Sensitization of visible and NIR lanthanide emission by InPZnS quantum dots in bi-luminescent hybrids

Jennifer K. Molloy,[a,b] Christophe Lincheneau,[a,c] Maria Moula Karimdjy,[a,b] Fabio Agnese,[a,c] Lucia Mattera,[a,c] Christelle Gateau,[a,b] Peter Reiss,[a,c] Daniel Imbert,*[a,b] and Marinella Mazzanti*[d]

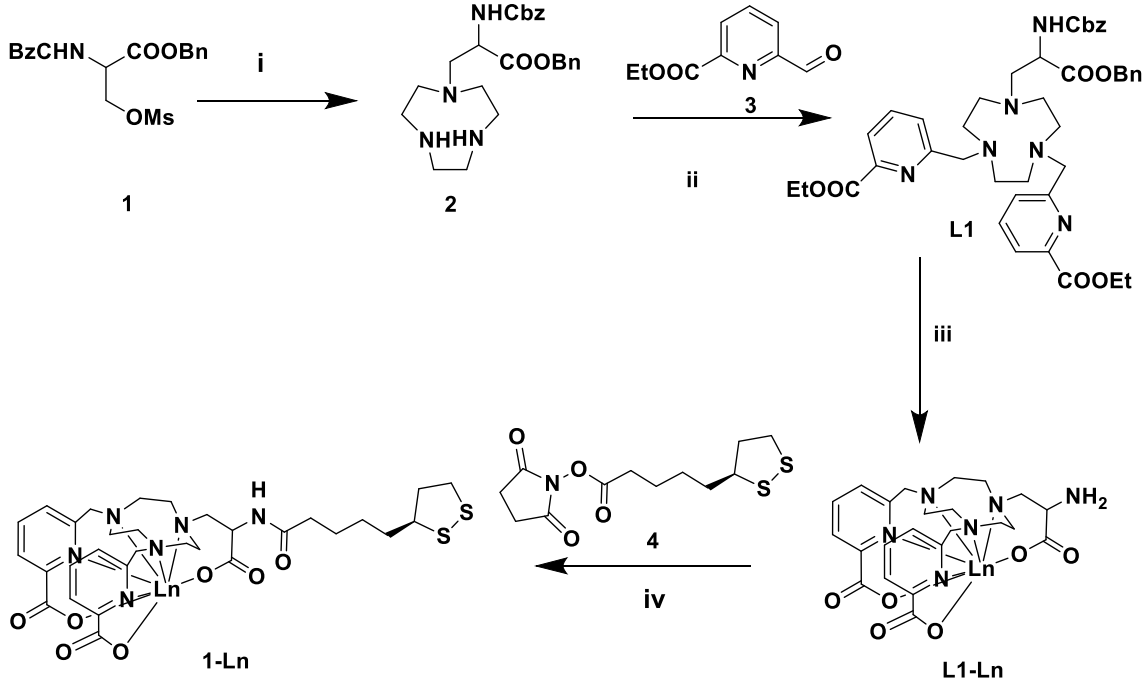
[a] Univ. Grenoble Alpes, INAC-SCIB, RICC, F-38000 Grenoble, France; [b] CEA, INAC-SCIB, RICC, F-38000 Grenoble, France.[c] CEA, INAC-SPrAM, LEMOH, F-38000 Grenoble, France. [d] Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

I. Synthesis

I.1. General information

Solvents and starting materials were purchased from Aldrich, Chematech, Fluka, Acros, Carlo Erba and Alfa Aesar and used without further purification. The lanthanide salts were purchased from Aldrich and were titrated by colorimetry with the xylenol orange as indicator. 2-Pyridinecarboxylic acid, 6-(hydroxymethyl)-, ethyl ester and the serine, *O*-(methylsulfonyl) -*N*-[(phenylmethoxy)carbonyl]-, phenylmethyl ester (**1**) were prepared according to the described procedure.[1] Flash chromatography was performed on silica gel 60 (40-63 μm, Merck) or silica gel 60 RP18 F_{254} or aluminium oxide F_{254} activated III (63-200 μm, Merck). All water solutions were prepared from ultrapure laboratory grade water that has been filtered and purified by reverse osmosis using Millipore MilliQ reverse-osmosis cartridge system (resistivity 18 MΩ cm). Thin layer chromatography (TLC) was performed on silica gel 60 F254 or aluminium oxide 60 F254 neutral (Merck). The analytical high performance liquid chromatography (HPLC) on organic compounds and lanthanide complexes was carried out on an Hypersil Gold column (250x4.6 mm, particle size 5 μ) at 1 mL/min using a gradient from water TFA (99.9/0.1) to acetonitrile/water/TFA (90: 9.9: 0.1) for L1-Ln or from water (100 %) to acetonitrile (100 %) for **1-Ln**, with an excitation wavelength at 270 nm. The preparative HPLC on organic compounds and lanthanide complexes was carried out on a Hypersil Gold column (250x21.6 mm, particle size 5 μm) at 15 mL/min, using the same gradient, with an excitation wavelength at 270 nm.

I.2. Synthesis of 1-Ln



Scheme S1: *Synthesis of [Ln(ebpatcnSS)(H_2O)]: i) tacn, K_2CO_3, CH_3CN ; ii) NaBH(OAC)$_3$, 1-2 dichloroethane ; iii) HCl (1M, reflux), KOH, $LnCl_3$ (Ln=Eu, Tb, Gd, Yb); iv) DIEA, CH_3CN*

benzyl 2-(((benzyloxy)carbonyl)amino)-3-(1,4,7-triazacyclononane)propanoate (2)

To a solution of tacn.3HCl (2.22 g, 9.30 mmol, 3.0 eq) in dry acetonitrile (60 mL), potassium carbonate (1.93 g, 13.5 mmol, 4.5 eq) was added. The reaction mixture was heated at 50°C and stirred for 1 h. Then the crude mesylate **1** (3.10 mmol, 1.0 eq) was added. The reaction was stirred at 50°C overnight, filtrated and evaporated under reduced pressure. The resulting oily product was solubilized in AcOEt (200 mL). The organic phase was washed with water (5x100 mL) and brine (2x100 mL), dried over Na_2SO_4, filtered and reduced under pressure to give the compound **2** (1.00 g, 73%) as colourless oil and used without further purification.
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) = 7.45-7.27 (m, 10H, $10H_{Ar}$), 6.73 (s broad, 1H, N*H*), 5.22-5.02 (m, 4H, $2CH_2Ar$), 4.50-4.40 (m, 1H, C*H*CH_2), 3.14-2.59 (m, 14H, CHC*H*$_2$ and 6 C*H*$_2$ tacn). **ES-MS** (m/z): 441.4 [**2**+H]$^+$

2-Pyridinecarboxylic acid, 6-formyl- ethyl ester (**3**)

To a solution of 2-pyridinecarboxylic acid, 6-(hydroxymethyl)-,ethyl ester (5.06 g, 27.93 mmol, 1.0 eq) in 1,4-dioxane (140 mL), SeO_2 (1.52 g, 13.68 mmol, 0.49 eq) was added. The reaction was stirred overnight at reflux. After filtration over celite and evaporation under reduced pressure, the crude product was purified over silica gel (200 g, gradient CH_2Cl_2/EtOH from 100/0 to 90/10, v/v) to give the compound **3** (4.49 g, 92%) as a yellow solid.
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K), δ (ppm): 10.19 (s, 1H, CHO), 8.34 (dd, J=1.4 Hz, 7.6 Hz, 1H, H_3), 8.18 (dd, J=1.4 Hz, 7.6 Hz, 1H, H_5), 8.08 (t, J=7.6 Hz, 1H, H_4), 4.53 (q, J=7.2 Hz, 2H, COOC*H*$_2$CH$_3$) 1.50 (t, J= 7.2 Hz, 3H, COOCH$_2$C*H*$_3$) **ES-MS** (m/z): 179.9 [**3**+H]$^+$; 201.9 [**3**+Na]$^+$

Benzyl-2-(((benzyloxy)carbonyl)amino)-3-(1,4,7-triazacyclononane-1,4 diethylbis(methylene)) dipicolinate) propanoate (L1)

To a solution of the crude compound **2** (1.03 g, 2.34 mmol, 1.0 eq) in dry 1-2 dichloroethane (100 mL), aldehyde **3** (0.860 g, 4.80 mmol, 2.05 eq) was added. After stirring the resulting reaction mixture for 1 h at room temperature, $NaBH(OAc)_3$ (1.24 g, 5.85 mmol, 2.5 eq) was added. The reaction mixture was stirred at room temperature overnight. A saturated aqueous $NaHCO_3$ solution (100 mL) was added to the reaction mixture. After decantation and separation, the aqueous layer was extracted with dichloromethane (4 x 100 mL). The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure to give the crude compound **4** (2.52 g, quant.) as an orange oil. The crude product was purified over activated III alumina (150 g, AcOEt/EtOH, 95/5, v/v) to give the compound **4** (0.90 g, 50%) as a yellow oil.
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K), δ (ppm): 7.92 (d, J=7.6Hz, 2H, H_3), 7.67 (t, J=7.6Hz, 2H, H_4), 7.58 (d, J=7.6Hz, 2H, H_5), 7.34-7.30 (m, 10H, $10H_{Ar}$), 5.14-5.04 (m, 4H, 2C*H*$_2$Ar), 4.44 (q, J=7.2Hz, 4H, 2xCOOC*H*$_2$CH$_3$), 4.43-4.32 (m, 1H, C*H*CH$_2$), 3.86 (s, 4H, 2C*H*$_2$Py), 2.96-2.65 (m, 14H, CHC*H*$_2$ and 6C*H*$_2$ tacn), 1.39 (t, J=7.2Hz, 6H, 2COOCH$_2$C*H*$_3$)
ES-MS (m/z): 767.5 [**L1**+H]$^+$

Ln[(6,6'-((7-(2-amino-2-carboxyethyl)-1,4,7-triazacyclononane-1,4-diyl)bis(methylene))dipicolinic acid] L1-Ln (Ln=Eu, L1-Eu; Ln= Tb, L1-Tb;Ln=Gd, L1-Gd; Ln=Yb, L1-Yb)

A solution of **4** (0.300 g, 0.391 mmol, 1 eq) in a 1 M solution of HCl (5 mL) was stirred at reflux for 6 h. The reaction was monitored by analytical HPLC. The pH of the reaction mixture was raised to 6.5 using a concentrated solution of KOH. Then $LnCl_3.6H_2O$ (Ln= Eu^{III}, Tb^{III}, Gd^{III}, Yb^{III}) (0.430 mmol, 1.1 eq) was added to the mixture and the pH was again raised to 6.5 using a 0.5 M solution of KOH in water. The resulting reaction mixture was purified by preparative HPLC to afford the complexes **L1-Ln** (L1-Eu: 60 mg, 25 %, L1-Tb: 27 mg, 15 %, L1-Yb: 29 mg, 15 %), L1-Gd: 32 mg, 15 %.
^{1}H NMR (Eu complex, D_2O, 400 MHz, 298 K, pD =7.4), δ (ppm): -13.74 (s, 1H, CH_2), -7.97 (s, 1H, CH_2), -7.43 (s, 1H, CH_2), -4.64 (s, 1H, CH_2), -3.33 (s, 1H, CH_2), -1.63 (s, 1H, CH_2), -1.16 (s, 1H, CH_2), -0.65 (s, 1H, CH_2), -0.19 (s, 1H, CH_2), -0.01 (s, 1H, CH_2), 0.22 (s, 1H, CH_2), 0.95 (s, 1H, CH_2), 2.29 (s, 1H, CH_2), 3.88 (s, 1H, CH_2), 5.32 (s, 1H, CH_2), 5.94 (s, 1H, CH_2), 6.07-6.09 (m, 2H, H_3), 6.37-6.47 (m, 3H, H_6+CH_2), 7.71 (s broad, 2H, H_5), 10.33 (s, 1H, CH_2), 25.38 (s, 1H, CH_2). **ES-MS** (m/z): Eu: 637.3 [**5**+H]$^+$; Tb: 643.3 [**5**+H]$^+$; Yb: 658.3 [**5**+H]$^+$. **Analytical HPLC**: rt= 11.6 min, purity = 95% (method 1)

1,2-Dithiolane-3-pentanoic acid, 2,5-dioxo-1-pyrrolidinyl ester (4)

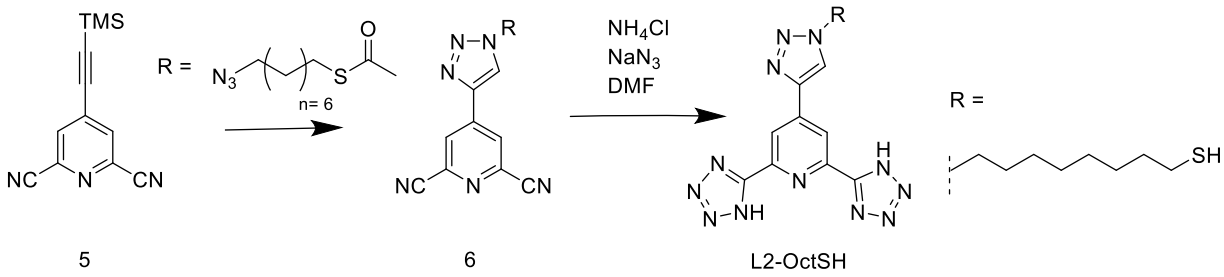
To a solution of lipoic acid (1.00 g, 4.85 mmol, 1.0 eq) in dry acetonitrile (70 mL), N-hydroxysuccinimide (0.781 g, 6.78 mmol, 1.4 eq) and 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.22 g, 6.31 mmol, 1.3 eq) were added. The reaction was stirred overnight at room temperature. The solvent was evaporated under reduce pressure and the residue was dissolved in dicholoromethane (150 mL). The organic phase was washed with a saturated solution of $NaHCO_3$ (100 mL) and with brine (100 mL), dried over Na_2SO_4, filtered and evaporated under reduce pressure to obtain the compound **5** as a yellow solid (1.46 g, 99%).
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K), δ (ppm): 3.57 (td, J=3.2, 7.2 Hz, 1H, H_5), 3.21-3.08 (m, 2H, H_1), 2.83 (s broad, 4H, NHS), 2.62 (t, J=7.2 Hz, 2H, H_7), 2.46 and 1.92 (ABXY$_2$, J_{AB}=6.4

Hz, J_{AX}=2.8 Hz, J_{BX}=3.4 Hz, J_{AY2}= J_{BY2}= 3.4 Hz, 1H, H_6), 1.82-1.75 (m, 2H, H_3), 1.74-1.68 (m,2H, H_2), 1.57 (m, 2H, H_4)

Ln(6,6'-((7-(2-(5-((R)-1,2-dithiolan-3-yl)pentanamido)-2-carboxyethyl)-1,4,7-triazacyclononane-1,4-diyl)bis(methylene))dipicolinic acid) (1-Ln)

To a solution of the complex **5-Ln** (44 mg, 0.069 mmol, 1.0 eq) in dry acetonitrile (2 mL), the activated lipoic acid **6** (23 mg, 0.076 mmol, 1.1 eq) and N,N-diisopropylethylamine (13 µL, 0.076 mmol, 1.1 eq) were added. The reaction mixture was stirred overnight then the solvent was removed under reduced pressure. The crude product was purified by preparative HPLC to obtain the compounds **1-Ln** (**1-Eu**: 15 %, **1-Tb**: 8 %, **1-Yb**: 8 %, **1-Gd**: 23 %).
^{1}H NMR (Eu^{III} complex, D_2O, 400 MHz, 298 K, pD =7.4), δ (ppm): -14.18 (s, 1H, CH_2), -9.54 (s, 1H, CH_2), -9.28 (s, 1H, CH_2), -7.07 (s, 1H, CH_2), -3.83 (s, 1H, CH_2), -2.34 (s, 1H, CH_2), -1.76 (s, 1H, CH_2), -1.63 (s, 1H, CH_2), -1.52 (s, 1H, CH_2), -0.02 (s, 1H, CH_2), 0.17 (s, 1H, CH_2), 0.34 (s, 1H, CH_2), 0.82 (s, 1H, CH_2), 1.21-1.11 (m, 3H, H_6), 1.43-1.30 (m, 2H, H_6), 1.56-1.47 (m, 2H, H_6), 1.68-1.56 (m, 1H, H_6), 2.24-2.16 (m, 1H, H_6), 2.73-2.66 (m, 1H, H_6), 3.67-3.54 (m, 2H, H_6), 3.89-3.79 (m, 2H, H_6+CH_2), 5.69 (s, 1H, CH_2), 6.15 (s, 1H, CH_2), 6.52 (m, 2H, H_3), 6.84 (d, J=7.6Hz, 1H, H_6), 7.00 (d, J=7.6Hz, 1H, H_6), 7.94 (t, J=7.6Hz, 1H, H_5), 8.08 (t, J= 7.6Hz, 1H, H_5), 8.18 (s, 1H, CH_2), 9.40 (s, 1H, CH_2), 26.86 (s, 1H, CH_2). **ES-MS** (m/z): Eu: 825.3 [**7**+H]$^+$; Tb: 831.3 [**7**+H]$^+$ 853.3 [**7**+Na]$^+$; 869.2 [**7**+K]$^+$; Yb: 846.2 [**7**+H]$^+$ 868.2 [**7**+Na]$^+$; 884.3 [**7**+K]$^+$
Analytical HPLC: rt= 21 min, purity = 99%

I.3. Synthesis of ligand L2-OctSH



Scheme S2: *Synthesis of ligand **L2-OctSH***

(8-bromooctyl)ethanethioate
1, 8-dibromooctane (3.4 mL, 18.4 mmoles, 3.5 eq.) was dissolved in acetonitrile (150 mL). Potassium thioacetate (0.6 g, 5.25 mmoles, 1 eq.) was added and the mixture refluxed at 80 ºC over 3 days stirring vigorously. After 3 days, the volume of MeCN was reduced in vacuo, dichloromethane added and the product washed with H_2O (3 x 20 mL), dried over Na_2SO_4, filtered and evaporated to yield an off-white oil. The product was purified using flash column chromatography on SiO_2 using hexane/ethyl acetate 95:5 as eluent to yield a clear oil, 1.01 g, 3.78 mmoles, 72 % yield. ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 3.4 ppm (2H, t, CH_2), 2.86 ppm (2H, t, CH_2), 2.36 (3H, s, CH_3), 1.87 (2H, m, CH_2), 1.36 (10 H, m, CH_2). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 196.5 (C=O), 34.5(CH_2), 31.1(CH_2), 29.9 (CH_3), 29.5 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.5 (CH_2). ES-MS spectroscopy m/z: 267.2 ($M + H^+$).

(8-azido)ethanthioate

The bromide (1.16 g, 4.3 mmoles, 1 eq.) was dissolved in EtOH (100 mL) and stirred vigorously upon the addition of NaN_3 (0.57 g, 8.7 mmoles, 2 eq.). The reaction mixture was stirred at 50 ºC for 16 hours. The solvent was removed in vacuo, dichloromethane added and the organic layer washed with H_2O (3 x 20 mL), dried over Na_2SO_4, filtered and the solvent removed to yield a clear oil, 0.936 g, 4.1 mmoles, 95 % yield. ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 3.25 (2H, t, CH_2), 2.85 (2H, t, CH_2), 2.47 (2H, m, CH_2), 2.31 (3H, s, CH_3), 1.32 (10 H, m, CH_2 chain). ^{13}C NMR ($CDCl_3$, 50 MHz), δ (ppm): 196.0 (C=O), 51.0 (CH_2), 29.2 (CH_2), 33(CH_2), 31 (CH_2), 30 (CH_3), 29.2 (CH_2), 26.7 (CH_2). ES-MS spectroscopy m/z: 202.1 (M+H - N_2)

4((trimethylsilyl)ethynyl)pyridine-2,6-dicarbonitrile (5) was prepared according to the published procedure.[7]

S-(8-(4-(2,6-dicyanopyridin-4-yl)-1H-1,2,3, triazol-1-yl)octyl)ethanethioate (6)

(8-azido)ethanthioate (0.24 mL, 1.7 mmoles, 1eq.) were added to a suspension of **1** (0.39 g, 1.7 mmoles, 1eq), $CuSO_4$ (0.055g, 0.35 mmoles 0.2 eq.) and Na ascorbate (0.135g, 0.68 mmoles, 0.4eq.) in 50 ml of a 1:1 mixture of ^{t}BuOH /H_2O. K_2CO_3 (0.24 g, 1.7 mmoles, 1eq.) was added and the resulting reaction mixture stirred at room temperature overnight. Dichloromethane and ammonium hydroxide (5 %) were added, the product was extracted into the organic layer, washed with H_2O and brine dried over $MgSO_4$, filtered and the solvent was removed to yield a yellow solid. Purification via flash column chromatography (Al_2O_3 dichloromethane: ethanol 99:1%) afforded compound **2** as a white solid in 62 % yield (0.33 g,

1.1 mmoles). ^{1}H NMR (DMSO, 200 MHz), δ (ppm): 9.05 ppm (s, 1H), 8.78 ppm (2H, Ar-H), 4.55 (2H, t, CH_2), 2.87 (2H, CH_2), 2.38 (3H, CH_3), 1.88 (2H, CH_2), 1.3-1.5 (10 H, CH_2). ^{13}C NMR (DMSO, 50 MHz), δ (ppm): 196.2 (Ar-C), 142.6 (Ar-C), 142.0 (Ar-C), 135.5(Ar-C), 128.3 (Ar-C), 126.4 (Ar-C), 117.0 (Ar-C), 50.8 (CH_2), 31.5 (CH_2), 30.3 (CH_2), 29.9 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 26.5 (CH_2). ES-MS spectroscopy m/z: 341.2 ($M-OCH_3+H^+$), 405.2 ($M+Na^+$).

L2-OctSH

A suspension of **2** (0.10 g, 0.26 mmoles, 1eq.), NaN_3 (0.085 g, 1.3 mmoles, 5eq.) and NH_4Cl (0.069 g, 1.3 mmoles, 5 eq.) was stirred under argon in anhydrous dimethylformamide (80 mL) overnight at 125 ºC. The resulting reaction mixture was cooled and the solvent removed in vacuo. 0.1 M HCl (50 mL) was added and the mixture was sonicated for 1 hour. The resulting white solid was filtered on a cellulose acetate filter and dried overnight under vacuum at 40° C to afford **L2-OctSH** as a white solid in quantitative yield 0.114 g, 0.26 mmoles. ^{1}H NMR (DMSO, 200 MHz), δ (ppm): 9.28 (1H, s, triazole), 8.79 (2H, s, Ar-H), 4.51 (2H, m, CH_2), 1.93 (2H, m, CH_2), 1.32 (12H, m, CH_2). ^{13}C NMR (DMSO, 50 MHz), δ (ppm): 213.7(C-Ar), 146.5(C-Ar), 143.7(C-Ar), 142.5 (C-Ar), 141.9 (C-Ar), 134.7 (C-Ar), 132.9 (C-Ar), 120.4 (C-Ar), 34.2 (CH_2), 31.5 (CH_2), 30.2 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 26.6 (CH_2), 24.6 (CH_2). ES-MS spectroscopy m/z: 425.2 $(M-H^+)^-$.

I.5. Synthesis of QD

The synthesis of the InPZnS/ZnSe/ZnS alloy core gradient shell NCs was based on the previously reported procedures.[2] This procedure consists of three distinctive steps: (1) Precursor preparation (2) QD core synthesis (3) Shell Growth (Steps 2 and 3 are performed in a one-pot reaction).

Synthesis of InPZnS alloy nanocrystals

In the glovebox, $In(MA)_3$ (indium myristate) (0.1 mmol, 1 mL of 0.1 M solution, 1 eq), $Zn(St)_2$ (zinc stearate)(0.1 mmol, 1 mL of 0.1 M solution, 1 eq), 1-dodecanethiol (DDT) (0.1 mmol, 1 eq) and of ODE (octadecene) (7-8 mL) were mixed into a 50 mL three-neck flask. Meanwhile, $P(TMS)_3$ (trimethylsilylphosphine)(0.1 mmol, 1 eq) was diluted in ODE (1 mL) in a sample tube under inert atmosphere. The three-neck flask was connected to a Schlenk line and the suspension was degassed at room temperature for 15 minutes. Ar was flushed into the flask and a fast Ar flow was set up. The resulting reactive mixture was heated up to 300°C in less than 2 minutes (Molten salt bath at 320°C). When the temperature in the flask reached 100°C, the solution of $P(TMS)_3$ was injected immediately into the flask. A yellow coloration significant of the NC formation was instantly observed. The resulting mixture was stirred 30 min at 300 °C to allow the growth of the QD. When the desired colour was obtained, the reaction mixture was cooled down below 220°C in order to stop the reaction and continue with the shell growth.

Growth of ZnSe/ZnS gradient shell

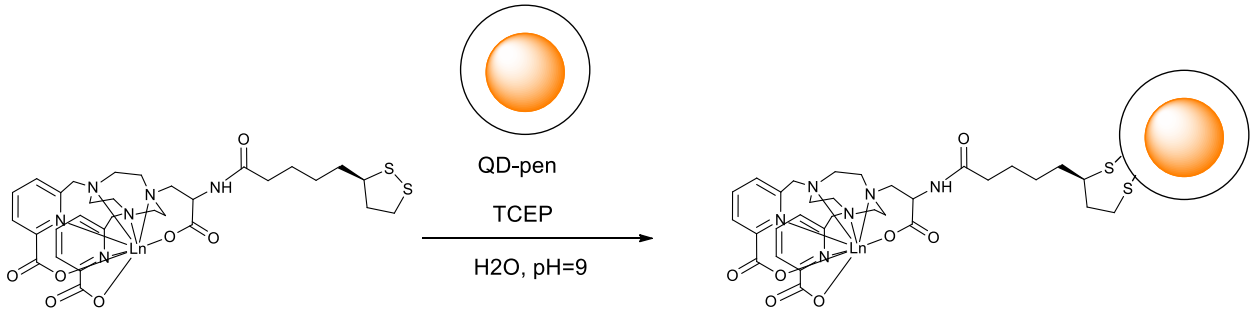
For the ZnSe/ZnS gradient shell growth, a high molar amount of precursors was used compared to the core synthesis, with a precursor ration of In:P:Zn:(Se + S) = 0.1:0.1:1:1 and the ratio Se/S of 0.2 was used. In a typical synthesis, Zn(oleic acid (OA))$_2$ (1 mmol, 2 mL of the 0.5 M stock solution, 1 eq), was added dropwise to the reactive mixture at 220°C. This was followed by the successive injection of TOP-Se (trioctylphosphine: TOP) (0.1 mmol, 0.1 mL of the 0.1 M solution, 0.1 eq) and TOP-S (0.9 mmol, 0.9 mL of the 0.1 M solution, 0.9

eq). The resulting mixture was slowly heated at 300°C (within 10 minutes). The shell growth was then allowed at 300°C for 20 more minutes (leading to a total time of reaction of approximatively 30 minutes), after which the reactive mixture was allowed to cool down slowly to room temperature. During both the core and the shell growth, the formation of the nanocrystals was followed using photoluminescence emission.
Once the mixture cooled down, the purification of the QD was performed via cycles of precipitation. Firstly, the mixture was suspended in 10 mL of a 1:1 (v/v) mixture of chloroform/methanol and 100 mL of acetone was added. Then the resulting suspension was centrifuged (8000 rpm for 5 minutes) and the obtained solid collected. This operation was repeated (usually 3 cycles) to afford the **QD-sur** quantum dots as a orange powder. In **QD-sur** the surface of the quantum dot is capped by a mixture of four different surfactants (Oleic Acid (OA), SA (stearic acid from the zinc stearate precursor), TOP (trioctylphosphine), DDT(dodecanethiol).

I.6. Synthesis of penicillamine–capped QDs (QD-pen)

Penicillamine capped QDs were prepared from QD-sur in 60% yield following the literature procedure.[3]

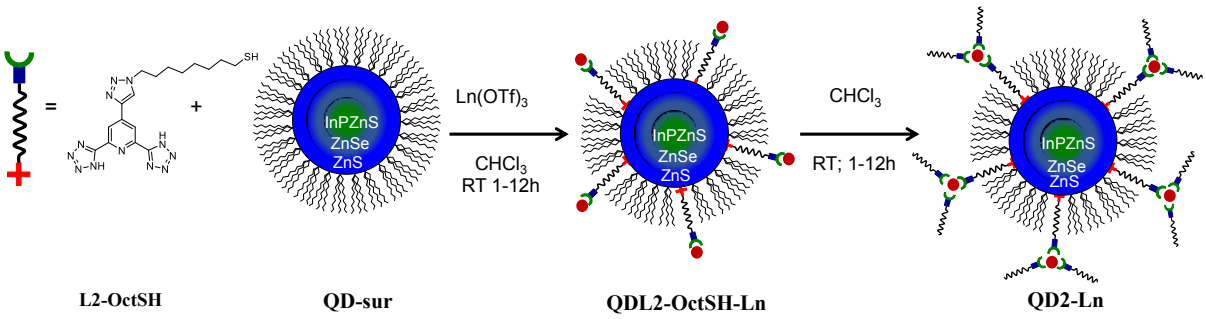
I.7. Synthesis of QD1-Ln (Ln= Eu^{III}, Tb^{III}, Gd^{III}, Yb^{III})



Scheme S3: Grafting of Ln complexes on quantum dots

Solutions of lanthanide complexes (0.25 mL, 2.1 mM, 200 eq) and TCEP (0.046 mL, 0.5 M, 9000 eq) in degassed water were added to the suspension of **QD-pen** (0.5 mL, 5.2 µM, 1 eq) in degassed water, and the pH of the resulting suspension was adjusted to 9 with 0.5M tetramethylammonium hydroxide solution. The mixture was shaken at 800 rpm overnight at 20°C. The resulting fine suspension was purified by size exclusion chromatography with a NAP^{TM}-25 columns (Sephadex^{TM} G-25 DNA Grade from GE Healthcare) eluted PBS buffer. The number of Ln^{III} complexes per QD was determined for independent syntheses by combined magnetic susceptibility measurements (on the Gd complex) and UV-visible spectroscopy (average number of grafted complexes = 115 complexes per QD).

I.8. Synthesis of QD2-Ln



Scheme S4**: Self-assembly of hybrid **QD2-Ln

The hybrids **QD2-Ln** (Ln= Eu^{III}, Tb^{III}, Yb^{III}) were synthesised via a partial cap exchange of the surface stabilising ligands (specify here which ligands). A 10^{-3} M solution of the deprotonated (by addition of 2 equivalents of NEt_3) ligand **L2-OctSH** in $CHCl_3$ was added to a 5 x 10^{-7} M^{-1} solution of the **QD-sur** in $CHCl_3$ with vigorous stirring. Immediately after addition of the ligand a decrease in the luminescence of the QD was observed. This sample was stirred over 12 hours to ensure cap exchange completion. After cap exchange the hybrid **QDL2-OctSH** was purified by several extractions into H_2O/MeOH to remove excess unreacted ligand and discarded stabilising ligands. The quantity of ligand per QD was determined by UV-vis absorption spectroscopy. Then 1eq. of $Ln(CF_3SO_3)_3$ (Ln= Eu^{III}, Tb^{III}, Yb^{III}) in MeOH per ligand was added *in situ* to a solution of the **QD-L2-OctSH** in $CHCl_3$, and the resulting **QDL2-OctSH-Ln** hybrid was extracted into $CHCl_3$. Addition of a solution of **L2-Oct** in $CHCl_3$ to the resulting hybrid solution yielded the final **QD2-Ln** complexes. The number of Ln^{III} complexes per QD was verified by UV-visible spectroscopy (200 **L2OctSH**/QD).

II. Characterisation of complexes

II.1. Characterization Methods

- ***Nuclear Magnetic Resonance (NMR)***

The ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance DMX 200 and Bruker Avance DMX 400 spectrometers. The chemical shifts are given in ppm by using the solvent as an internal reference. The following abbreviation are used for describing the multiplicity of the signal s (singulet), d (doublet), t (triplet), q (quadruplet), qt (quintuplet), dd (doublet of doublets), td (triplet of doublet), m (multiplet).

- ***Mass spectrometry (ES-MS)***

Mass spectra of organic compounds were recorded on a LXQ type THERMO SCIENTIFIC spectrometer, equipped with an electrospray ionization source and a linear-trap detector. Solutions were injected in the spectrometer at 10 µL min−1 flow rate. Ionization voltage and capillary temperature were about 2 kV and 250 °C, respectively. The source settings were the same (sheath gas, auxiliary gas, capillary voltage, and tube lens).

- ***Dynamic light scattering (DLS)***

The hydrodynamic diameter of nanoparticles dispersed in water was measured by dynamic light scattering (DLS), using a Malvern Zeta Sizer (NanoZS). The samples have been filtered with centrifugal filters from VWR (MWCO 30k) and dispersed in MilliQ water (18 mΩ) prior to the measurements. Given the sensitivity of the instrument, multiple runs (> 3) were performed to avoid erroneous results. The spectra have been corrected for viscosity (0.882 mPa.s at 298 K), absorption (at 532 nm), solvent (water), refractive index (1.33) and material (InP) refractive index (3.1). The data were collected in automatic mode and are expressed in number-percent.

- ***Transmission Electron Microscopy***

Conventional and high resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL 3010 LaB6 microscope operated at 300kV. Size distributions were determined manually on some hundred NCs using Fiji software; the low contrast of the InP-based QDs on the amorphous carbon film supported by a copper grid did not allow reliable binarisation of the images and automatic determination of the mean size and its standard deviation.

- ***UV-visible absorption spectroscopy***

UV-Vis absorption spectroscopy was performed on a HP 8452A spectrophotometer. It is a single beam spectrophotometer operating in the wavelength range 190-820 nm using a diode array for detection. The background run and the sample acquisition were performed in series on the same cuvette holder. For all the measurements, a quartz cuvette of 1 cm width has been used.

- ***Luminescence measurements***

Fluorescence spectra of the quantum dots were measured on a F-4500 spectrofluorometer (Hitachi) with a quartz cell of 1 cm by dispersing quantum dots in suitable organic solvent or aqueous medium. Luminescence data of the lanthanide complexes were recorded using a Perkin-Elmer LS50B luminescence spectrometer (using FLWINLAB for Windows v2.2) and a modular Fluorolog FL3-22 spectrometer from Horiba-Jobin Yvon-Spex. from Horiba-Jobin Yvon-Spex equipped with a double grating excitation monochromator and an iHR320 imaging spectrometer. Hamamatsu R928P and Hamamatsu R5509 photomultipliers were used for visible and NIR measurements, respectively. All spectra were corrected for detection and optical spectral response (instrumental functions) of the spectrofluorimeters. Quartz cells with an optical path of 1 cm and quartz capillaries 4 mm in diameter were used. For the acquisition of the excitation and emission spectra in the NIR, a longpass coloured filter was always used at 870 nm to block the signal of the 2nd harmonics. For each measurement of emission spectra of QD1-Ln and QD2-Ln we measured the emission of the pure QD as a control. In the case of the QD no emission was observed from the 2nd harmonics in the NIR. The direct excitation on the exciton at 456 nm results in a very weak and noisy signal due to the low concentration of QD used. Increasing the concentration of the QD results in a change of the lifetimes due to reabsorption, and measurements of the QD were carried out at low concentration.

Phosphorescence lifetimes of the lanthanides were measured in time-resolved mode and are the averages of three independent measurements that were taken by monitoring the decay at the maxima of the emission spectra. The signals were analyzed with the OriginLab Origin Pro

software. Lifetimes of the quantum dots were obtained using a SpectraLED source S-390 (FWHM 15 nm) from Horiba Scientific coupled to a Jobin Yvon NL-C2 Pulse Diode controller and a DH-HT TCSPC controller including a SpectraLED output. The output signal of the photomultiplier was fed to a PC and controlled and analyzed with the Data Station (v2.7) and Decay Analysis (v6.8) software from Horiba Scientific. Lifetimes are averages of 3 independent determinations with a calculated Chi-square < 2. The quantum yields were determined at room temperature through an absolute method using an integrating sphere from GMP S.A. (Switzerland) coupled to the spectrofluorimeter. The values reported are the average of three independent determinations for each sample.

The absolute quantum yields were calculated using the following expressions:

$$\Phi = E_c/(L_a-L_c) = E_c/L_a \times \alpha \qquad \alpha = (L_a-L_c)/L_a$$

where *Ec, Lc* and *La* are the emission spectra of the sample, the excitation wavelength of the sample and the excitation wavelength of the reference, respectively.

- ***Magnetic Susceptibility measurements***

The concentration of Gd(II) complexes were determined from bulk magnetic susceptibility (BMS) shift. The paramagnetic Ln(III) ions induce a susceptibility shift of the H_2O proton resonance frequency which is proportional to the concentration of the ions. This BMS shift was readily obtained as the difference of the measured frequencies in capillaries (1.7 mm OD, 1.3 mm ID, 110 mm in length) containing Gd content and a diamagnetic reference.
To a good approximation, the BMS shift Δ may be expressed by the equation:[i]

$$\Delta = \frac{4\pi cs}{T}\left(\frac{\mu_{eff}}{2.84}\right)^2 \times 10^3$$

$\Delta = \frac{4\pi cs}{T}\left(\frac{\mu_{eff}}{2.84}\right)^2 \times 10^3 \Delta = \frac{4\pi cs}{T}\left(\frac{\mu_{eff}}{2.84}\right)^2 \times 10^3$ where the concentration of paramagnetic solute is given by c in mol/L, s is dependent on the shape of the sample and its position in the magnetic field (s = 1/3, 1/6 and 0 for a cylinder parallel to the main field, a cylinder perpendicular to the main field and a sphere, respectively), T is the absolute temperature and μ_{eff} is the effective magnetic moment for a particular lanthanide ion. For superconducting magnets, s= 1/3. The theoretical effective magnetic moment of the gadolinium is 7.94.[ii]

The diamagnetic references are water for diluted solutions of Gd complexes, non-grafted oligonucleotides or quantum dots for the corresponding grafted object with Gd complexes and silica nanoparticles doped with yttrium complexes for the same nanoparticles doped with Gd complexes.

To lock the external magnetic field, a capillary filled with a 3mM solution of the $[Tb(ttha)]^{3-}$ complex (ttha = triethylene tetraamine hexaacetate) in D_2O was juxtaposed in the 5mm NMR holder tube, parallel to the first capillary containing the investigated solution (the reference or the Gd sample). The $[Tb(ttha)]^{3-}$ complex was used to induce a significant paramagnetic susceptibility shift of the resonance frequencies of the deuterium nuclei and residual HOD protons.[14] Then, the spectrometer field could be locked to the deuterium frequency of the auxiliary solution, the residual HOD protons giving a signal well separated from that of the H_2O protons in the sample.
The concentration of the samples needs to be at least 0.5 mM to have an accurate measurement by BMS shift. The error on the measurement is ±0.1 mM.

II.2. NMR of europium complexes

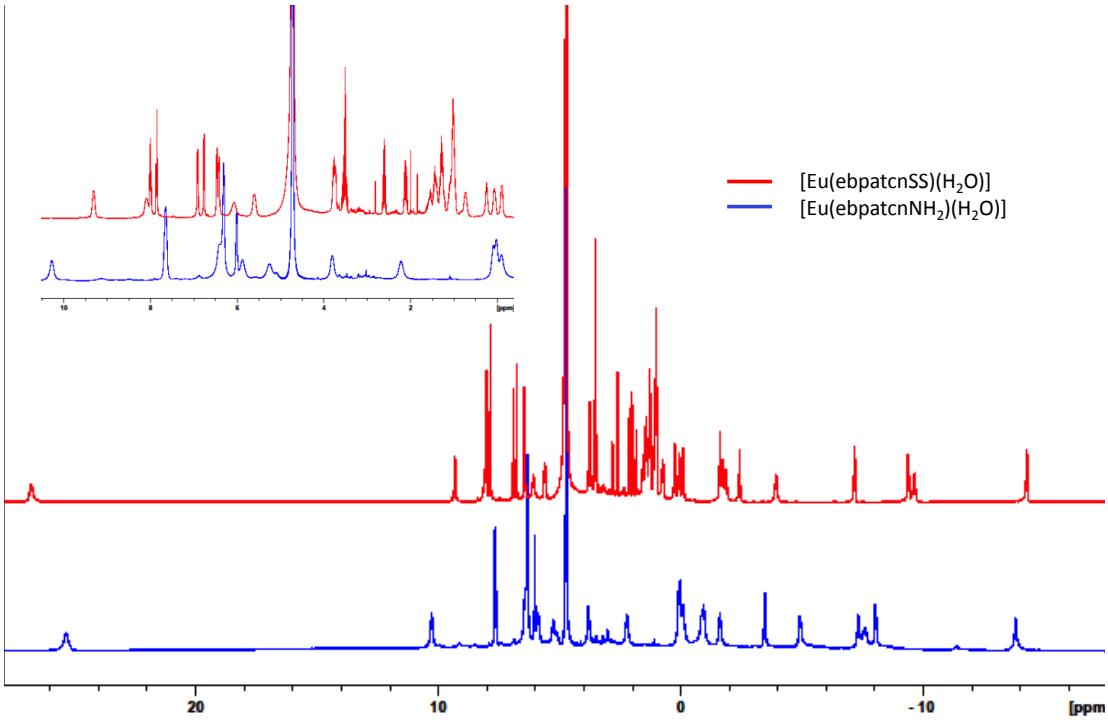


Figure S1*: NMR spectra of Eu complexes (400 MHz, 25°C, pD=7.4)*

II.3. Formation of L2-OctSH-Ln complexes

Triethylamine (3 eq.) was added to a suspension of the ligand **L2-OctSH** in MeOH to yield a 2.35 x 10^{-5} M solution of the deprotonated ligand. Aliquots of 4 mM solutions of $[Ln(CF_3SO_3)_3]$ (1.1 eq.) were progressively added at room temperature. The formation of the **L2OctSH-Ln** complexes was monitored by UV-visible and fluorescence spectroscopy.
^{1}H NMR of a 1:1 mixture of deprotonated ligand and **L2-OctSH** (MeOD, 200 MHz) δ (ppm): 8.73(Ar-H), 8.58 (Ar-H), 8.2 (Ar-H), 5.6 (CH_2), 4.4(CH_2), 2.5(CH_2), 2.3(CH_2), 1.9(CH_2), 1.55(CH_2), 1.4(CH_2), 1.33(CH_2). ES-MS spectroscopy m/z: 999.3 $(L2\text{-}octSH)_2^{4-} + Eu^{III}$)

The formation of the 3:1 complexes **L2-OctSH-Ln** in solution was followed via absorption and emission spectroscopy.

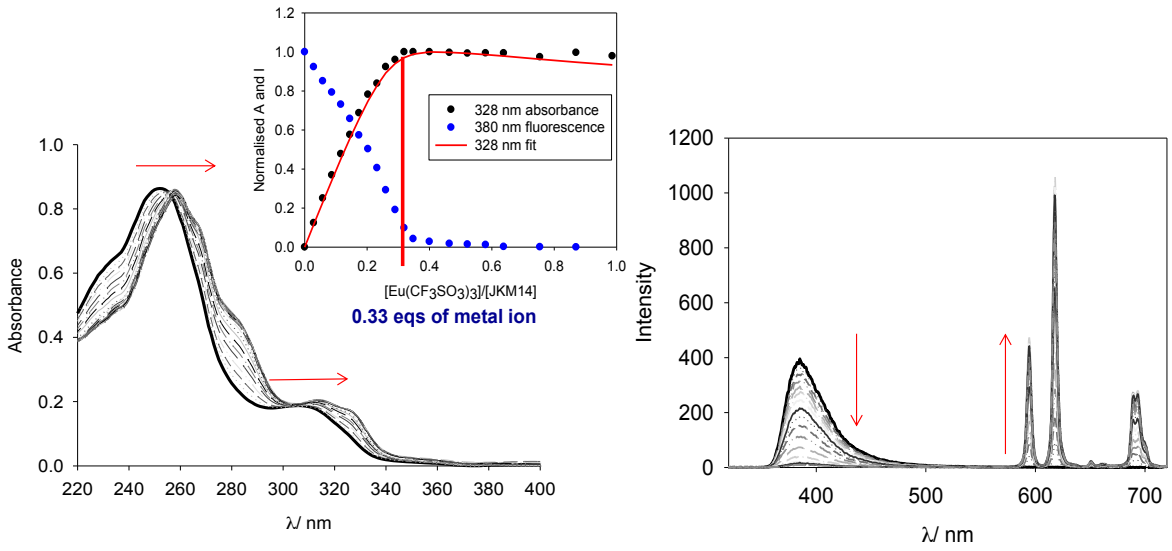


Figure S2: *Changes in the UV-Vis absorption (left) and emission (right) spectra upon addition of a 4 mM solution of $Eu(CF_3SO_3)_3$ to a 2.35 x 10^{-5}M solution of deprotonated* ***L2-OctSH*** *ligand in $CHCl_3$. Inset: Plot and fit of data at 328 nm demonstrating formation of complex at 0.33 eq of metal ion.*

III. Characterization of hybrids from QD-pen

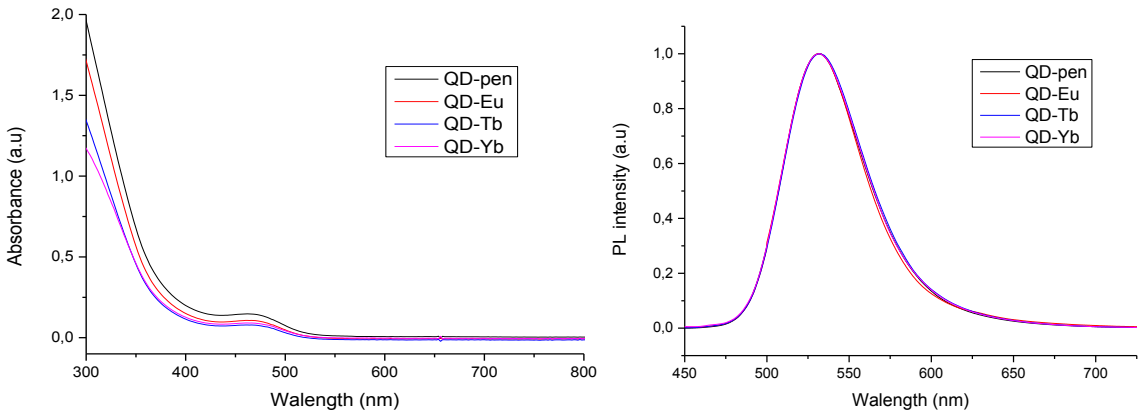


Figure S3*: Absorbance and luminescence spectra of* ***QD-pen*** *and* ***QD1-Ln*** *in PBS1X buffer (λ_{exc}=400 nm). Calculation with of the QD concentration with ε_{450}=415970 $M^{-1}cm^{-1}$*

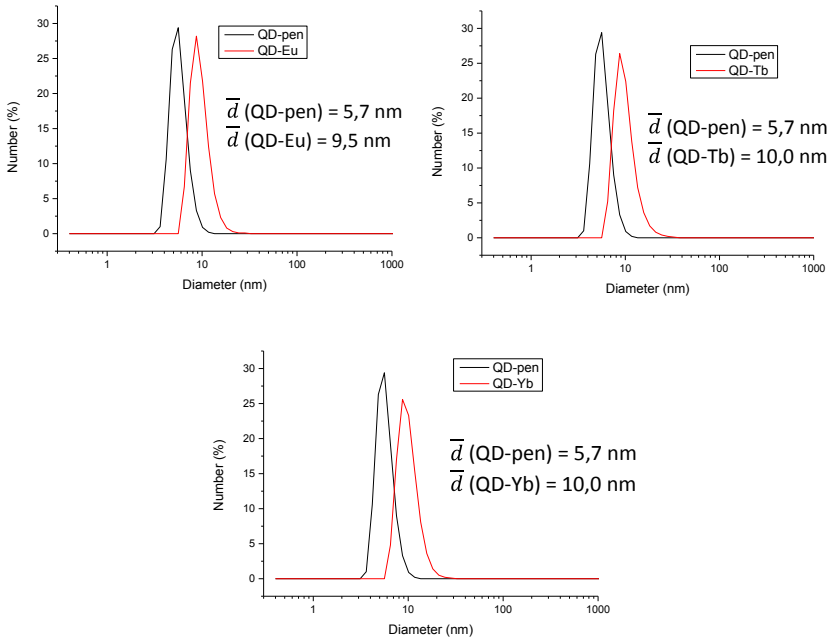


Figure S4: *DLS spectra of the* ***QD-pen*** *and* ***QD1-Ln*** *in PBS1X buffer*

Table S1: Polydispersity indices for 3 different samples of each hybrid

QD1-Eu	PdI	0,434	0,475	0,472
QD-Pen	PdI	0,326	0,442	0,444
QD1-Tb	PdI	0,498	0,499	0,501
QD1-Yb	PdI	0,421	0,395	0,43
QD1-Gd	PdI	0,41	0,439	0,451

IV. Characterization of hybrids from QD-sur

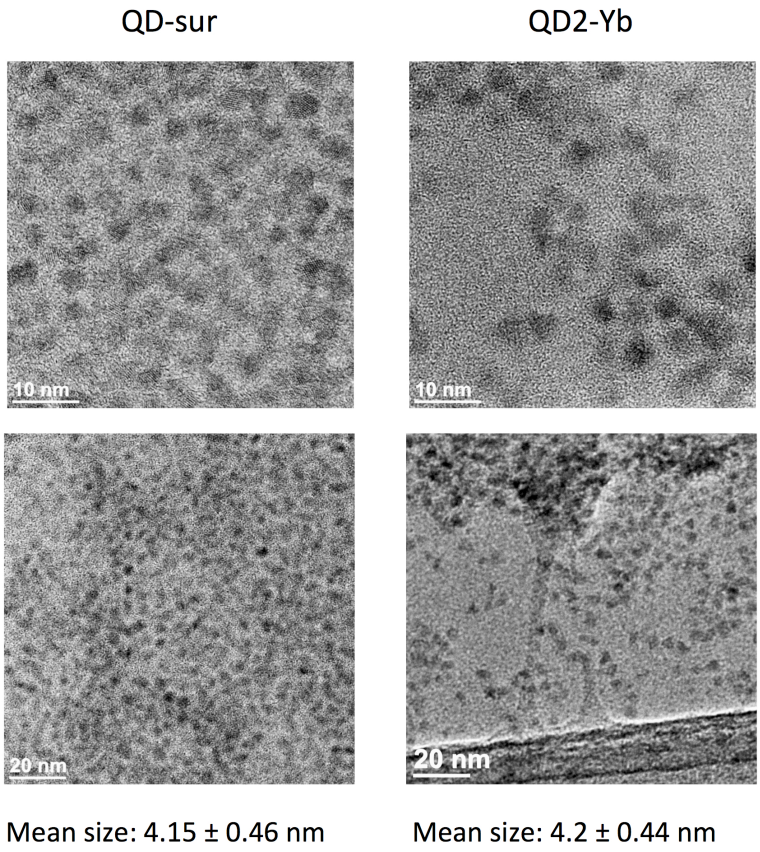


Figure S5: *Transmission electron micrographs of* ***QD-sur*** *and* ***QD2-Yb****, i.e. the identical sample after functionalization, at two different magnifications.*

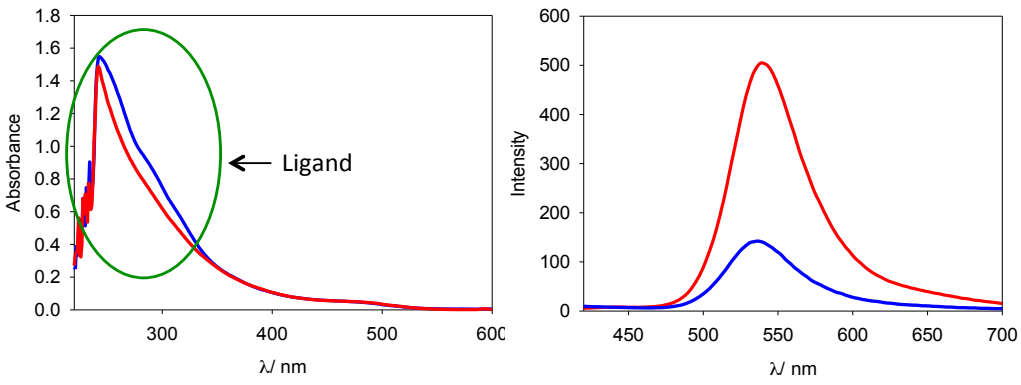


Fig S6: *Absorption and emission of* ***QD-sur*** *(red) and* ***QDL2-OctSH*** *(blue) at 4 x 10^{-8} M in $CHCl_3$, after functionalisation by the ligand* ***L2-OctSH.*** *The epsilon values have been calculated (8020 $M^{-1}\cdot cm^{-1}$ for ligand L2 and 416 900 $M^{-1}\cdot cm^{-1}$ for the QD-sur)*

The samples do not demonstrate any aggregation, as the absorption spectrum would clearly show an increase in baseline upon precipitation or aggregation. The TEM would not be a reasonable assessment of aggregation as the drying process can cause the particles to aggregate while evaporating and not because the samples are aggregated in solution. The most reliable measurement of aggregation is the absorption and emission spectra, which would show baselines and bandwidths indicative of aggregation that are not observed.

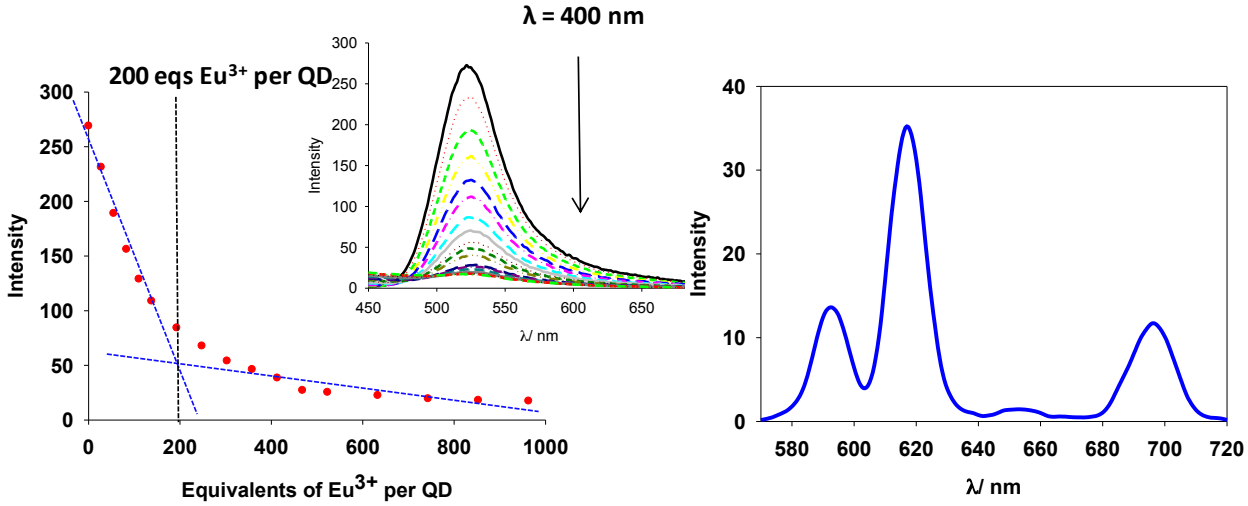


Fig S7: Changes in the *QD luminescence of **QDL2-OctSH** upon the addition of europium triflate in $CHCl_3$ ($c = 10^{-7}$M) to afford the complex **QDL2-OctSH-Eu** Right: Weak luminescence of Eu^{III} complex upon excitation at 306 nm.*

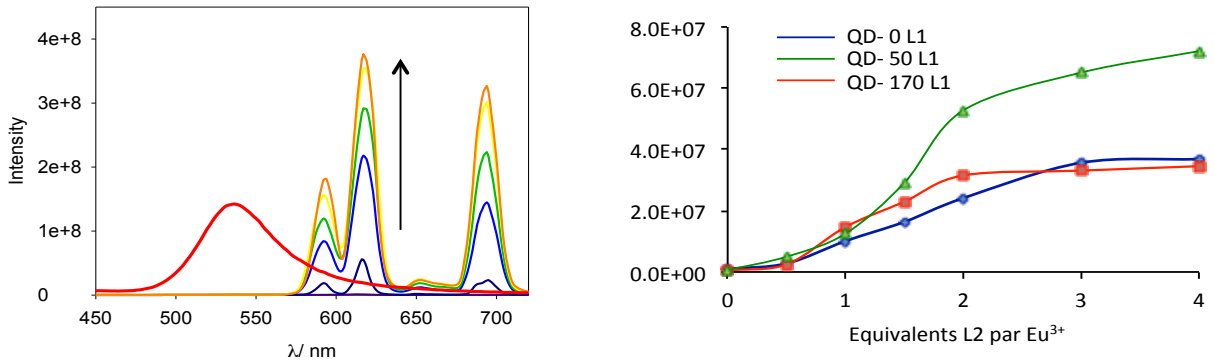


Fig. S8: *Changes in the emission spectra of **QDL2-OctSH-Eu** in $CHCl_3$ upon addition of capping agent **L2-Oct** demonstrating a dramatically increased Eu^{III} luminescence. Right: Plot of intensity versus eqs. of capping agent.*

V. Photophysical Characterisation of QD1-Ln

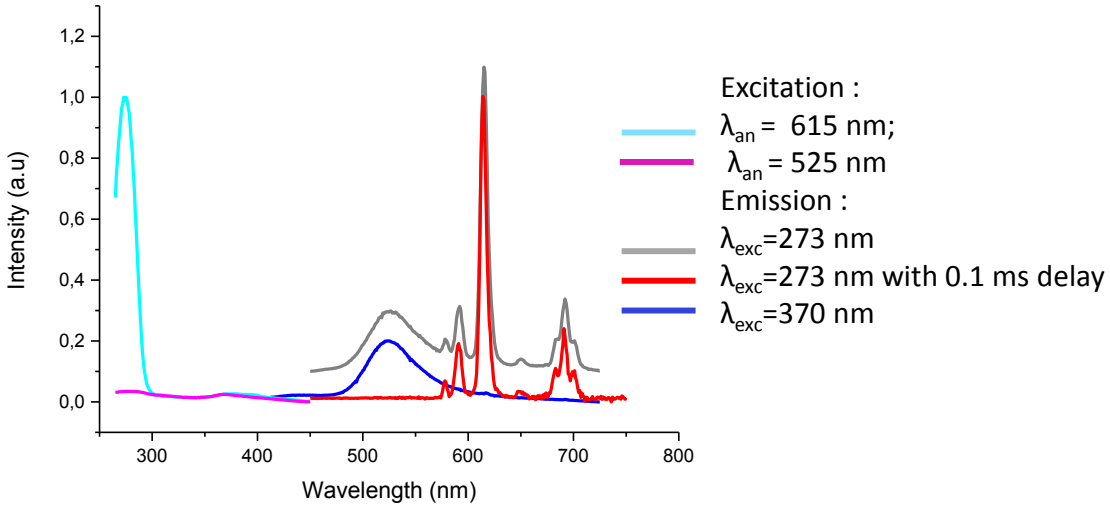


***Figure S9**: Excitation and emission spectra of **QD1-Eu** in PBS1X buffer*

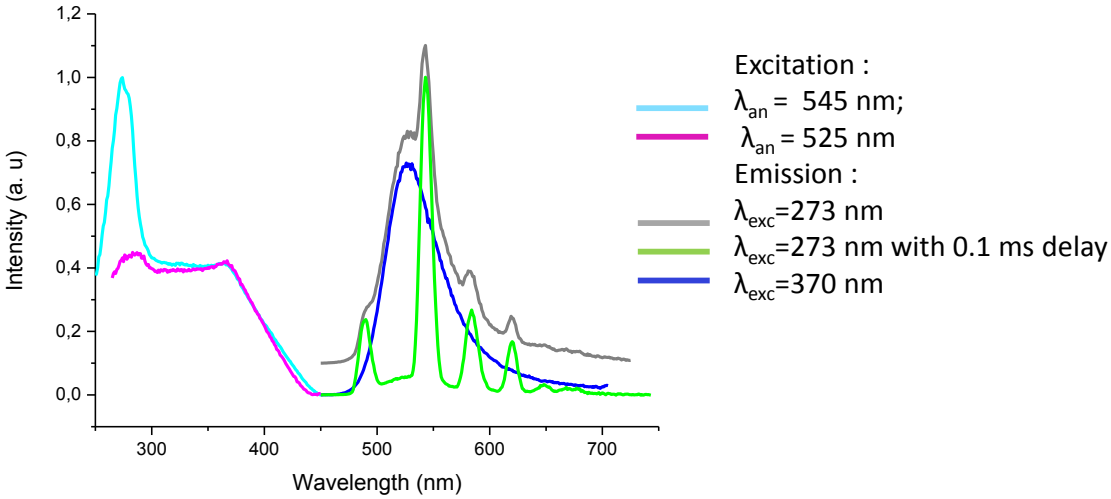


***Figure S10**: Excitation and emission spectra of **QD1-Tb** in PBS1X buffer*

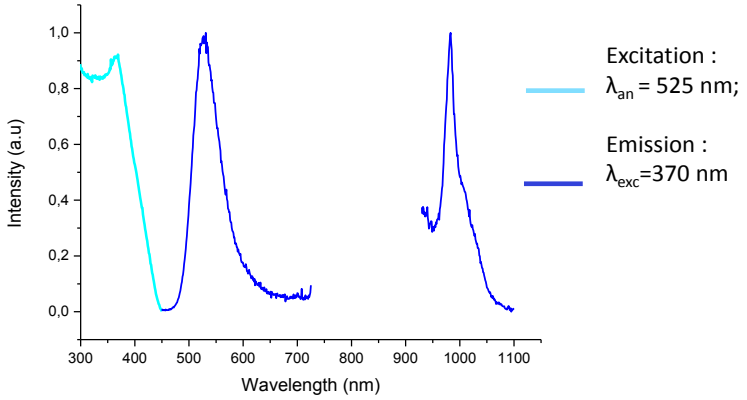


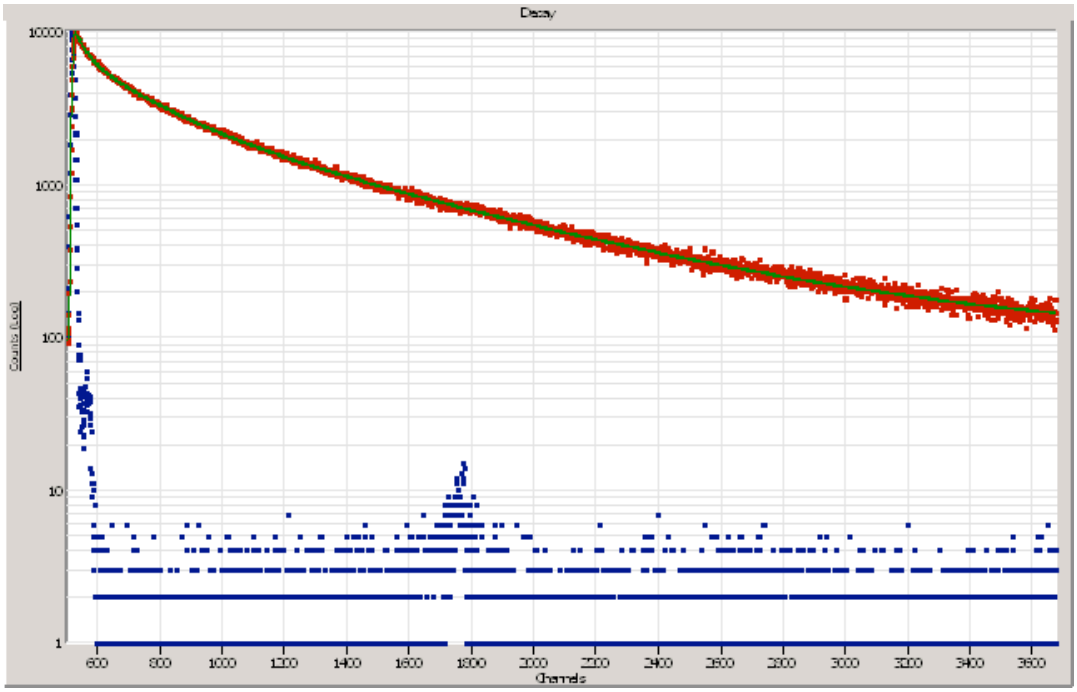
***Figure S11**: Excitation and emission spectra of **QD1-Yb** in PBS1X buffer*

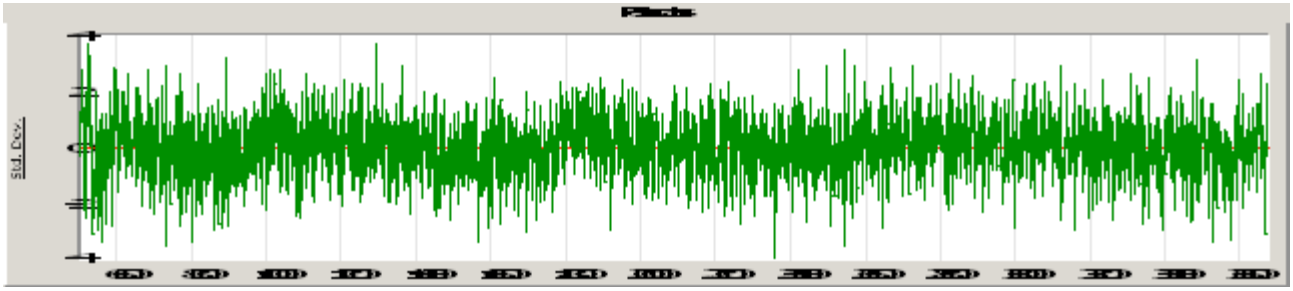
Table S2: *Lifetimes (λ_{exc}=273 nm for Ln complexes, λ_{exc}=370 nm for QD), calculated q-values and quantum yields (measurements were done in PBS1X buffer for QD1 and in $CHCl_3$ for QD2 samples)*

	τ(H_2O)		τ(D_2O)	q	Φ (H_2O)		τ ($CHCl_3$)	Φ ($CHCl_3$)
	Ln (ms)	QD (ns)	Ln (ms)	Ln	Ln(%)	QD (%)	QD (ns)	QD (%)
QD-pen		3.9±0.1 22.9±0.1 83.6±0.1				15 ± 2		
QD-sur							0.3 ±0.1 16.9±0.1 75.0±0.1	40 ± 4
[Eu(ebpatcnNH_2)(H_2O)]	0.53±0.01		1.45±0.02	1.0±0.1	8.0±0.5			
[Tb(ebpatcnNH_2)(H_2O)]	1.55±0,02		2.57±0.02	1.0±0.1	25±1			
[Eu(ebpatcnSS)(H_2O)]	0.49±0.02		1.17±0,02	1.0±0.1	9.8±0.5			
[Tb(ebpatcnSS)(H_2O)]	0.92±0,02		1.21±0.02	1.0±0.1	19±1			
QD1-Eu	0.48±0.01	0.9±0.1 5.6±0.1 30.1±0.1				1±1		
QD1-Tb	0.66±0.01	3.3±0.1 18.9±0.1 71.8±0.1	-	-	-	10±1		
QD1-Yb	-	3.2±0.1 16.4±0.1 61.8±0.1	-	-	-	5±1		
QD1.Gd	-	3.9±0.1 23±0.1 84±0.1	-	-	-	15±2		
QD2.Eu	-		-	-	-		0.2±0.1 4.2±0.1 31.3±0.1	
QD-L2-OctSH	-		-	-	-		0.2±0.1 5.1±0.1 50.3±0.1	
QD-L2OctSH-Eu	-		-	-	-		0.2±0.1 4.1±0.1 30.0±0.1	
QD2.Tb	-	-	-	-	-			40±4
QD2.Yb	-	-	-	-	-			5±2

VI. Representative fits and residuals for QD-pen, QD-sur, QD1-Ln and QD2-Ln

QD-pen





Calculated using 3 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

Shift Value = 0 ch
0 sec
Shift Limit = 10 ch
1.097394E-09 sec

T1 Estimate = 235.8273 ch
2.587954E-08 sec
T2 Estimate = 471.6545 ch
5.175907E-08 sec
T3 Estimate = 943.3091 ch
1.035181E-07 sec

A Free
B1 Free
B2 Free
B3 Free

Prompt and decay LO = 505 ch
5.541838E-08 sec
Prompt and decay HI = 3683 ch
4.041701E-07 sec

Background on prompt = 103
Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

Hi reduced to: 3673 ch

SHIFT = 0.6067011 ch
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S.Dev = 2.8093E-12 sec

T1 = 208.9265 ch
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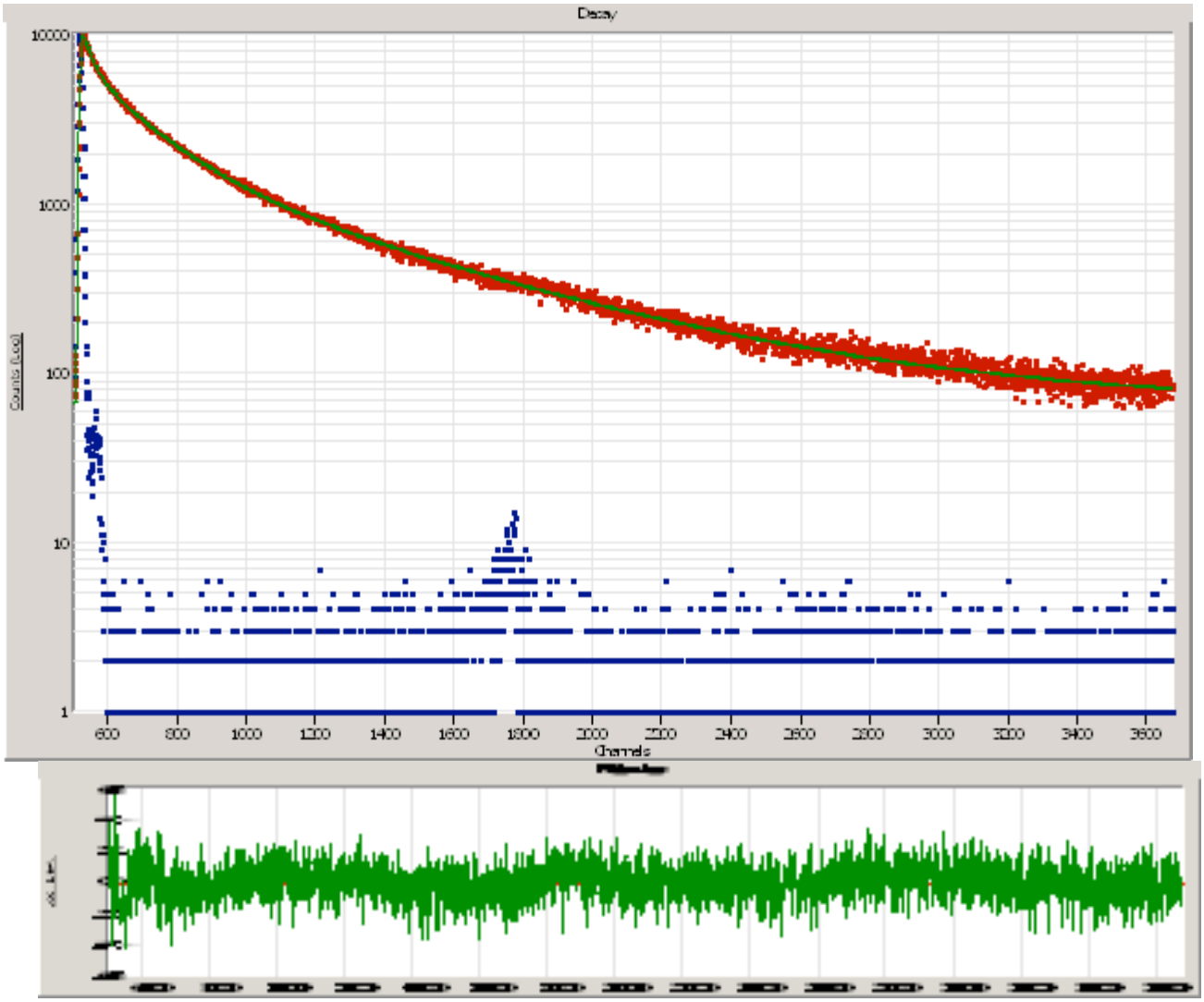
S.Dev = 4.666007E-10 sec
T2 = 762.1183 ch
8.363439E-08 sec
S.Dev = 3.363963E-10 sec
T3 = 35.81285 ch
3.930079E-09 sec
S.Dev = 7.409934E-11 sec

A = 96.06313
S.Dev = 0.4766235

B1 = 3.564032E-02
[25.43 Rel.Ampl]
S.Dev = 1.206659E-04
B2 = 2.705625E-02
[70.42 Rel.Ampl]
S.Dev = 3.997642E-05
B3 = 3.394978E-02
[4.15 Rel.Ampl]
S.Dev = 2.709133E-04

CHISQ = 1.142489
[3161 degrees of freedom]
Chi-squared Probability = 2.9218E-06%
Durbin-Watson Parameter = 1.87062
Negative residuals = 48.40644%
Residuals < 1 s.dev = 66.26696% Residuals < 2 s.dev = 93.78353% Residuals < 3 s.dev = 99.46355% Residuals < 4 s.dev = 100%

QD1-Tb



Calculated using 3 exponentials

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Decay data : Decay

The initial parameters are:

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Shift Limit = 10 ch
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T2 Estimate = 393.545 ch
4.318738E-08 sec
T3 Estimate = 787.09 ch
8.637475E-08 sec

A Free
B1 Free
B2 Free
B3 Free

Prompt and decay LO = 505 ch
5.541838E-08 sec
Prompt and decay HI = 3683 ch
4.041701E-07 sec

Background on prompt = 103
Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

Hi reduced to: 3673 ch

SHIFT = 0.8466126 ch
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S.Dev = 2.726488E-12 sec

T1 = 171.8271 ch
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S.Dev = 2.824468E-10 sec
T2 = 654.6436 ch
7.184017E-08 sec
S.Dev = 3.474242E-10 sec
T3 = 30.10322 ch
3.303508E-09 sec
S.Dev = 5.262543E-11 sec

A = 67.25849
S.Dev = 0.3136325

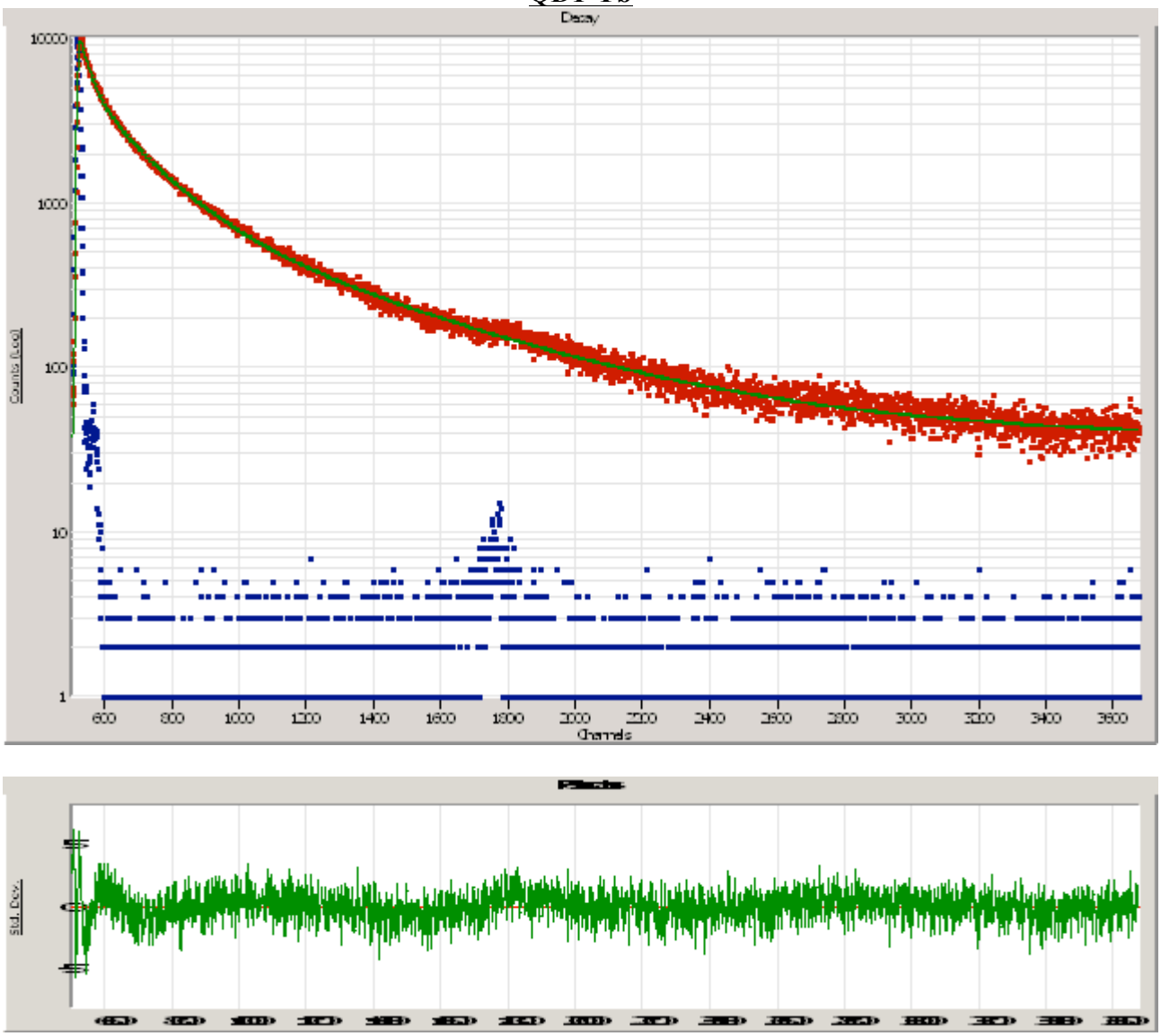
B1 = 4.140266E-02
[37.55 Rel.Ampl]
S.Dev = 1.129855E-04
B2 = 1.604643E-02
[55.45 Rel.Ampl]
S.Dev = 3.12779E-05
B3 = 4.399402E-02
[6.99 Rel.Ampl]
S.Dev = 2.872061E-04

CHISQ = 1.242417
[3161 degrees of freedom]

Chi-squared Probability = 1.6220E-17%
Durbin-Watson Parameter = 1.712338
Negative residuals = 47.55443%

Residuals < 1 s.dev = 64.53139% Residuals < 2 s.dev = 92.64752% Residuals < 3 s.dev = 98.92711% Residuals < 4 s.dev = 99.90533%

QD1-Yb



Calculated using 3 exponentials

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Decay data : Decay

The initial parameters are:

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0 sec
Shift Limit = 10 ch
1.097394E-09 sec

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T2 Estimate = 292.3239 ch
3.207943E-08 sec

T3 Estimate = 584.6477 ch
6.415887E-08 sec

A Free
B1 Free
B2 Free
B3 Free

Prompt and decay LO = 505 ch
5.541838E-08 sec
Prompt and decay HI = 3683 ch
4.041701E-07 sec

Background on prompt = 103
Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

Hi reduced to: 3673 ch

SHIFT = 0.6711709 ch
7.365387E-11 sec
S.Dev = 2.821251E-12 sec

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1.644156E-08 sec
S.Dev = 2.423524E-10 sec
T2 = 562.8245 ch
6.176401E-08 sec
S.Dev = 3.872729E-10 sec
T3 = 28.74618 ch
3.154588E-09 sec
S.Dev = 3.912131E-11 sec

A = 38.33287
S.Dev = 0.2038842

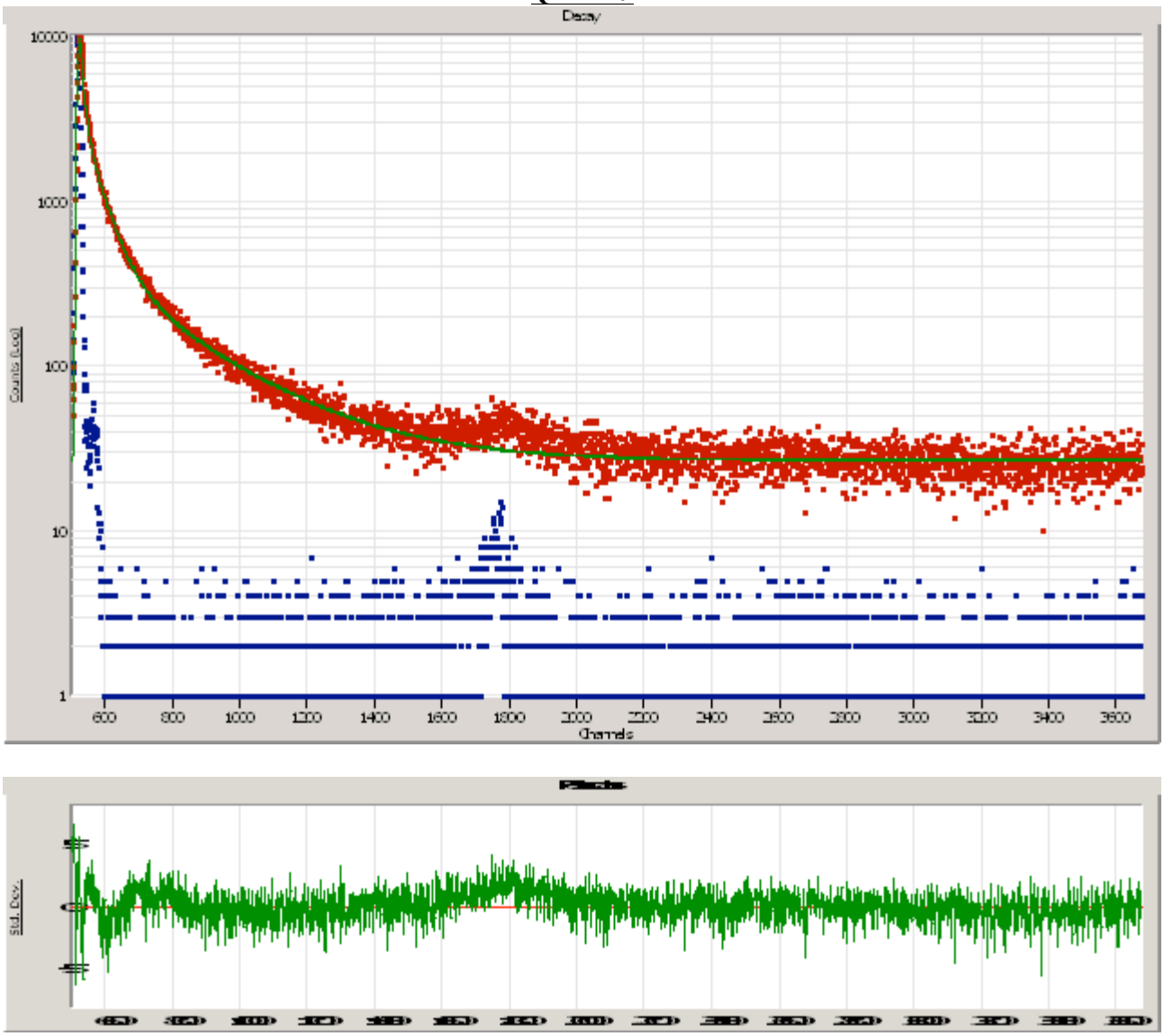
B1 = 0.0381377
[45.18 Rel.Ampl]
S.Dev = 1.059102E-04
B2 = 9.407024E-03
[41.86 Rel.Ampl]
S.Dev = 2.537956E-05
B3 = 5.704587E-02
[12.97 Rel.Ampl]
S.Dev = 2.862744E-04

CHISQ = 1.340333
[3161 degrees of freedom]

Chi-squared Probability = 1.9288E-20%

Durbin-Watson Parameter = 1.607309
Negative residuals = 46.89177%
Residuals < 1 s.dev = 63.93184% Residuals < 2 s.dev = 92.36353% Residuals < 3 s.dev = 98.67466% Residuals < 4 s.dev = 99.62133%

QD1-Eu



Calculated using 3 exponentials

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Decay data : Decay

The initial parameters are:

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T2 Estimate = 26.06921 ch
2.860819E-09 sec
T3 Estimate = 52.13843 ch
5.721638E-09 sec

A Free
B1 Free
B2 Free
B3 Free

Prompt and decay LO = 505 ch
5.541838E-08 sec
Prompt and decay HI = 3683 ch
4.041701E-07 sec

Background on prompt = 103
Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

Hi reduced to: 3673 ch

SHIFT = 0.6789979 ch
7.451281E-11 sec
S.Dev = 2.709658E-12 sec

T1 = 8.218687 ch
9.019135E-10 sec
S.Dev = 2.183695E-11 sec
T2 = 50.64579 ch
5.557837E-09 sec
S.Dev = 7.27332E-11 sec
T3 = 274.8343 ch
3.016014E-08 sec
S.Dev = 3.136449E-10 sec

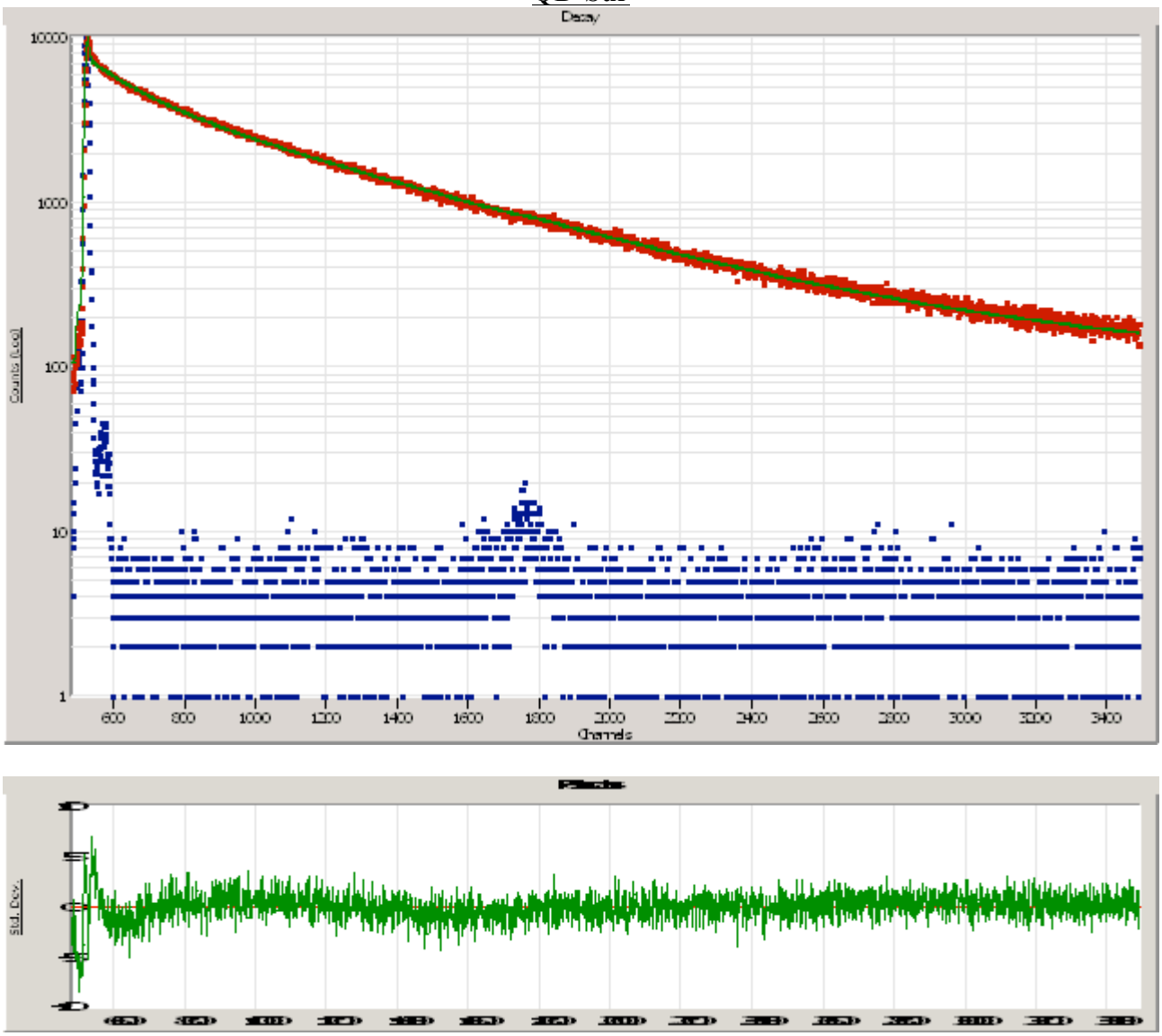
A = 27.0055
S.Dev = 0.1121194

B1 = 0.1413318
[31.26 Rel.Ampl]
S.Dev = 6.022909E-04
B2 = 3.087652E-02
[42.08 Rel.Ampl]
S.Dev = 1.310314E-04
B3 = 3.604485E-03
[26.66 Rel.Ampl]
S.Dev = 1.837196E-05

CHISQ = 1.514197
[3161 degrees of freedom]

Chi-squared Probability = 1.9288E-20%
Durbin-Watson Parameter = 1.380074
Negative residuals = 46.03976% Residuals < 1 s.dev = 59.67182%Residuals < 2 s.dev = 90.50173% Residuals < 3 s.dev = 97.91733%
Residuals < 4 s.dev = 99.55822%

QD-Sur



Calculated using 3 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

Shift Value = 0 ch
0 sec
Shift Limit = 10 ch
1.097394E-09 sec

T1 Estimate = 252.5045 ch
2.770969E-08 sec
T2 Estimate = 505.0091 ch
5.541938E-08 sec
T3 Estimate = 1010.018 ch
1.108388E-07 sec

A Free
B1 Free
B2 Free
B3 Free

Prompt and decay LO = 490 ch
5.377229E-08 sec
Prompt and decay HI = 3500 ch
3.840878E-07 sec

Background on prompt = 13
Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

Hi reduced to: 3490 ch

SHIFT = 5.500054E-02 ch
6.035724E-12 sec
S.Dev = 2.847161E-12 sec

T1 = 153.9326 ch
1.689247E-08 sec
S.Dev = 4.684418E-10 sec
T2 = 683.3344 ch
7.498868E-08 sec
S.Dev = 2.039914E-10 sec
T3 = 3.154093 ch
3.461281E-10 sec
S.Dev = 2.394547E-11 sec

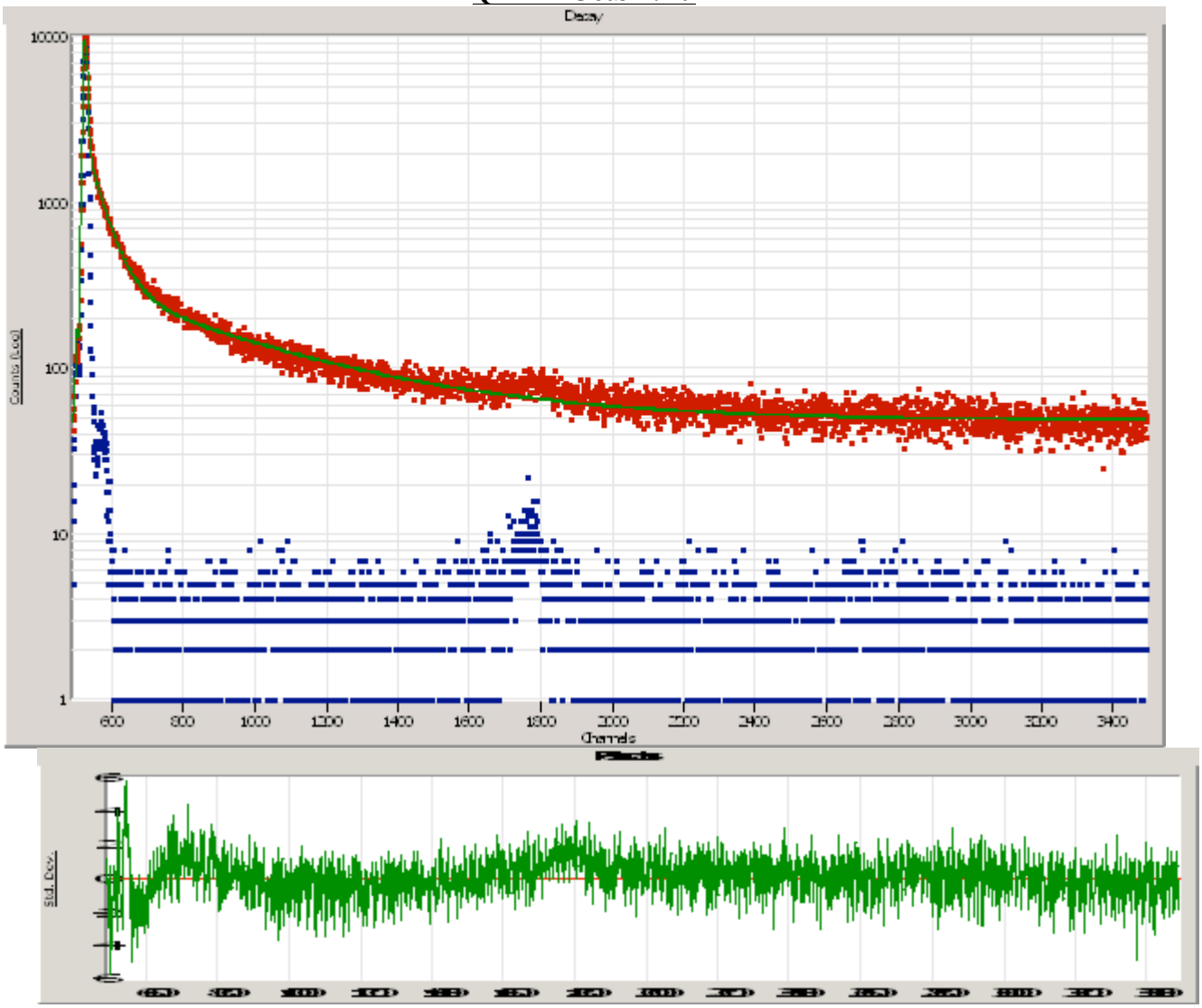
A = 105.9044
S.Dev = 0.4890929

B1 = 2.637648E-02
[13.20 Rel.Ampl]
S.Dev = 1.094555E-04
B2 = 0.0381922
[84.83 Rel.Ampl]
S.Dev = 3.986968E-05
B3 = 0.192239
[1.97 Rel.Ampl]
S.Dev = 1.329289E-03

CHISQ = 1.569924
[2993 degrees of freedom]

Chi-squared Probability = 1.9288E-20%
Durbin-Watson Parameter = 1.398911
Negative residuals = 47.81739%
Residuals < 1 s.dev = 63.51216%Residuals < 2 s.dev = 91.13629% Residuals < 3 s.dev = 97.6008% Residuals < 4 s.dev = 98.96701%

QD-L2-OctSH.Eu



Calculated using 3 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

Shift Value = 0 ch
0 sec
Shift Limit = 10 ch
1.097394E-09 sec

T1 Estimate = 100.3195 ch
1.1009E-08 sec
T2 Estimate = 200.639 ch
2.201799E-08 sec
T3 Estimate = 401.278 ch
4.403599E-08 sec

A Free
B1 Free
B2 Free
B3 Free

Prompt and decay LO = 490 ch
5.377229E-08 sec
Prompt and decay HI = 3500 ch
3.840878E-07 sec

Background on prompt = 16
Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

Hi reduced to: 3490 ch

SHIFT = -0.8325657 ch
-9.136524E-11 sec
S.Dev = 2.518535E-12 sec

T1 = 46.82586 ch
5.138641E-09 sec
S.Dev = 7.99797E-11 sec
T2 = 458.5007 ch
5.031558E-08 sec
S.Dev = 6.017948E-10 sec
T3 = 2.07266 ch
2.274524E-10 sec
S.Dev = 1.154525E-11 sec

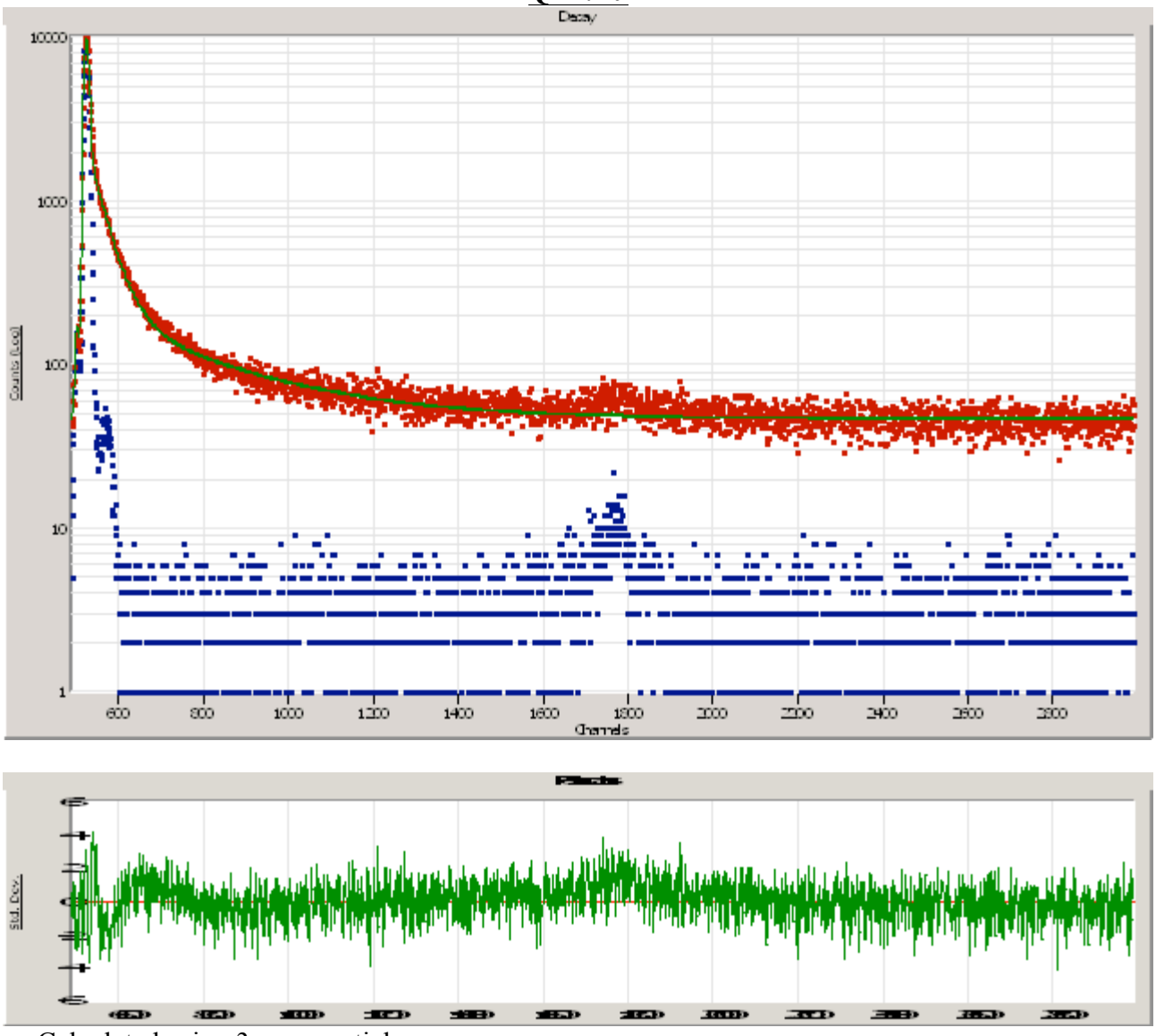
A = 48.89741
S.Dev = 0.1746036

B1 = 1.768186E-02
[27.71 Rel.Ampl]
S.Dev = 8.588928E-05
B2 = 2.188136E-03
[33.57 Rel.Ampl]
S.Dev = 1.090046E-05
B3 = 0.5583137
[38.72 Rel.Ampl]
S.Dev = 1.993275E-03

CHISQ = 1.387543
[2993 degrees of freedom]

Chi-squared Probability = 1.9288E-20%
Durbin-Watson Parameter = 1.43172
Negative residuals = 46.55115%
Residuals < 1 s.dev = 62.67911% Residuals < 2 s.dev = 91.23625% Residuals < 3 s.dev = 98.53382% Residuals < 4 s.dev = 99.63345%

QD2.Eu



Calculated using 3 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

Shift Value = 0 ch
0 sec

Shift Limit = 10 ch
1.097394E-09 sec

T1 Estimate = 0.0995 ch
1.091907E-11 sec
T2 Estimate = 0.199 ch
2.183814E-11 sec
T3 Estimate = 0.398 ch
4.367627E-11 sec

A Free
B1 Free
B2 Free
B3 Free

Prompt and decay LO = 490 ch
5.377229E-08 sec
Prompt and decay HI = 3000 ch
3.292181E-07 sec

Background on prompt = 16
Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

Hi reduced to: 2990 ch

SHIFT = -0.5571195 ch
-6.113794E-11 sec
S.Dev = 2.290939E-12 sec

T1 = 1.601316 ch
1.757274E-10 sec
S.Dev = 1.226306E-11 sec
T2 = 37.92106 ch
4.161433E-09 sec
S.Dev = 6.334484E-11 sec
T3 = 285.4896 ch
3.132945E-08 sec
S.Dev = 6.798131E-10 sec

A = 46.92601
S.Dev = 0.1692408

B1 = 0.7794363
[54.17 Rel.Ampl]
S.Dev = 2.757321E-03
B2 = 1.752777E-02
[28.85 Rel.Ampl]
S.Dev = 9.522807E-05
B3 = 1.370481E-03

[16.98 Rel.Ampl]
S.Dev = 1.262753E-05

CHISQ = 1.297522
[2493 degrees of freedom]

Chi-squared Probability = 3.2806E-20%
Durbin-Watson Parameter = 1.620719
Negative residuals = 46.54138%
Residuals < 1 s.dev = 64.05437% Residuals < 2 s.dev = 91.36346% Residuals < 3 s.dev = 98.84046% Residuals < 4 s.dev = 99.92003%

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