Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Lighting up Eu^{3+} luminescence through remote sensitization in silica nanoarchitectures

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Transmission Electron Microscopy

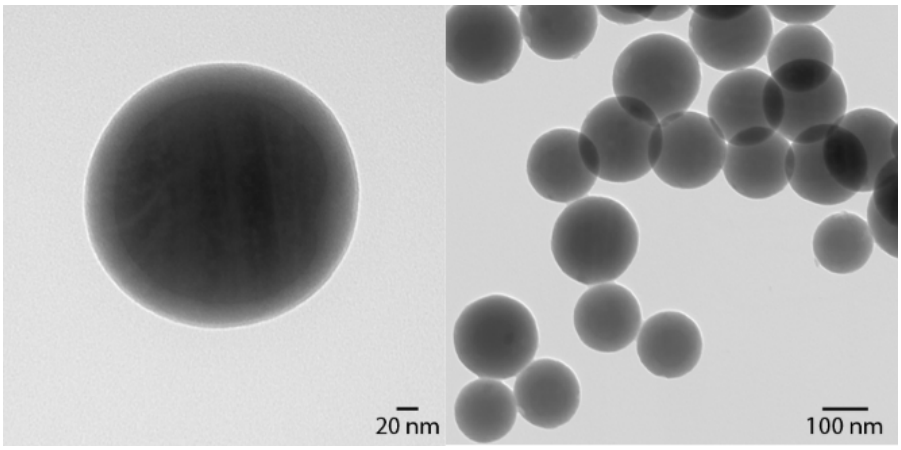

Figure S1. TEM micrographs of core Stöber NPs at different magnifications.

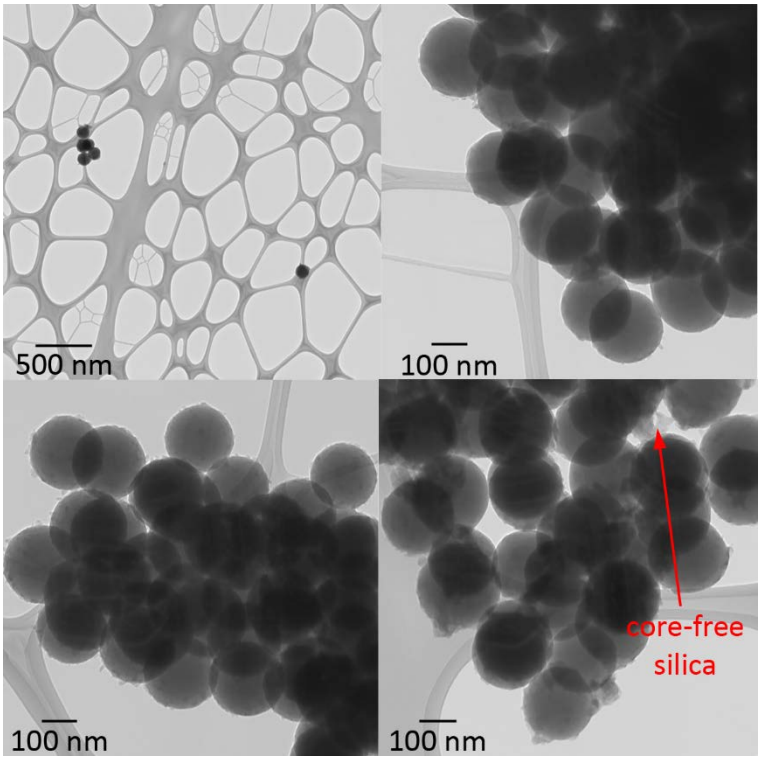

Figure S2. Additional TEM micrographs of S@SEu_900 NPs showing isolated particles and the low amount of core-free silica (red arrow, bottom right panel) in the rare NPs aggregates found on the TEM grid.

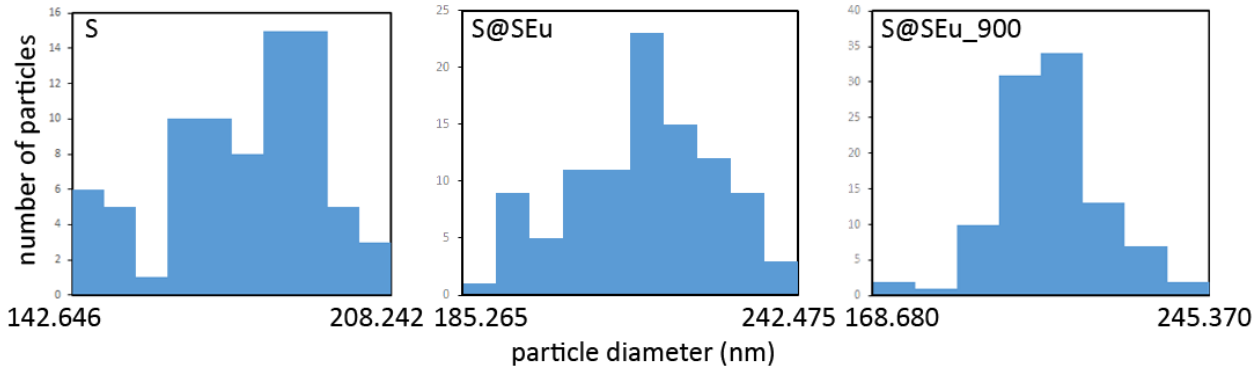

Figure S3. Size distribution histograms (100 particles) for core silica (S) NPs (left), S@SEu (center) and S@SEu_900 (right) NPs.

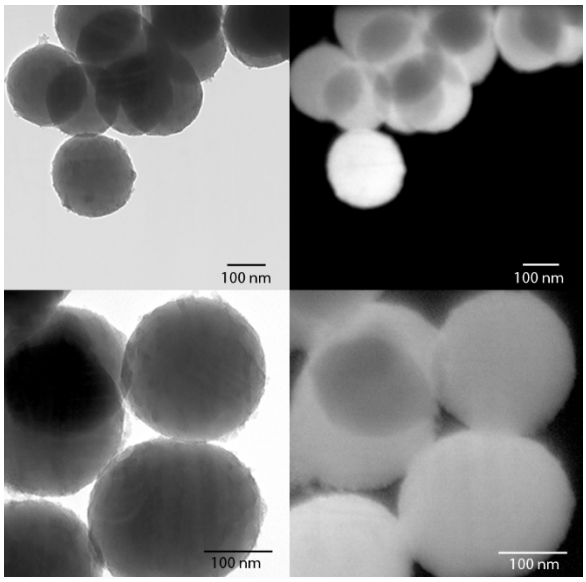

Figure S4. TEM micrographs of S@SEu_900 in bright field (left) and dark field (right) modes at different magnifications.

Vibrational Spectroscopy

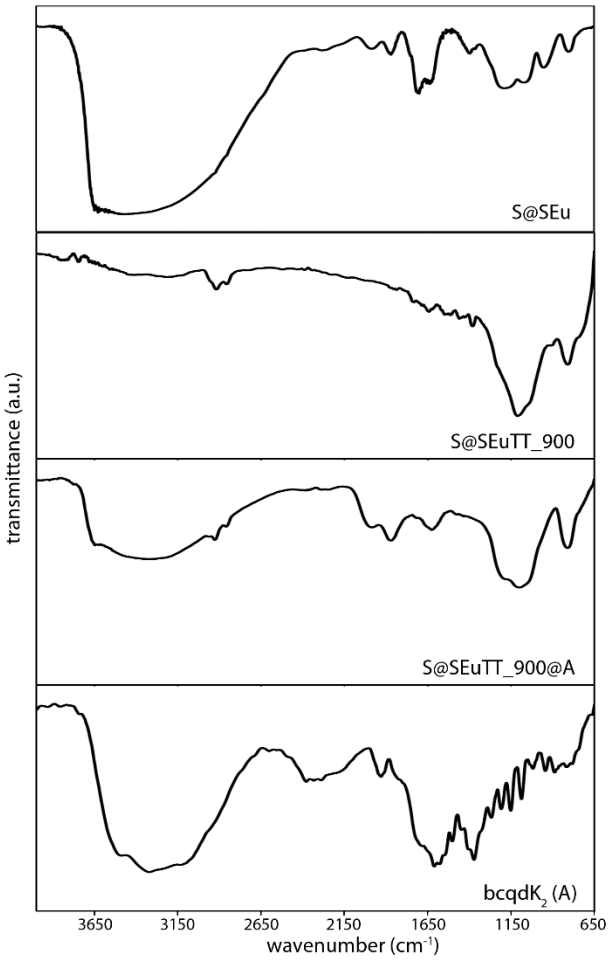

Figure S5. FT-IR spectra of the investigated NPs and of the free antenna molecule ($bcqdK_2$).

The spectra of the silica NPs are all characterized by the typical bands related to the Si-O-Si asymmetric stretching around 1100 cm^{-1} and the Si-O-Si symmetric stretching at ~800 cm^{-1}. The spectrum of the "fresh“ S@SEu NPs shows an intense broad band centered at 3460 cm^{-1} relatable to the stretching modes of trapped water molecules and OH groups, whereas the split band around 1650 cm^{-1} can be attributed to the bending of H_2O and to the stretching mode of residual carbonyls of acetic acid used as a catalyst during the synthesis. Moreover, the typical band attributed to Si-OH stretching (~950 cm^{-1}) appears. This band is much reduced in intensity in the spectrum of thermally treated S@SEuTT_900 NPs and disappears completely for the grafted S@SEuTT_900@A NPs. In addition, a small sharp peak typical of the free (i.e. not involved in hydrogen bonding) SiOH groups

at 1740 cm^{-1}, becomes clearly visible in the spectrum of S@SEuTT_900 NPs but is not recognizable in the spectrum of S@SEuTT_900@A NPs. These observations suggest that thermal treatment is effective in removing silanols groups (and trapped water molecules, as evidenced by the absence of the related broad band in S@SEuTT_900 NPs) from the bulk of the silica particle, and in inducing the formation of free SiOH on the surface. These free surface silanols then provide an active substrate for the covalent anchoring of $bcqd^{2-}$ by esterification with carboxylate groups. Since only negligible amount of water is found in the grafted S@SEuTT_900@A NPs (see discussion on thermal gravimetric analysis and diffuse reflectance spectroscopy), the broad band around 3400 cm^{-1} and the peak at 1650 cm^{-1} may be attributed to vibrational modes of the carboxylate groups of bonded bcqd molecules. Weak bands related to CH stretching in the region 2900-3000 cm^{-1} are attributed to superficial sample contamination.

Thermal analysis

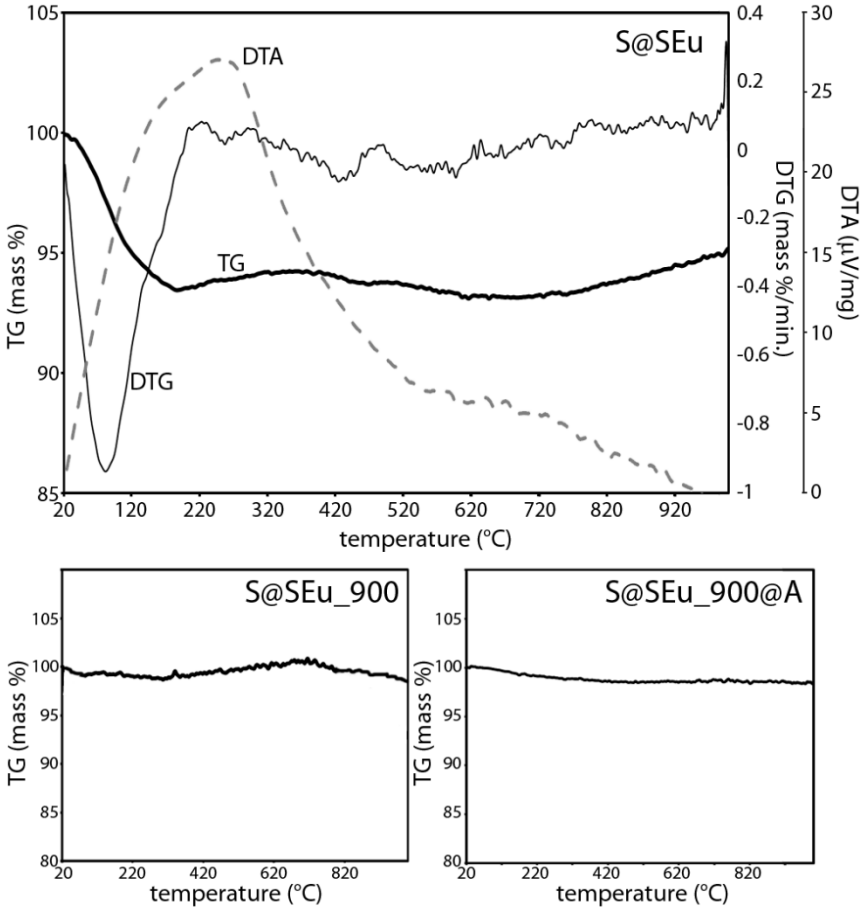

Figure S6. TG/DTG and DTA curves for S@SEu NPs (above) and TG curves for S@SEu_900 (below, left) and S@SEu_900@A NPs in the 20-1000°C temperature range.

The thermal gravimetric (TG) curve and simultaneous differential thermal analysis (DTA) for S@SEu NPs in the 20-1000°C temperature range show a weight loss of about 6.5% below 100 °C, accompanied by an endothermic peak and attributed to the loss of water molecules entrapped in the silica matrix. A small weight loss around 500 °C is instead attributed to the combustion of residual organic groups. Only negligible weight decrements attributable to the loss of water molecules below 100°C are instead observed in the TG curves of thermally treated NPs, which show no other significant peaks, indicating the high thermal stability of these materials.

X-ray diffraction

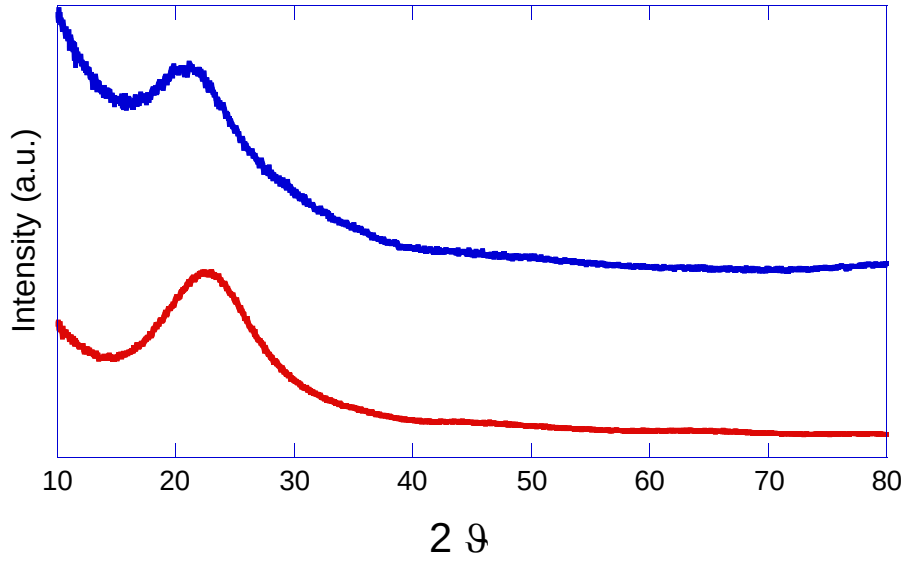

Figure S7. X-ray diffraction patterns of S NPs (red) and S@SEu_900 NPs (blue) in the 10–80° (2θ) range, showing the broad halo of amorphous silica.

Electronic spectroscopy

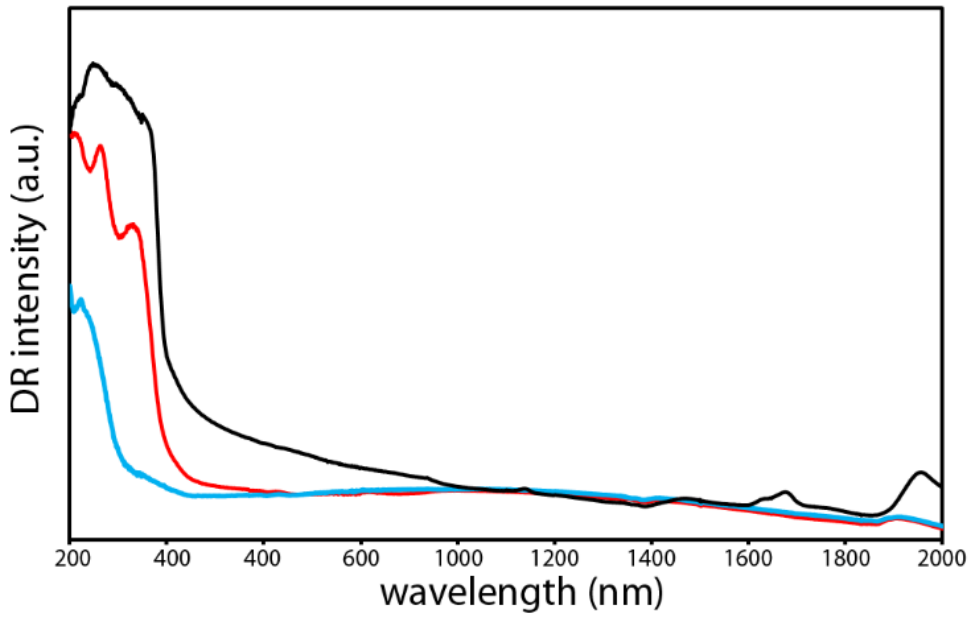

Figure S8. Solid state diffuse reflectance spectra of S@SEu_900 (blue), S@SEu_900@A (red) NPs and of bcqdK_2 in the UV-vis-NIR region. Bands in the region 1900-2000 nm are attributed to overtone/combination bands of the vibrational modes of OH groups and/or H_2O molecules.

Photoluminescence

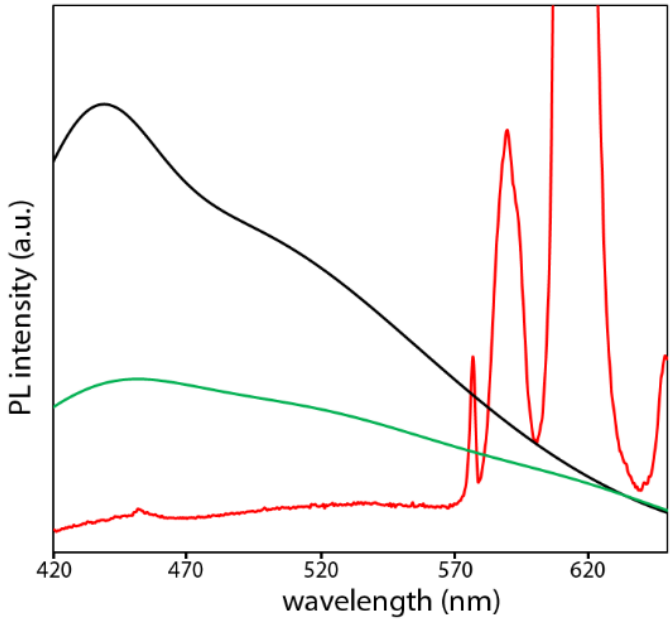

Figure S9. PL spectra of S@SEu_900@A (red) S@SGd_900@A (green) NPs and bcqdK_2 in the solid state (black). Excitation wavelength was 343 nm.

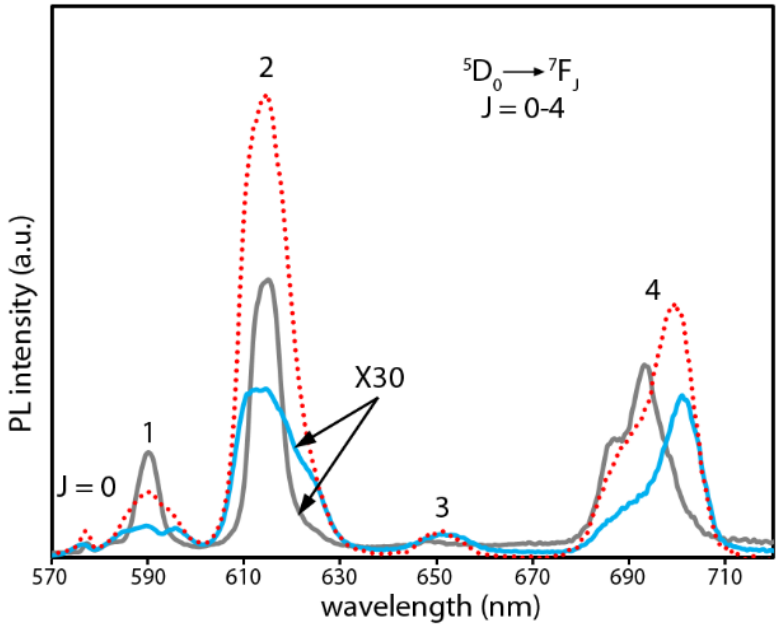

Figure S10. PL spectra of S@SEu_900@A (dotted red line), S@SEu_900 (blue) and S@SEu (grey) NPs excited at 392 nm. Spectral intensity of S@SEu_900 and S@SEu NPs is enhanced by a factor of 30.

Table S1. Main spectral and photophysical parameters

Sample	I_{TOT}	$I_{0\text{-}2}$	I_{MD}	$I_{0\text{-}2}/I_{MD}$	I_{TOT}/I_{MD}	k_{RAD} (s^{-1})	τ_{RAD} (ms)
S@SEu_900@A (λ_{ex} = 343 nm)	$1.88\cdot10^{7}$	$1.00\cdot10^{7}$	$1.36\cdot10^{6}$	7.34	13.8	648	1.54
S@SEu_900@A (λ_{ex} = 392 nm)	$4.52\cdot10^{6}$	$2.62\cdot10^{6}$	$3.70\cdot10^{5}$	7.08	12.2	574	1.74
S@SEu_900 corrected	$9.93\cdot10^{4}$	$4.24\cdot10^{4}$	$7.76\cdot10^{3}$	5.46	12.8	602	1.66
S@SEu corrected	$1.18\cdot10^{5}$	$3.90\cdot10^{4}$	$1.16\cdot10^{4}$	3.36	10.2	477	2.09

Intensity ratios	S@SEu_900@A/ S@SEu_900	S@SEu_900@A/ S@SEu	S@SEu_900@A$_{\lambda ex = 343\ nm}$ /S@SEu_900@A$_{\lambda ex=392\ nm}$
	189	159	4.15

Table S2. Decay time constants the samples at 1.9 mol% Eu^{3+} doping concentration.

Sample	τ_{OBS} (ms)	average τ_{OBS} (ms)
S@SEu_900@A λ_{ex} = 343 nm	0.883 (68%), 0.259 (30%), 0.040 (2%),	0.680
S@SEu_900	1.214 (5%), 0.004 (95%)	0.065
S@SEu	0.140 (20%), 0.004 (80%)	0.031

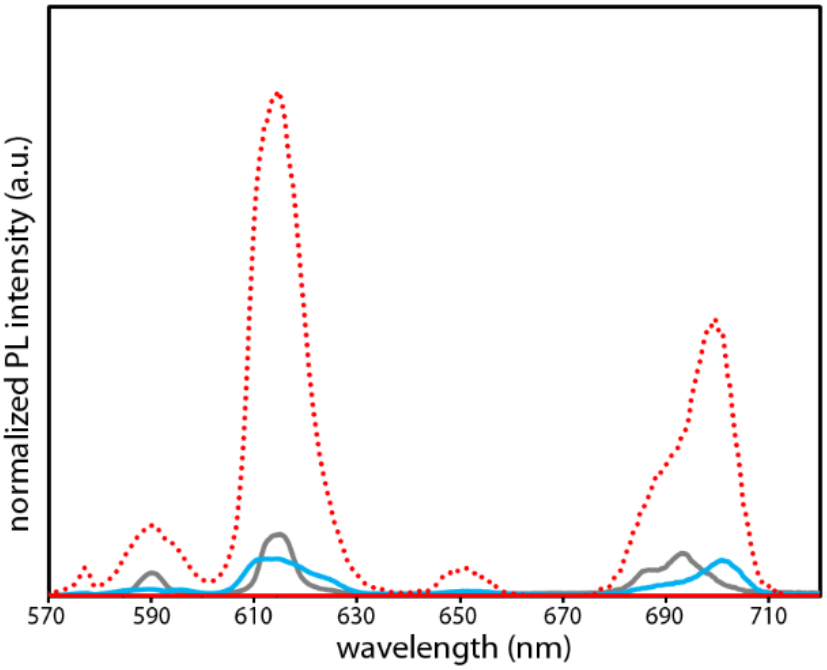

Figure S11. PL spectra of S@SEu_900@A NPs excited at 343 (red) and 392 nm (dotted red line), S@SEu_900 (blue) and S@SEu (grey) NPs excited at 392 nm normalized for optical density at excitation wavelength. Spectral intensity is representative of the population of excited Eu^{3+} ions in the sample, other than emission efficiency and oscillator strength, under the rough assumption that both direct and indirect sensitization efficiencies are unitary.

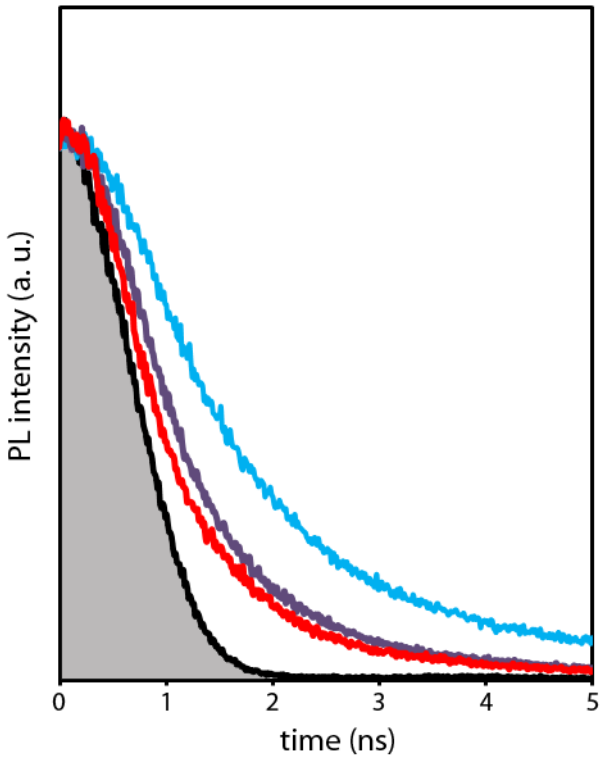

Figure S12. Decay dynamics of the emission at 420 nm of the free bcqdK_2 salt (blue), S@SEu_900@A (red) and S@SGd_900@A (purple). The shaded grey area represents the instrument response function (IRF).

Curve fitting

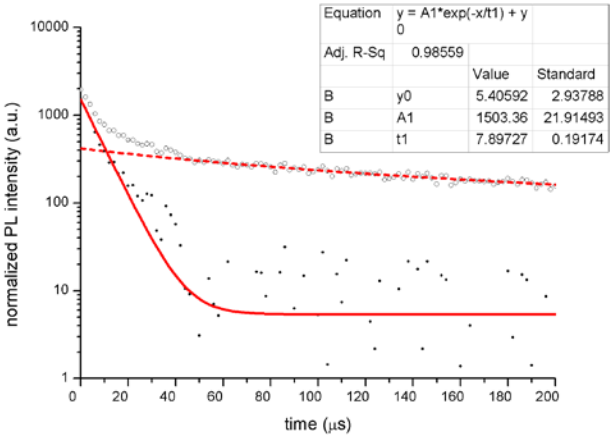

Figure S13. Curve fitting (solid red line) for the short-time components of the decay signal of S@SEu_900@A excited at 392 nm. The fitted data set (black dots) was extracted from the total signal (black circles) by subtracting the longer-lived component as retrieved from data fit (dashed red line).

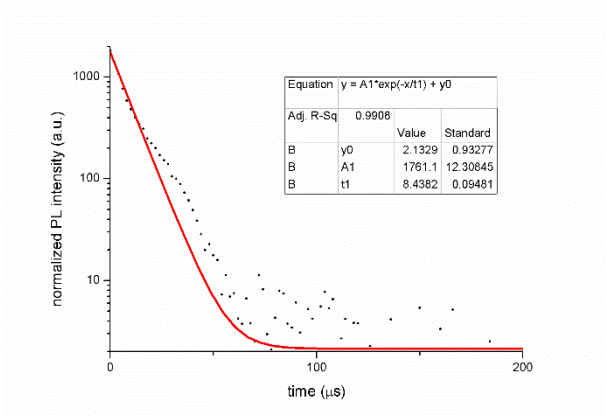

Figure S14. Curve fitting (solid red line) for the short-time components of the decay signal of S@SEu_900 (black dots) extracted from the total signal by subtracting the longer-lived component as retrieved from data fit.

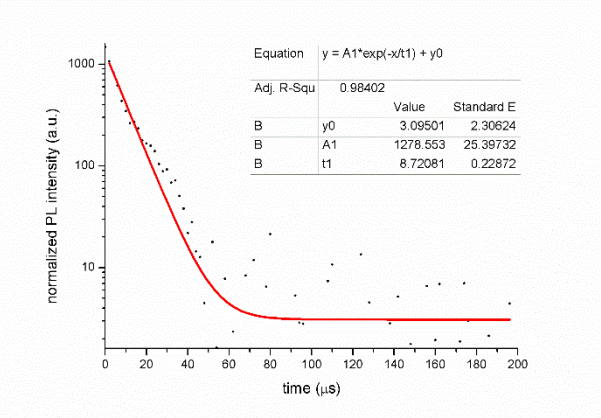

Figure S15. Curve fitting (solid red line) for the short-time components of the decay signal of S@SEu (black dots) extracted from the total signal by subtracting the longer-lived component as retrieved from data fit.

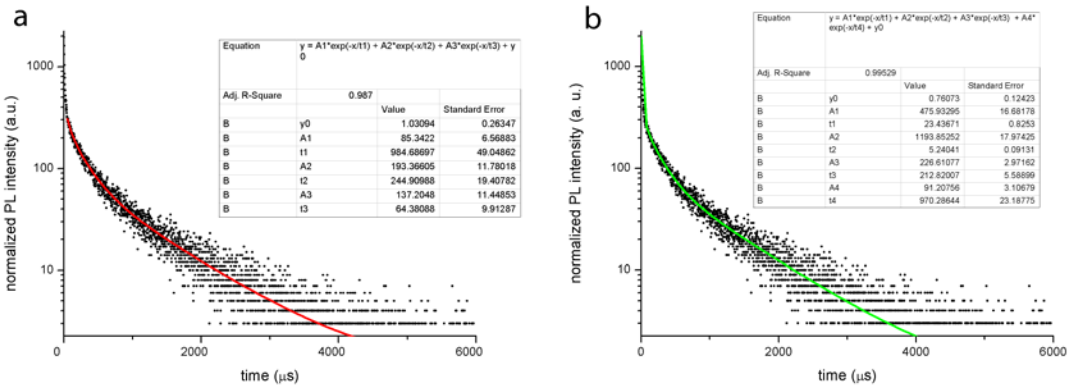

Figure S16. Comparison of the curve fittings of the decay signal of S@SEu_900@A excited at 392 nm as referred to the longer-lived component only (a) and to the entire data set (b).

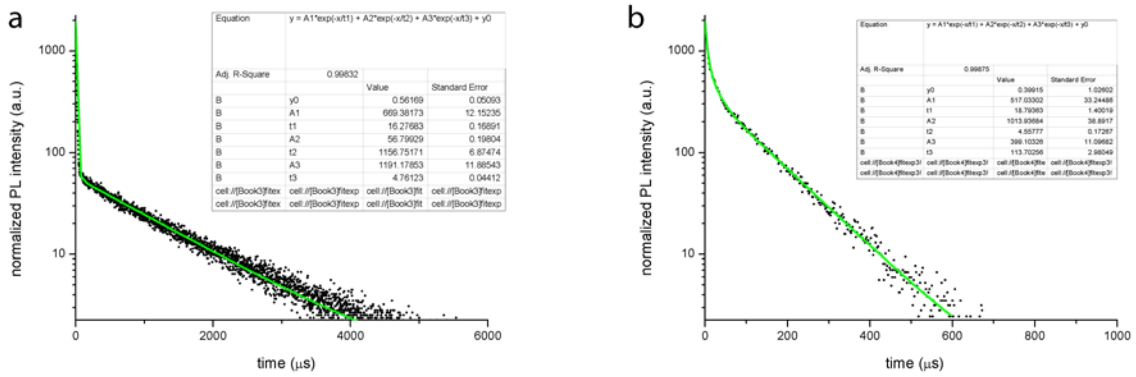

Figure S17. Curve fitting referred to the entire data set for the decay signal of S@SEu_900 (a) and S@SEu (b) excited at 392 nm.