nm



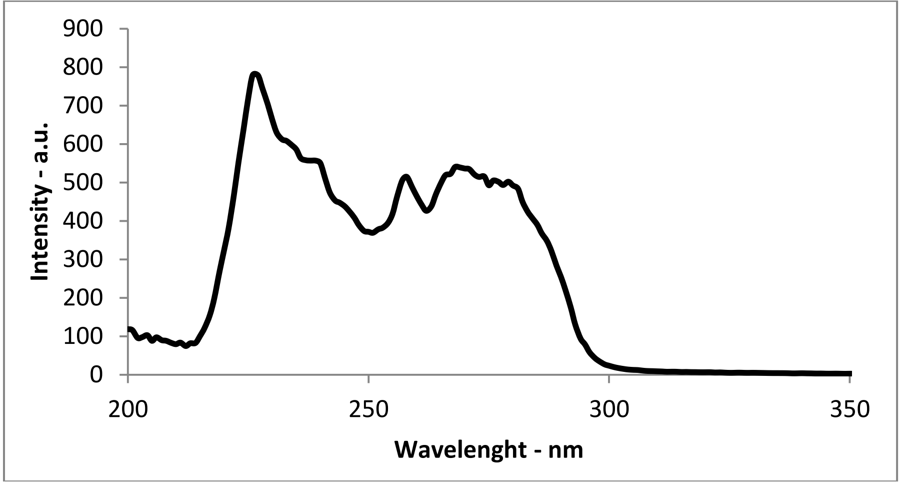
Luminescence decay with λ_{exc} = 226 nm and λ_{em} = 616 nm.



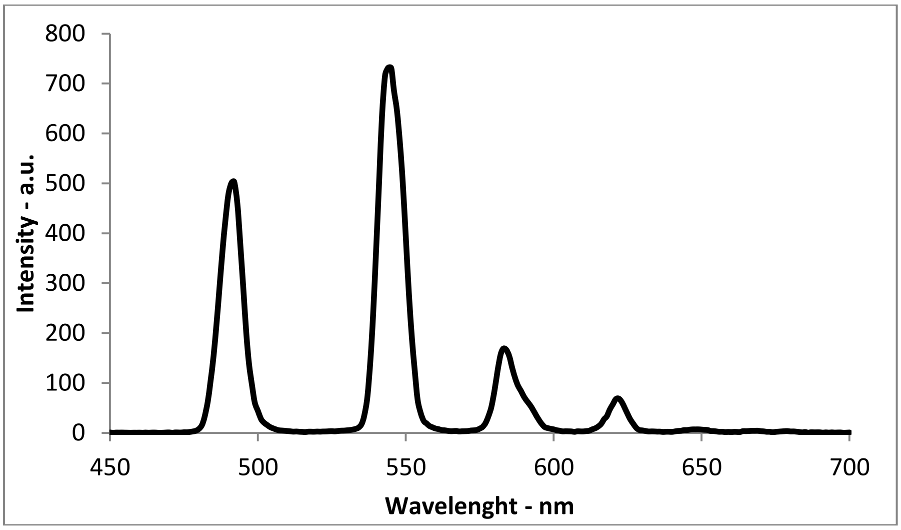
τ_1 = 1.15 ms ; τ_2 = 0.25 ms

Luminescence properties of tris[4-(4-(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylate]terbiate(III) – Tb(**4**)$_3$, Na$_3$

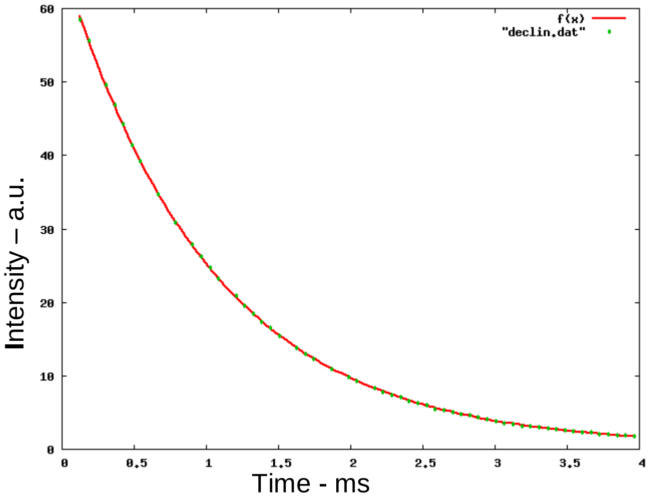
Excitation spectrum at 545 nm



Emission at 226 nm



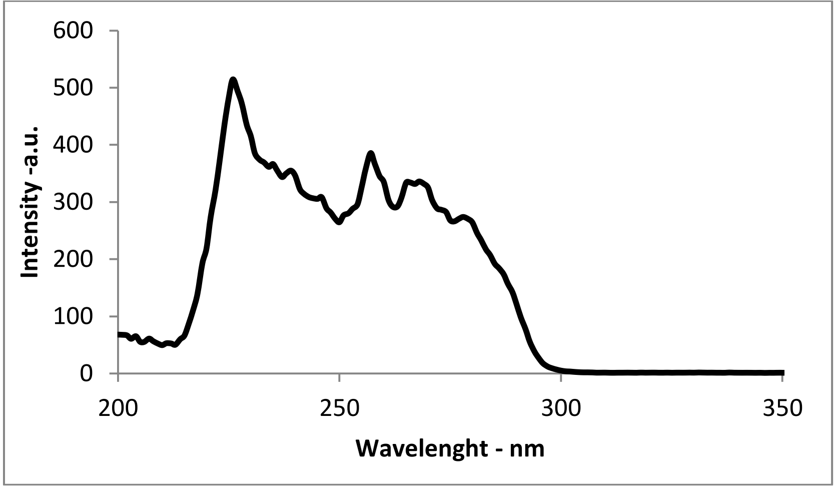
Luminescence decay with λ_{exc} = 226 nm and λ_{em} = 545 nm.



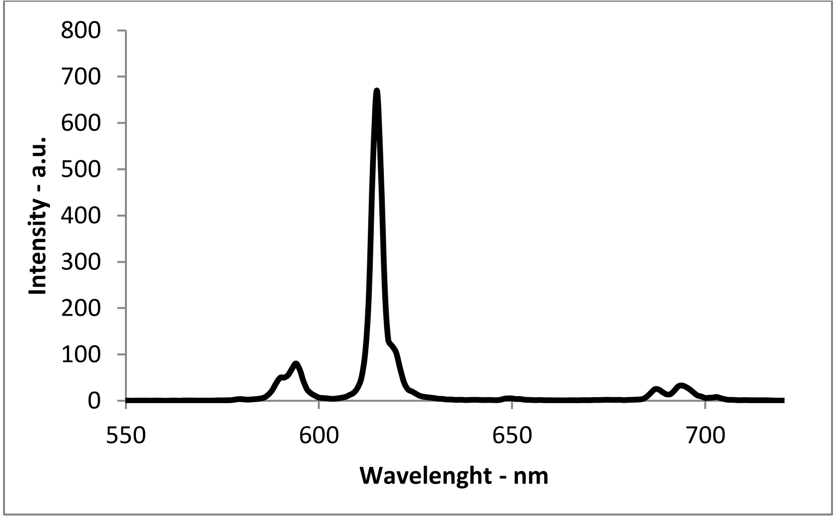
τ_1 = 1.02ms

Luminescence properties of tris[4-(4-(*N*-2-hydroxyethyl-*N*,*N*-dimethylamminiomethyl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylate]europium(III) – Eu(5)$_3$

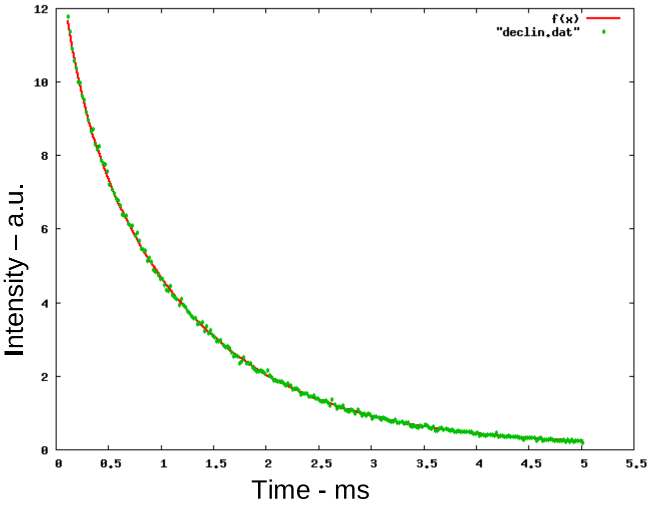
Excitation spectrum at 616 nm



Emission spectrum at 226 nm



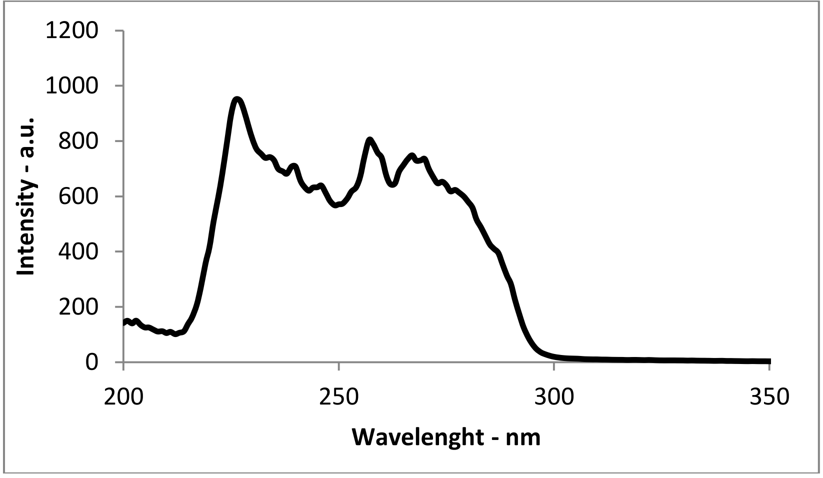
Luminescence decay with λ_{exc} = 226 nm and λ_{em} = 616 nm.



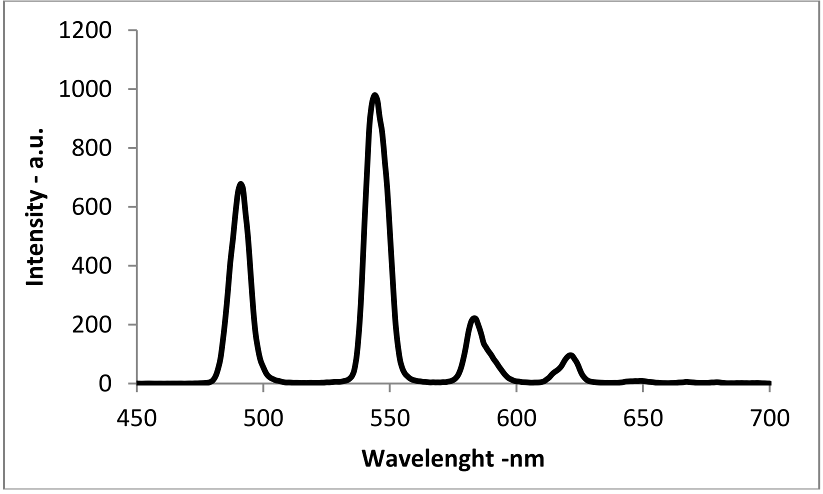
τ_1 = 1.22 ms ; τ_2 = 0.29 ms

Luminescence properties of tris[4-(4-(*N*-2-hydroxyethyl-*N*,*N*-dimethylamminiomethyl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylate]terbium(III) – Tb(5)$_3$

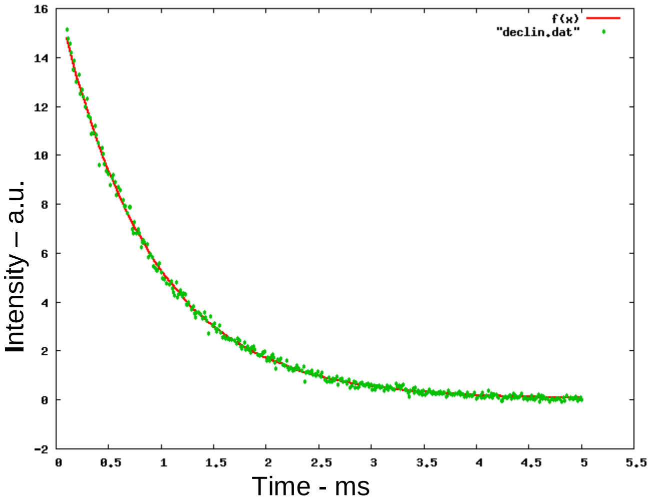
Excitation spectrum at 545 nm



Emission spectrum at 226 nm



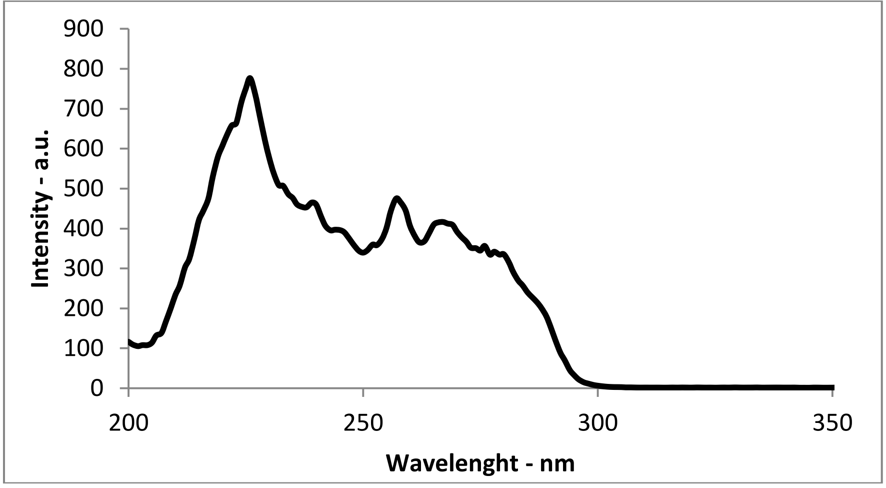
Luminescence decay with λ_{exc} = 226 nm and λ_{em} = 545 nm.



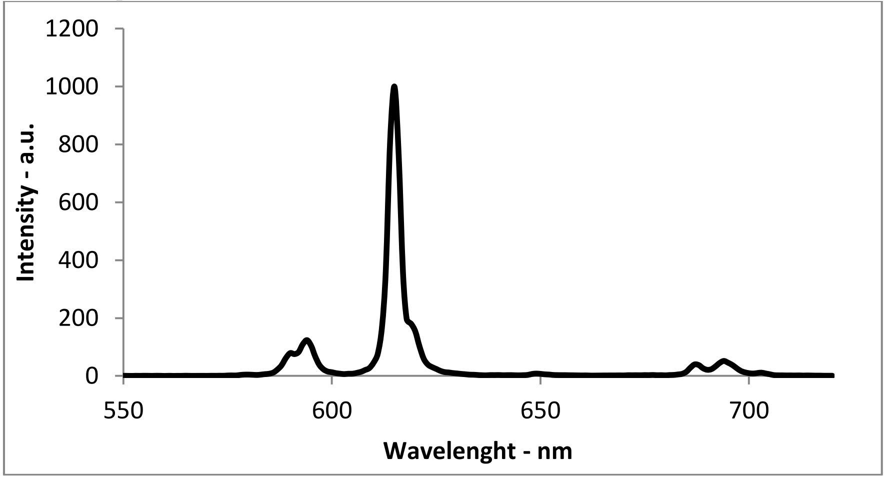
τ_1 = 0.87 ms

Luminescence properties of tris[4-(4-(*N*,*N*,*N*-trimethylamminiomethyl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylate]europium(III) – Eu(**6**)$_3$

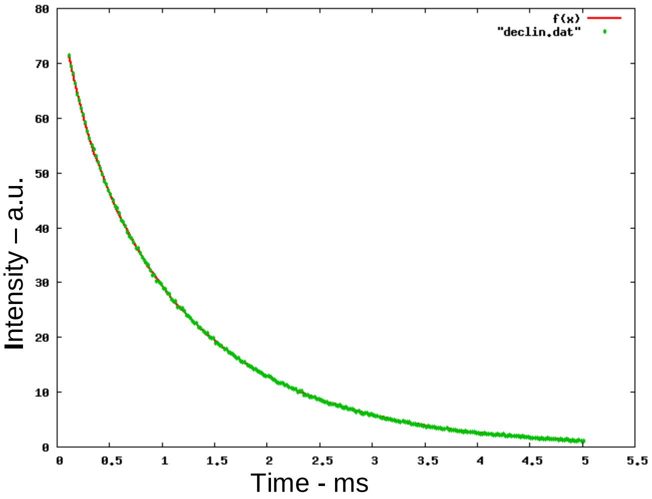
Excitation spectrum at 616 nm



Emission spectrum at 226 nm



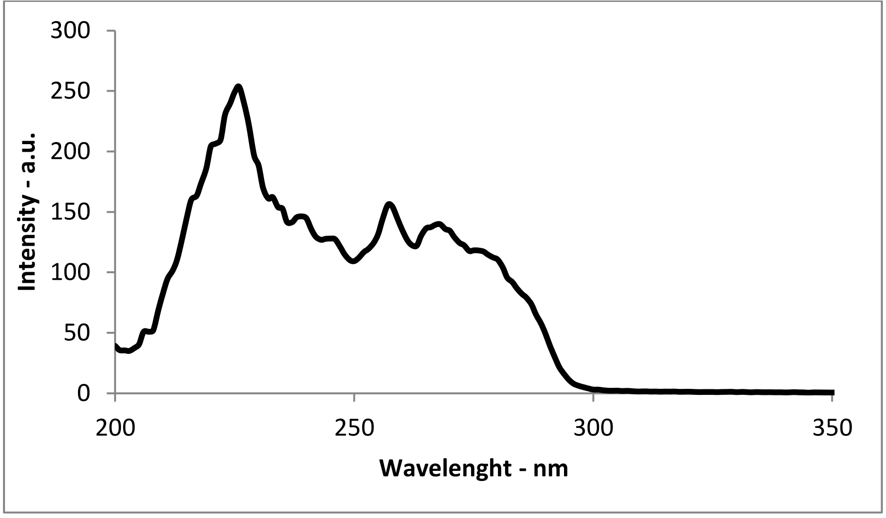
Luminescence decay with λ_{exc} = 226 nm and λ_{em} = 616 nm.



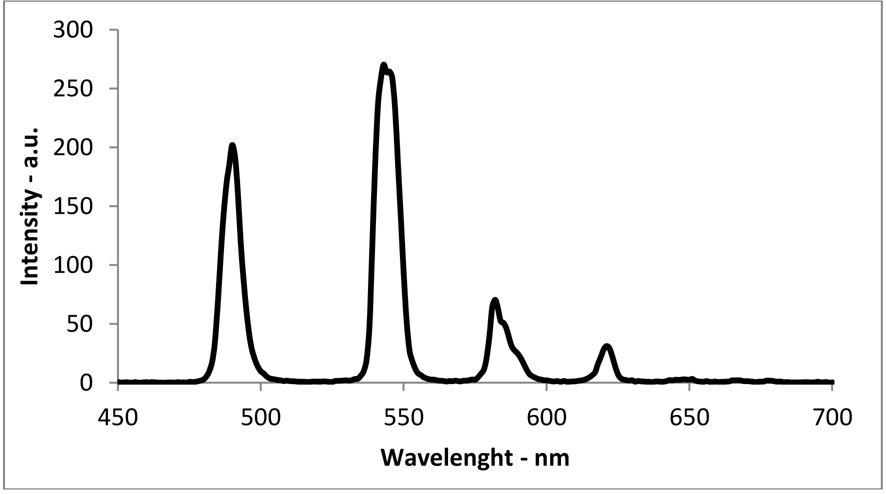
τ_1 = 1.25 ms ; τ_2 = 0.30 ms

Luminescence properties of tris[4-(4-(*N*,*N*,*N*-trimethylamminiomethyl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylate]terbium(III) – Tb(**6**)$_3$

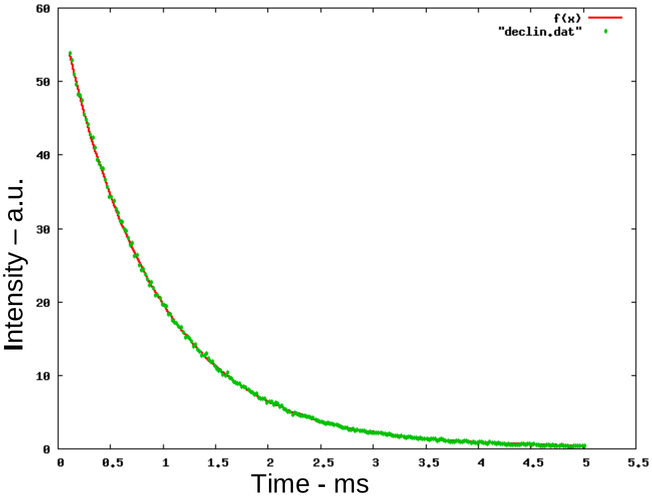
Excitation spectrum at 545 nm



Emission spectrum at 226 nm



Luminescence decay with λ_{exc} = 226 nm and λ_{em} = 545 nm.

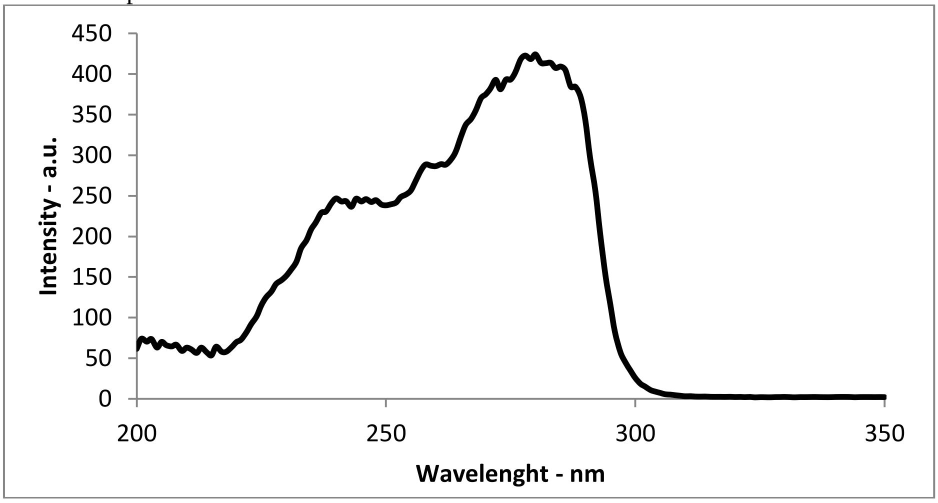


τ_1 = 0.89 ms

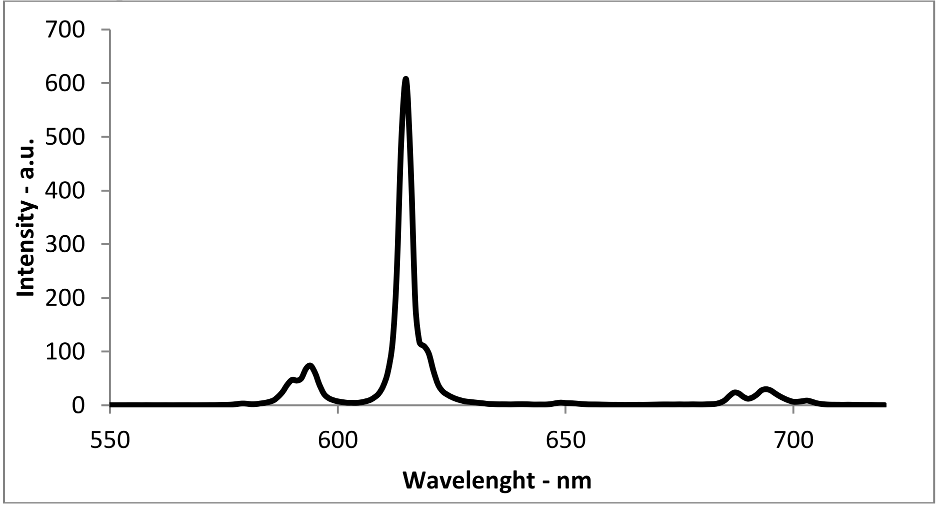
S4. Luminescence studies of nanoparticles

Luminescence properties of NP-Eu(5)$_3$

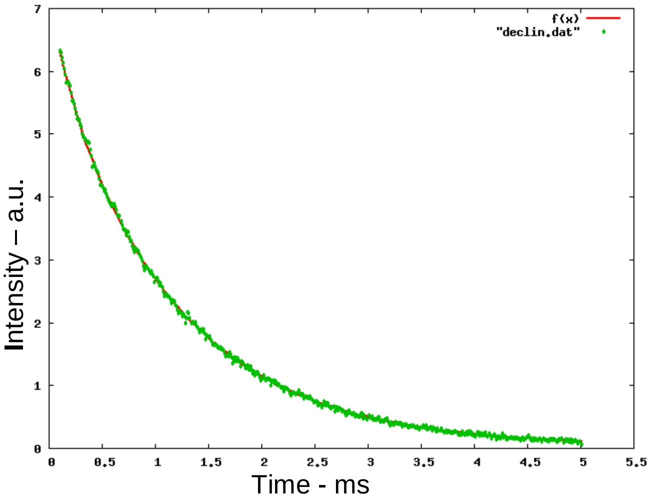
Excitation spectrum at 616 nm



Emission spectrum at 280 nm



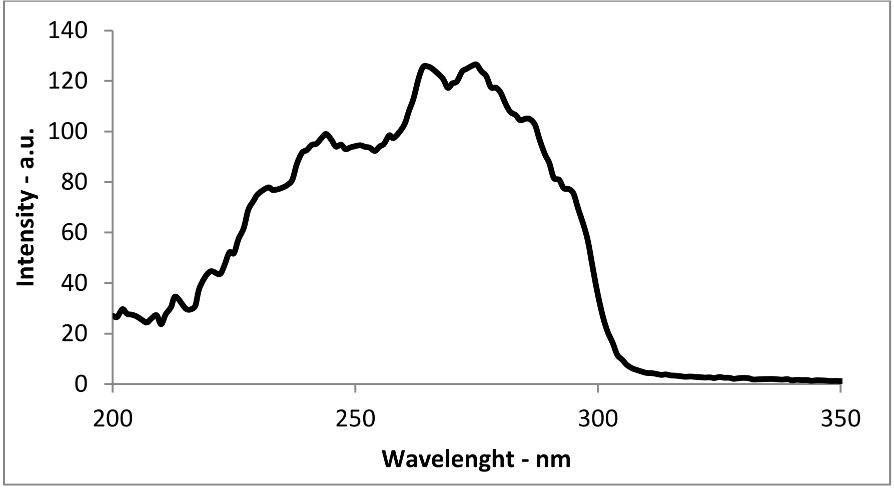
Luminescence decay with λ_{exc} = 280 nm and λ_{em} = 616 nm.



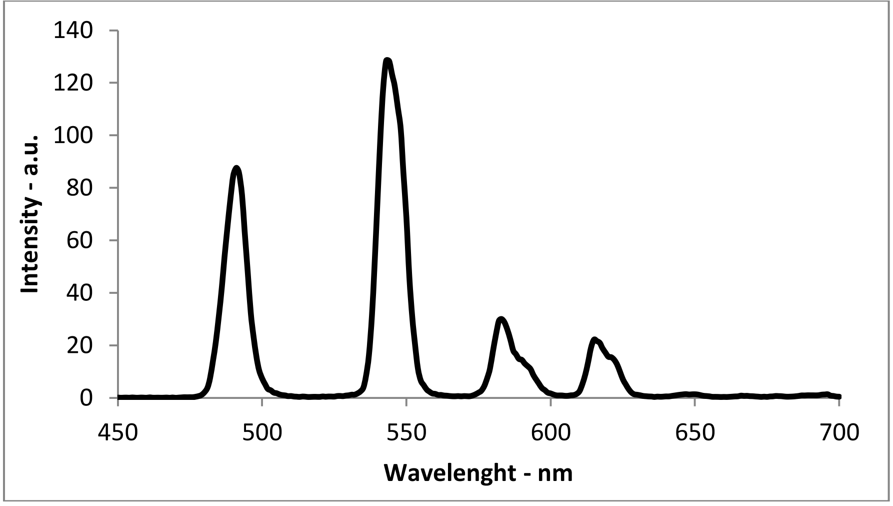
τ_1 = 1.15 ms; τ_2 = 0.20 ms

Luminescence properties of NP-Tb(5)$_3$

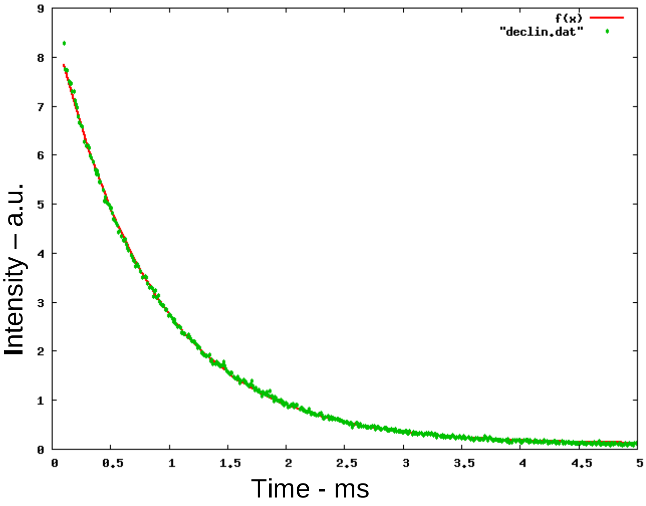
Excitation spectrum at 545 nm



emission spectrum t 278 nm.



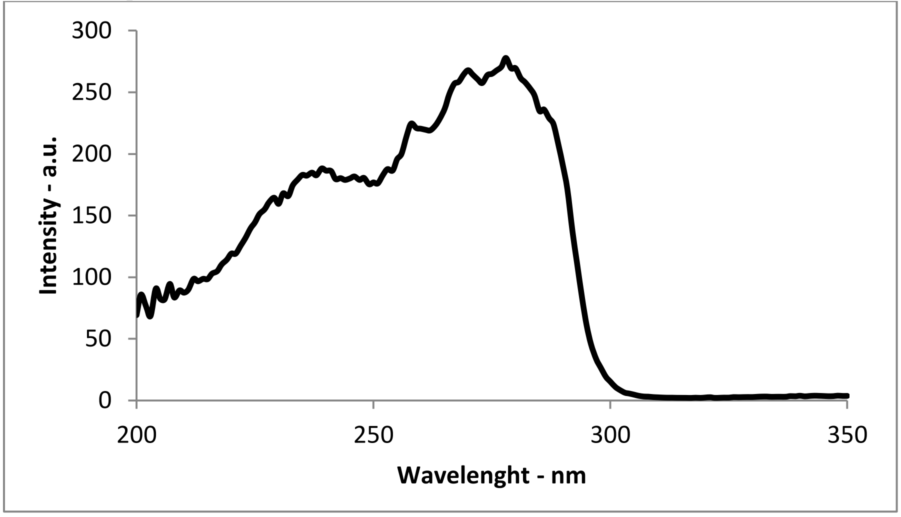
Luminescence decay with λ_{exc} = 278 nm and λ_{em} = 545 nm.



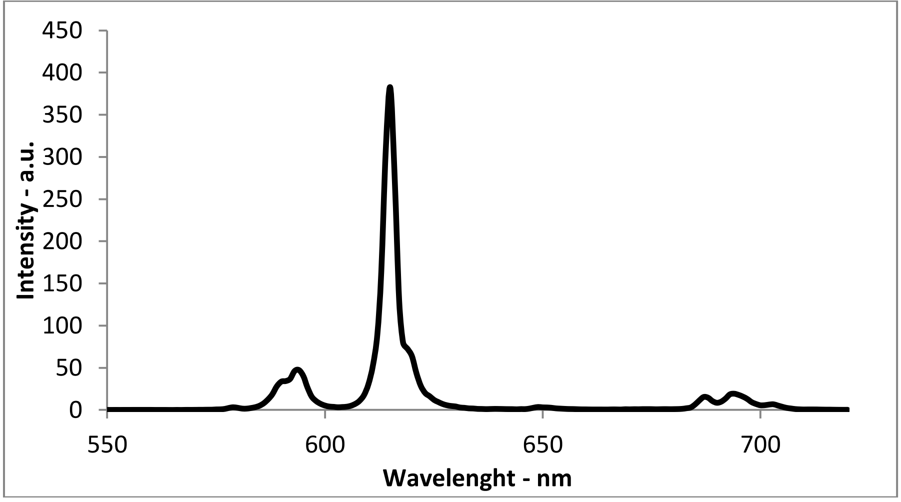
τ_1 = 0.84ms

Luminescence properties of NP-Eu(6)$_3$

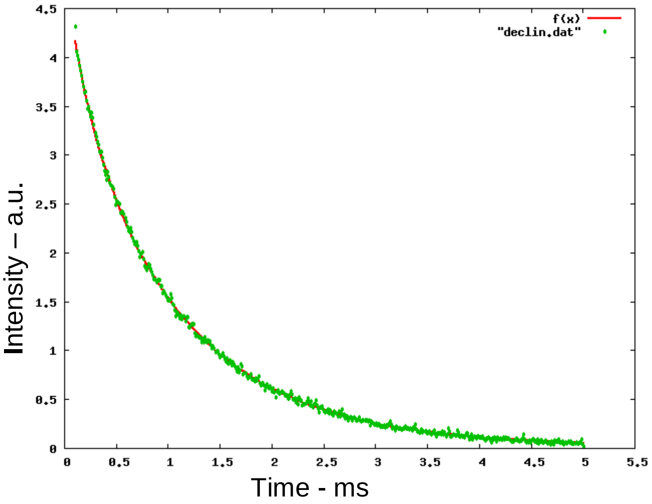
Excitation spectrum at 616 nm



Emission spectrum at 278 nm

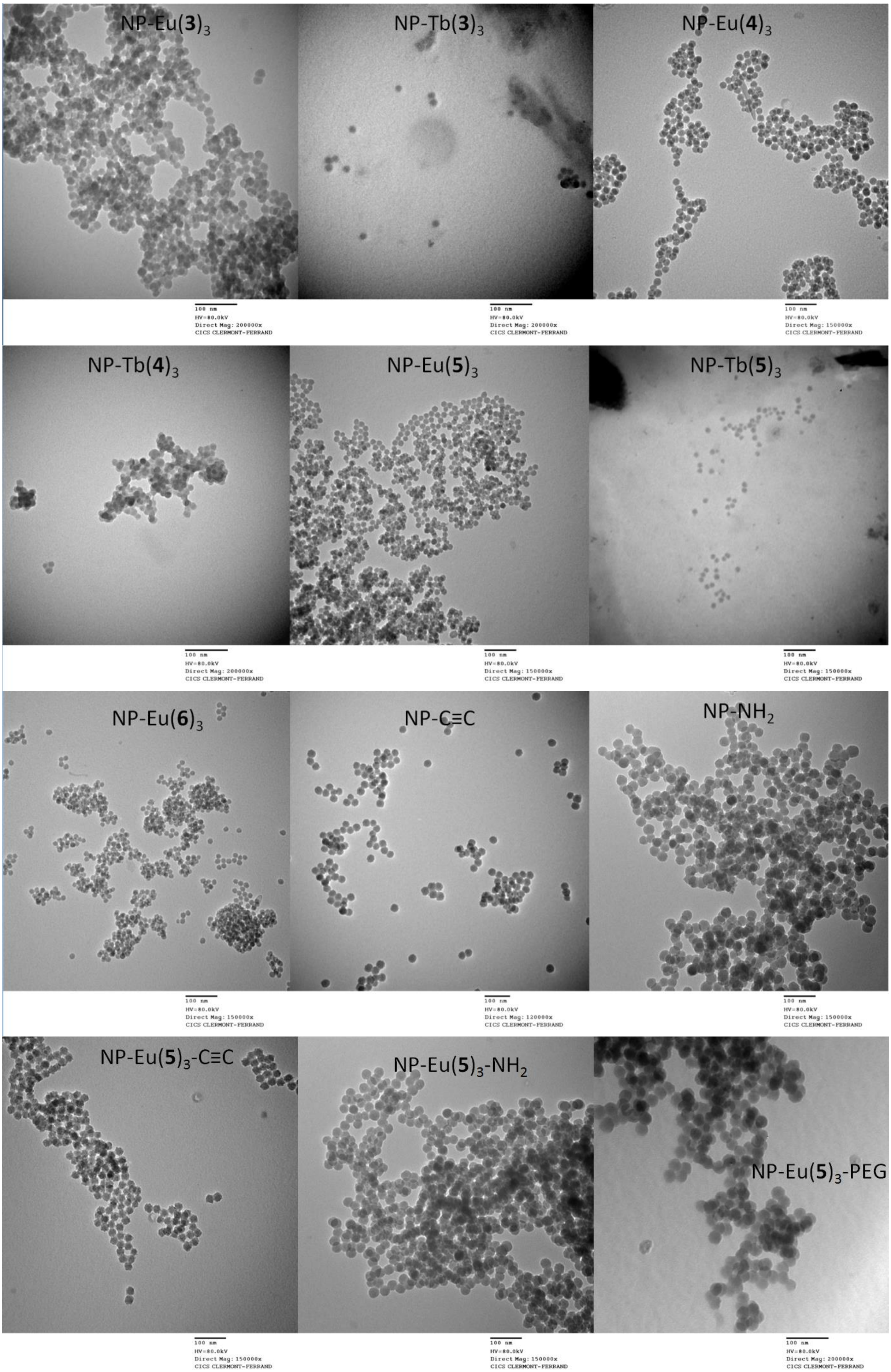


Luminescence decay with λ_{exc} = 278 nm and λ_{em} = 616 nm.

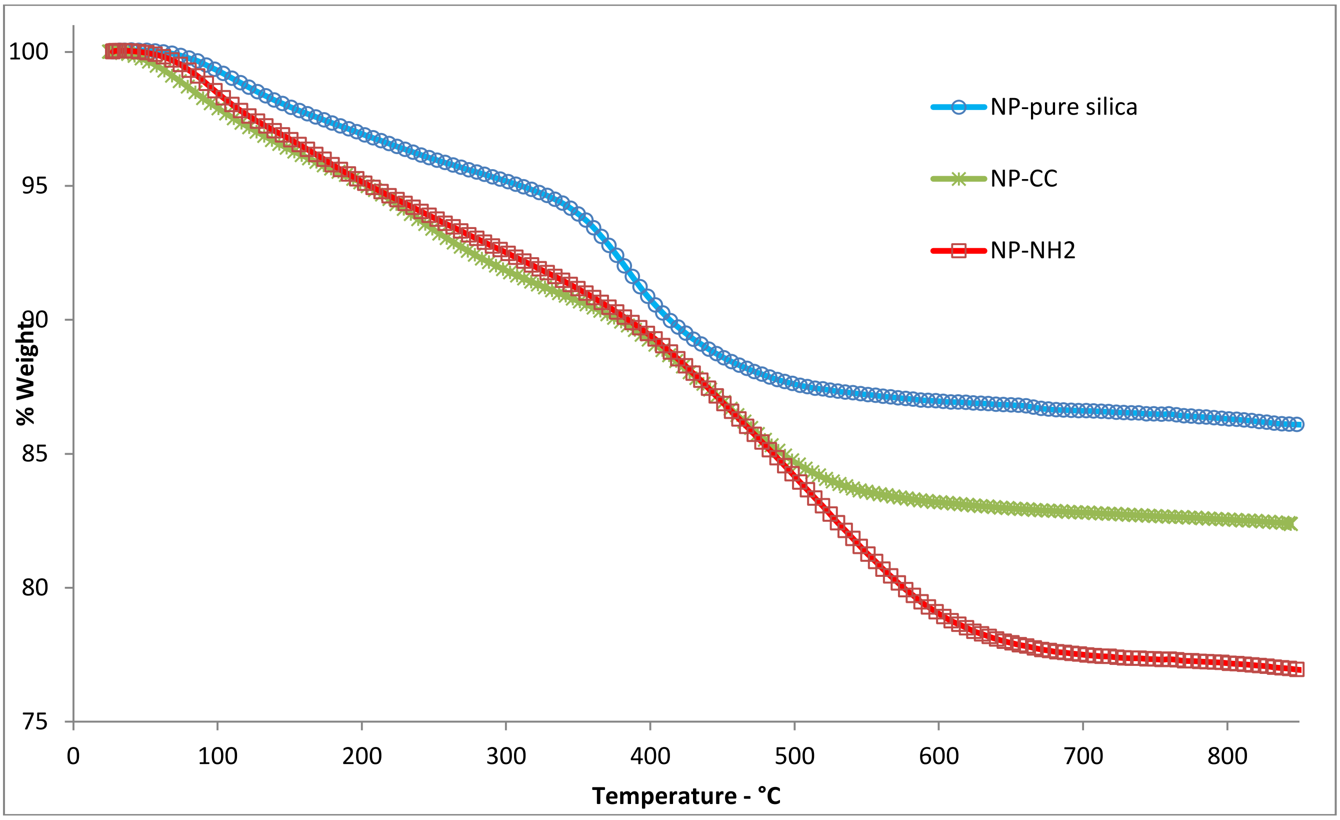


τ_1 = 1.08 ms, τ_2 = 0.25 ms

S5. TEM micrographs



S6. Thermogravimetric analysis

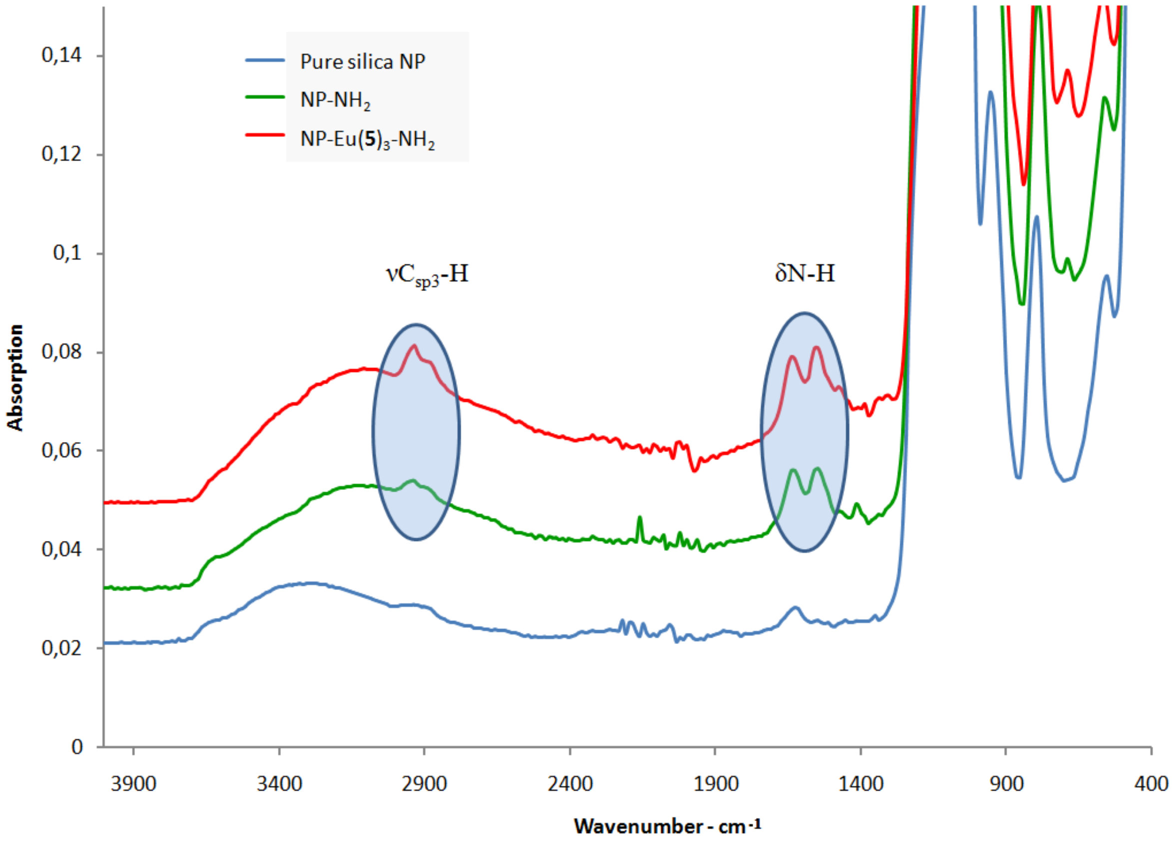


S7. Zeta potential

Samples were prepared by suspending 3 mg of nanoparticles in 1mL of Tris.HCl buffer (pH 7.5).

	Zeta potential - mV
NP- pure silica	-21.7
NP-Eu(**5**)$_3$	-19.6
NP -C≡C	-6.5
NP - Eu(**5**)$_3$-C≡C	-6.3
NP-NH$_2$	+25.7
NP-Eu(**5**)$_3$-NH$_2$	+26.0
NP-Eu(**5**)$_3$-PEG-COOH	-24.5

S8. Infrared spectroscopy



S9. Raman spectroscopy

Raman spectrum of NP-C≡C