

Supporting Information

Multi-functional GdEu_xTb_{1-x}O₃ (x = 0 to 1) nanoparticles: colour tuning optical properties, water proton spin relaxivities, and X-ray attenuation properties

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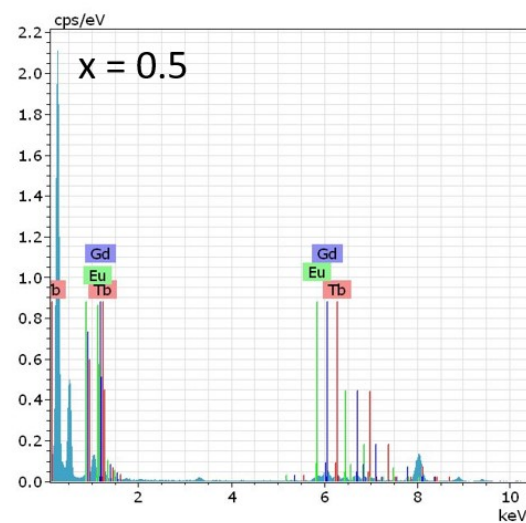
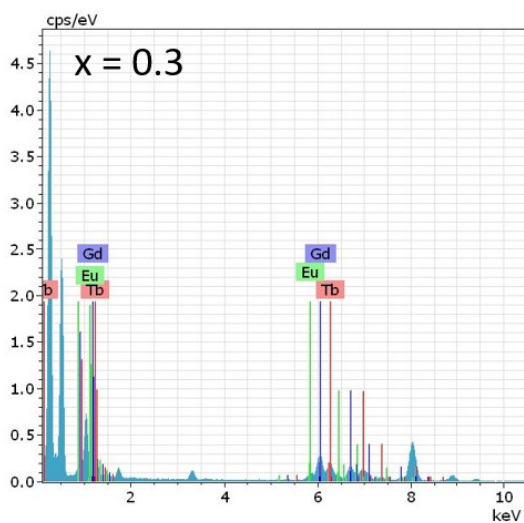
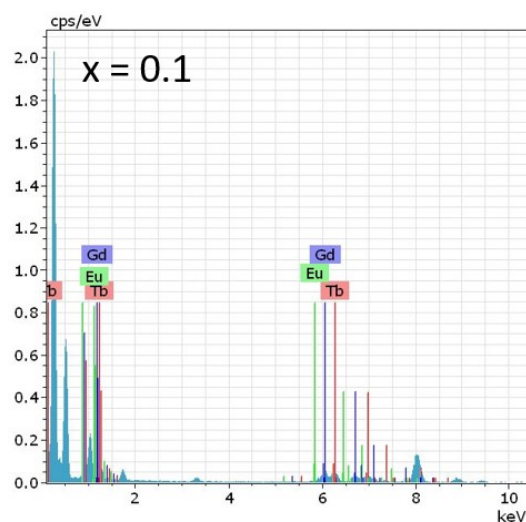
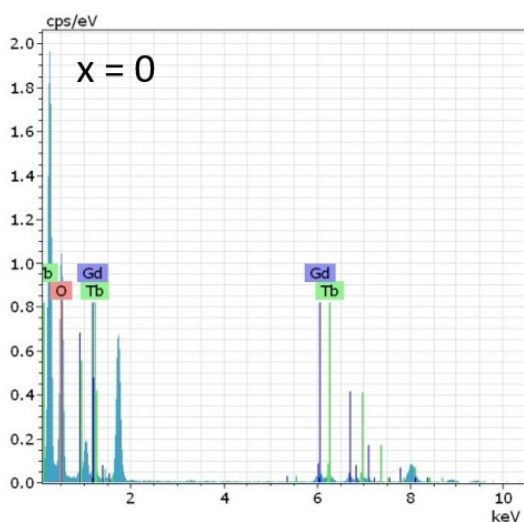
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(1) EDS spectra of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@PAA/PDA$ nanoparticles

EDS spectra of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@PAA/PDA$ nanoparticles ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9,$ and 1) confirmed the presence of Eu, Gd, and Tb within the nanoparticles (Figure S1).



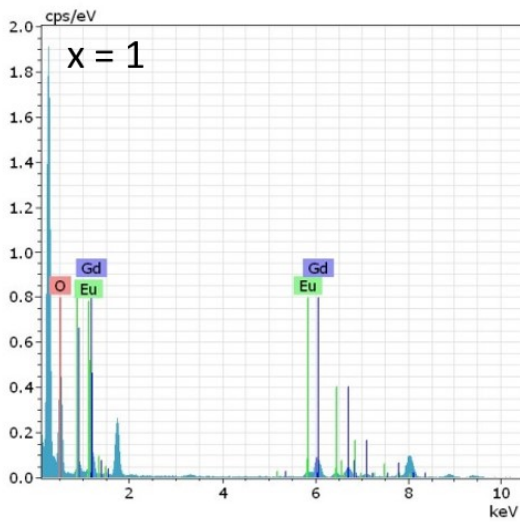
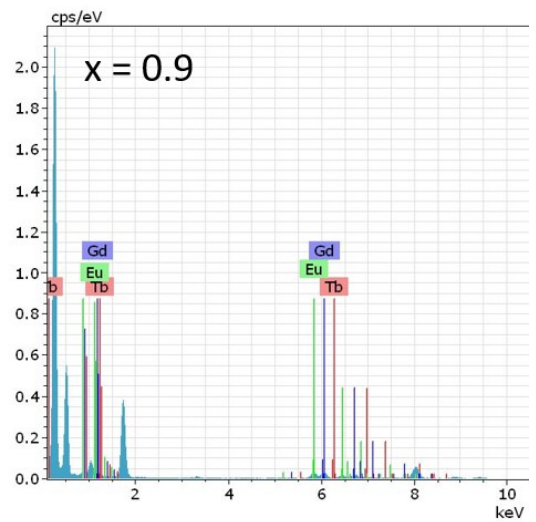
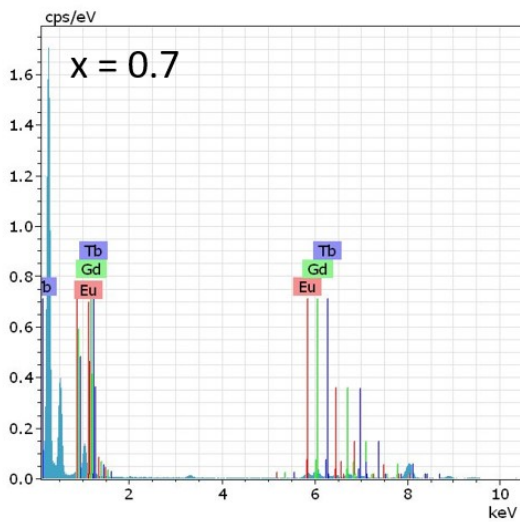


Figure S1. EDS spectra of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@PAA/PDA$ nanoparticles ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9,$ and 1).

(2) Laser light scattering (i.e., Tyndall effect)

The laser light scattering was only observed for nanoparticle solutions, but not for triple-distilled water, proving good colloidal dispersion of the nanoparticles in aqueous media (Figure S2).

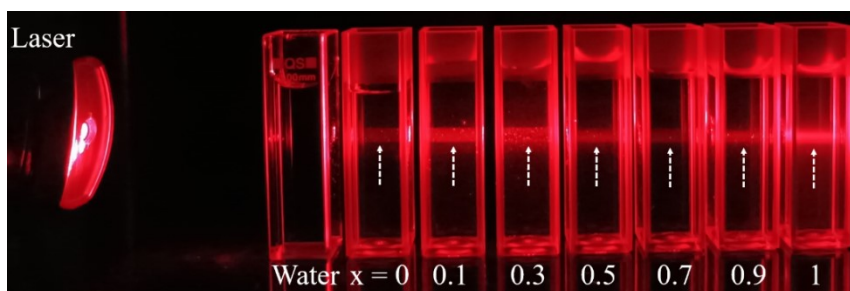


Figure S2. Photographs of laser light scattering (i.e., Tyndall effect) of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@PAA/PDA$ nanoparticle solution samples and water as reference, showing Tyndall effect only for the nanoparticles in aqueous media ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9,$ and 1), but not for water. The arrows indicate laser light scattering.

(3) XRD patterns of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@PAA/PDA$ nanoparticles before and after TGA

XRD patterns were taken before (Figure S3a) and after (Figure S3b) TGA. All peaks after TGA could be assigned with (hkl) Miller indices of cubic structure and the peak positions were mole% average values of those of bulk Ln_2O_3 ($\text{Ln} = \text{Eu}, \text{Gd},$ and Tb).¹⁻³ The (hkl) assignments and 2θ values of four main peaks and the estimated lattice constants are provided in Table S1.

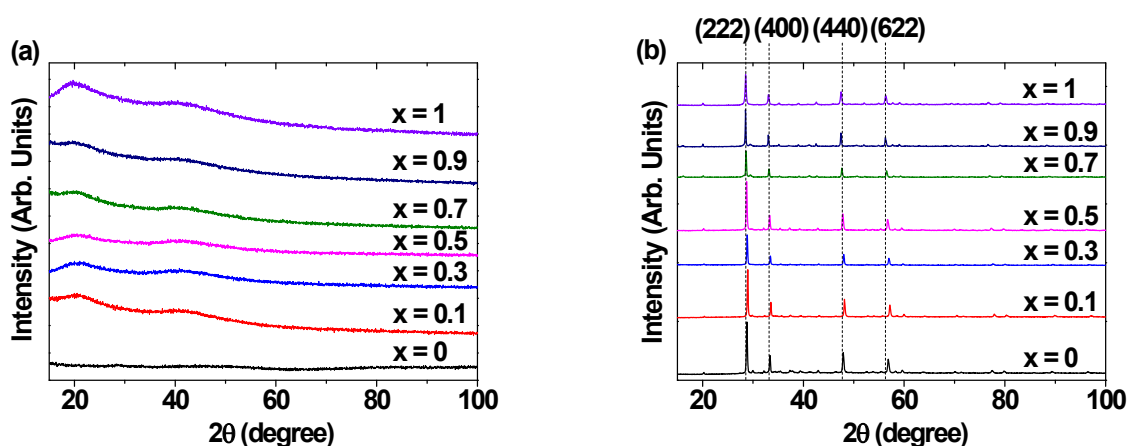


Figure S3. XRD patterns of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@PAA/PDA$ nanoparticles ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9,$ and 1) (a) before and (b) after TGA. All peaks after TGA could be assigned with (hkl) Miller indices of cubic structure and only the four main peaks were representatively assigned.

Table S1. Observed peak positions (2θ) of four main peaks and estimated lattice constants of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@PAA/PDA$ nanoparticles after TGA.

x	(hkl) and 2θ in degree	Lattice	Mole %-averaged lattice	Ref.
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	(222)	(400)	(440)	(622)	constant (Å)	constant (Å) ^a	
0	28.794	33.370	47.923	56.874	10.739	10.790	This study
0.1	28.950	33.550	48.175	57.183	10.685	10.780	This study
0.3	28.853	33.441	48.021	56.993	10.718	10.793	This study
0.5	28.743	33.313	47.834	56.768	10.758	10.806	This study
0.7	28.635	33.186	47.647	56.542	10.798	10.819	This study
0.9	28.523	33.055	47.462	56.320	10.838	10.831	This study
1	28.543	33.081	47.495	56.359	10.831	10.828	This study
Eu ₂ O ₃	28.450	32.968	47.316	56.139	10.859	-	1
Gd ₂ O ₃	28.560	33.096	47.507	56.371	10.813	-	2
Tb ₂ O ₃	28.804	33.382	47.921	56.875	10.730	-	3

^aMole % or atomic % values are obtained from ICP-AES data listed in Table 1 in the text.

(4) FT-IR absorption peak frequencies and assignments

Characteristic FT-IR absorption peak frequencies, supporting the successful grafting of PAA and PDA on the nanoparticles, are provided in Table S2.

Table S2. Observed characteristic FT-IR absorption peak frequencies in cm⁻¹.

x	O–H		C–H		C=O		COO ⁻ antisymmetric stretching		COO ⁻ symmetric stretching	
	No PDA	With PDA	No PDA	With PDA	No PDA	With PDA	No PDA	With PDA	No PDA	With PDA
PAA	3450		2955		1689		-		-	
PDA	-		-		1700		-		-	
0	3305	3335	2939	2948	1709	1709	1548	1548	1396	1396
0.1	3334	3387	2948	2939	1709	1709	1548	1548	1396	1386
0.3	3315	3350	2940	2948	1709	1709	1548	1555	1396	1386
0.5	3334	3341	2939	2939	1709	1709	1548	1548	1396	1386
0.7	3315	3334	2940	2948	1709	1709	1548	1557	1396	1386
0.9	3350	3340	2949	2940	1709	1709	1548	1548	1390	1386
1	3315	3315	2948	2939	1709	1709	1540	1540	1396	1405

Table S3. The lanthanide ion concentrations used for measurements of colour tuning, absolute QYs, PL spectra, UV-visible absorption spectra, and lifetimes.

	Without PDA (mM [Ln])			With PDA (mM [Ln])			
	Gd (mM)	Tb (mM)	Eu (mM)	Gd (mM)	Tb (mM)	Eu (mM)	PDA (mM)
0	1.99	2.00	0.00	1.99	2.00	0.00	7.10
0.1	2.13	1.78	0.22	2.13	1.78	0.22	7.50
0.3	2.09	1.34	0.66	2.09	1.34	0.66	7.50
0.5	2.03	0.93	1.07	2.03	0.93	1.07	5.00
0.7	2.00	0.54	1.46	2.00	0.54	1.46	10.00
0.9	1.95	0.17	1.83	1.95	0.17	1.83	7.50
1	1.97	0.00	2.00	1.97	0.00	2.00	3.70

Ln = Eu or Gd or Tb.

(5) The CIE (1931) chromaticity coordinate (a,b)

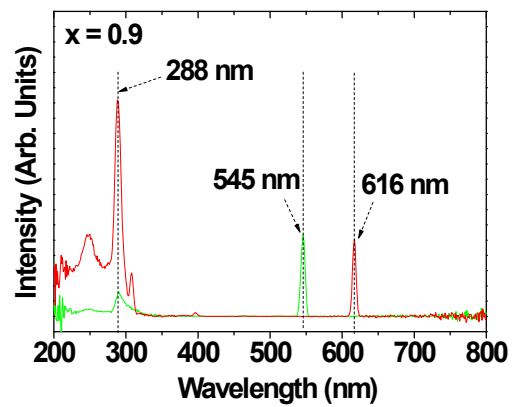
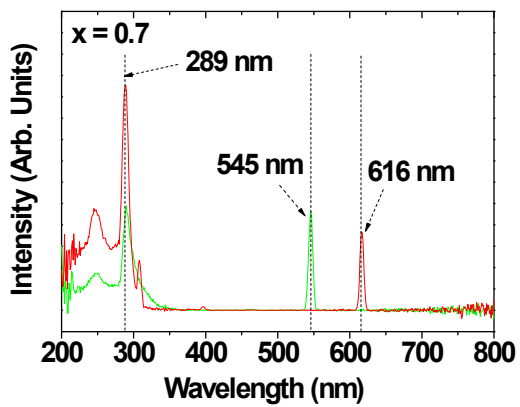
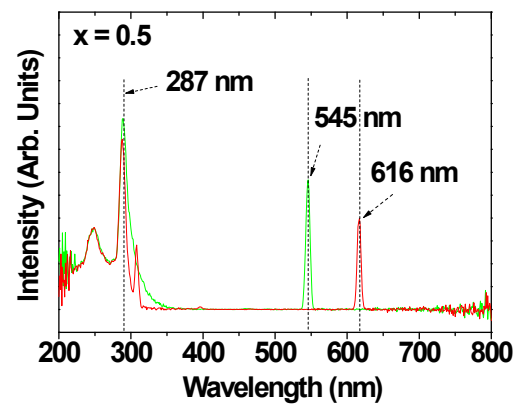
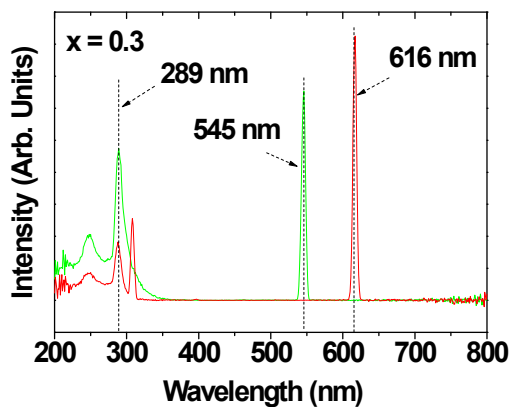
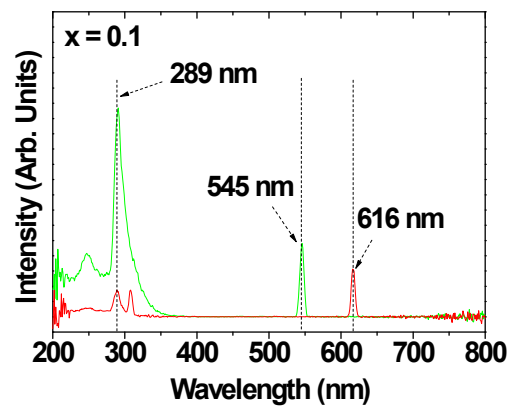
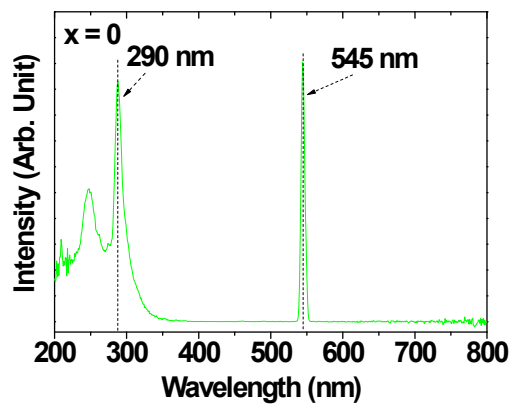
The CIE (1931) chromaticity coordinates (a,b) of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@\text{PAA/PDA}$ nanoparticles estimated from PL spectra in aqueous media are provided in Table S4.

Table S4. The CIE (1931) chromaticity coordinate (a,b) of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@\text{PAA/PDA}$ nanoparticles estimated from PL spectra in aqueous media.

x	a	b	Approximate colour
0	0.3141	0.5674	Yellowish green
0.1	0.3542	0.5494	Yellowish green
0.3	0.3755	0.5319	Yellow green
0.5	0.4295	0.4992	Greenish yellow
0.7	0.5030	0.4487	Yellowish orange
0.9	0.5823	0.3975	Orange
1	0.6197	0.3706	Reddish orange

(6) Excitation spectra of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@\text{PAA/PDA}$ nanoparticles in aqueous media

The λ_{ex} s were determined from the most intense peaks in excitation spectra (Figure S4) except peaks from Eu [i.e., 308 (= 616/2) and 616 nm] and Tb (i.e., 545 nm).



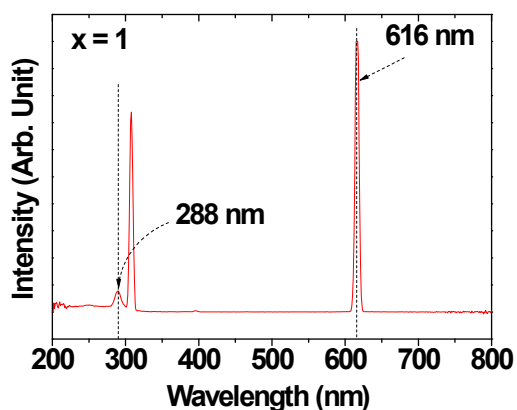


Figure S4. Excitation spectra of $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@\text{PAA/PDA}$ nanoparticles in aqueous media ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9,$ and 1) based on 545 nm peak for Tb and 616 nm peak for Eu.

(7) UV-visible absorption spectrum of PDA (0.1 mM) and $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@\text{PAA/PDA}$ nanoparticles ($x = 0$ and 1) in aqueous media

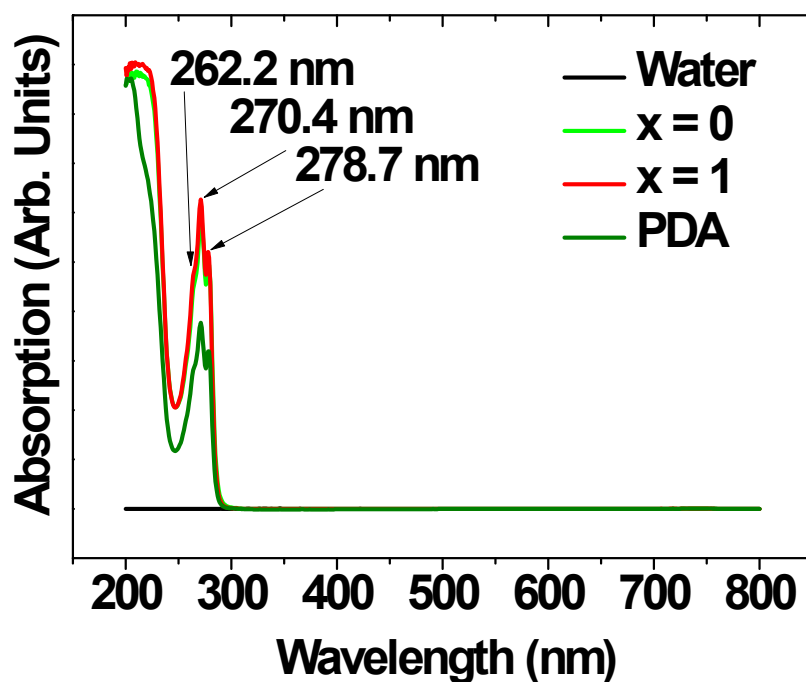


Figure S5. UV-visible absorption spectra of PDA (0.1 mM) and $\text{GdEu}_x\text{Tb}_{1-x}\text{O}_3@\text{PAA/PDA}$ nanoparticles ($x = 0$ and 1) in aqueous media and water as reference.

(8) The transition wavelengths and peak assignments in PL spectra

Table S5. The transition wavelengths and peak assignments of GdEu_xTb_{1-x}O₃@PAA/PDA nanoparticles (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1) in PL spectra in aqueous media.

x	Tb (⁵ D ₄ → ⁷ F ₆)	Tb (⁵ D ₄ → ⁷ F ₅)	Tb (⁵ D ₄ → ⁷ F ₄)	Tb (⁵ D ₄ → ⁷ F ₃)	Eu (⁵ D ₁ → ⁷ F ₁)	Eu (⁵ D ₁ → ⁷ F ₂)	Eu (⁵ D ₀ → ⁷ F ₀)	Eu (⁵ D ₀ → ⁷ F ₁)	Eu (⁵ D ₀ → ⁷ F ₂)	Eu (⁵ D ₀ → ⁷ F ₃)	Eu (⁵ D ₀ → ⁷ F ₄)
0	490	545	583	622	-	-	-	-	-	-	-
0.1	490	545	583	622	-	-	-	-	615	-	-
0.3	490	545	583	622	-	-	-	-	615	-	694
0.5	490	545	583	-	-	-	-	593	615	-	694
0.7	490	545	583	-	-	-	-	593	615	-	694
0.9	490	545	582	-	-	-	-	593	615	-	694
1	-	-	-	-	537	556	583	593	615	650	694

(9) The energy transfer efficiency (η_{ET}) from Tb^{3+} to Eu^{3+} in $GdEu_xTb_{1-x}O_3@PAA/PDA$ nanoparticles ($x = 0.1, 0.3, 0.5, 0.7,$ and 0.9)

The η_{ET} values were estimated using the lifetimes τ .

$$\eta_{ET} = 1 - \tau_x/\tau_0, \quad x = 0.1 \text{ to } 0.9$$

The obtained η_{ET} values are provided in Table S6 and plotted in Figure S6.

Table S6. The energy transfer efficiency (η_{ET}) from Tb^{3+} to Eu^{3+} in $GdEu_xTb_{1-x}O_3@PAA/PDA$ nanoparticles ($x = 0.1, 0.3, 0.5, 0.7,$ and 0.9).

x	η_{ET}
0	-
0.1	0.218
0.3	0.339
0.5	0.260
0.7	0.264
0.9	0.228
1	-

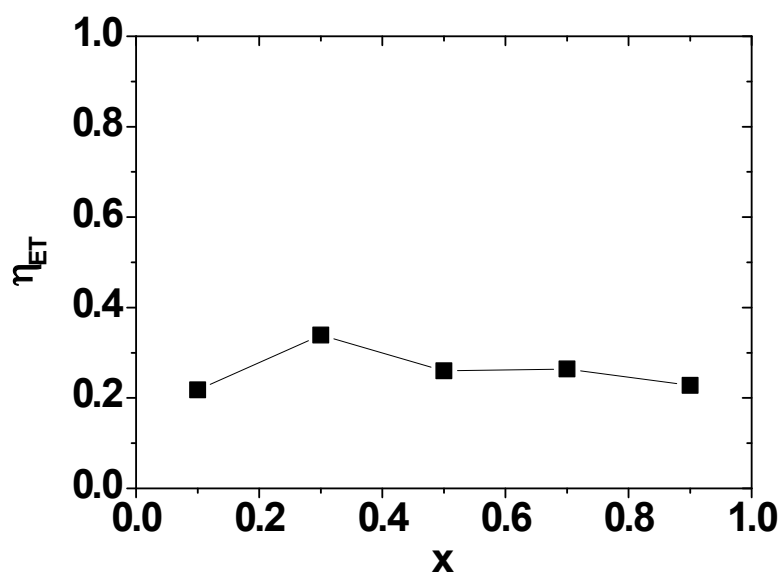


Figure S6. Plot of the energy transfer efficiency (η_{ET}) from Tb^{3+} to Eu^{3+} in $GdEu_xTb_{1-x}O_3@PAA/PDA$ nanoparticles ($x = 0.1, 0.3, 0.5, 0.7,$ and 0.9).

References

- 1 Eu_2O_3 , 1977 JCPDS-International Centre for Diffraction Data, card no. 43-1008, the lattice constant = 10.859 Å.
- 2 Gd_2O_3 , 1977 JCPDS-International Centre for Diffraction Data, card no. 43-1014, the lattice constant = 10.813 Å.
- 3 Tb_2O_3 , 1977 JCPDS-International Centre for Diffraction Data, card no. 43-1032, the lattice constant = 10.730 Å.