

ELECTRONIC SUPPLEMENTARY INFORMATION

Novel light-emitting clays with structural Tb³⁺ and Eu³⁺ for chromate anion detection

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1) Experimental Approach

Synthesis of Na-TbEuSAP clay: the saponite clay containing Tb^{3+} and Eu^{3+} ions was synthesized by a modified *one-pot* hydrothermal method, adapted from the literature (Scheme S1).¹⁻³

The synthesis gel was prepared with the following molar composition: $[SiO_2:MgO:Al_2O_3:Na_2O:TbCl_3:EuCl_3:H_2O]$ 1:0.835:0.056:0.056:0.01:0.01:20, and H_2O/Si molar ratio of 20. In detail, 6.68 g (0.10 mol) of amorphous silica (SiO_2 fumed, 99.8%) were gradually dispersed in a solution prepared by dissolving 0.63 g (0.01 mol) of sodium hydroxide (NaOH) in 45.00 g (2.50 mol) of ultrapure water (equal to 5/6 of the total water content). The obtained gel was then mixed accurately. After 30 min, 24.86 g (0.09 mol) of magnesium acetate tetrahydrate ($Mg(CH_3COO)_2 \cdot 4H_2O$, 99%) and 3.20 g (0.01 mol) of aluminium isopropoxide ($Al[OCH(CH_3)_2]_3$, $\geq 98\%$) were added to the reaction mixture. Simultaneously, a solution with 1:1 molar ratio of anhydrous terbium chloride ($TbCl_3$; 0.363 g, 0.001 mol) and europium chloride ($EuCl_3$; 0.353 g, 0.001 mol) in tetraethyl orthosilicate (TEOS; 6.03 mL, 0.03 mol) was prepared. The pH was then corrected between 2-3 with 1-2 drops of concentrated H_2SO_4 solution and the mixture was left under stirring at RT for 5 min. 0.50 g (0.03 mol) of ultrapure water were added to the suspension, stirred for another 5 min and, finally, introduced into the clay synthesis gel. The remaining ultrapure water (5.00 g, 0.28 mol) was then added to the reaction mixture. After 4 h, the gel, with a pH between 8-9, was introduced in a Teflon cup (125 mL capacity) of an autoclave (Anton Paar 4748) and heated in an oven for 72 h at 240 °C. After hydrothermal treatment, the product was filtered, washed with hot ultrapure water up to neutral pH and dried in an oven overnight at 100 °C.

The so-produced material, called TbEuSAP, was submitted to cation-exchange procedure in the presence of a saturated sodium chloride (NaCl) solution, in order to ensure a chemical uniformity of the exchange sites: in detail, 2.50 g of TbEuSAP were dispersed in 250 mL of saturated NaCl solution, and stirred for 36 h at RT to replace all possible cations present in the interlayer space (*i.e.* Al^{3+} , Mg^{2+} , H_3O^+) with Na^+ . The final solid (named Na-TbEuSAP) was filtered, washed with hot ultrapure water until complete elimination of chlorides (confirmed by silver nitrate spot test) and finally dried in an oven overnight at 100 °C.

- **Synthesis of Na-TbSAP clay:** The preparation of the sample containing only Tb^{3+} in the framework (hereafter named Na-TbSAP) followed the same procedure described before, using only the anhydrous TbCl_3 (0.363 g, 0.001 mol).
- **Synthesis of Na-SAP clay:** Na^+ -exchanged synthetic saponite clay, with a cationic exchange capacity (CEC) of 87.9 ± 2.3 meq/100 g, was synthesized following the classical hydrothermal method adopted in the literature by D. Costenaro *et al.*⁴
- **Photoluminescence sensing tests of chromate anion (CrO_4^{2-}) in water:** Preliminary studies related to the optical detection of CrO_4^{2-} anion in water by Na-TbSAP and Na-TbEuSAP samples were conducted by photoluminescence analyses in aqueous suspensions at room temperature (RT), under continuous stirring (to maintain good dispersions stability through the tests) and excitation at 270 nm (λ_{max} Tb^{3+}) and 395 nm (λ_{max} Eu^{3+}) and by monitoring the evolution of the main emission bands of Tb^{3+} (545 nm) and Eu^{3+} (615 nm) with progressive CrO_4^{2-} concentrations.

For the tests, five CrO_4^{2-} solutions were prepared: a starting solution of 500 mM of CrO_4^{2-} (sol. A) was prepared by dissolving 3.6773 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 50 mL of ultrapure water and then correcting the pH to 7 with NaOH 1 M, which converts $\text{Cr}_2\text{O}_7^{2-}$ (orange) to CrO_4^{2-} species (yellow). From sol. A, four solutions were prepared by successive dilutions: sol. B (50 mM), sol. C (5 mM), sol. D (0.5 mM) and sol. E (0.05 mM).

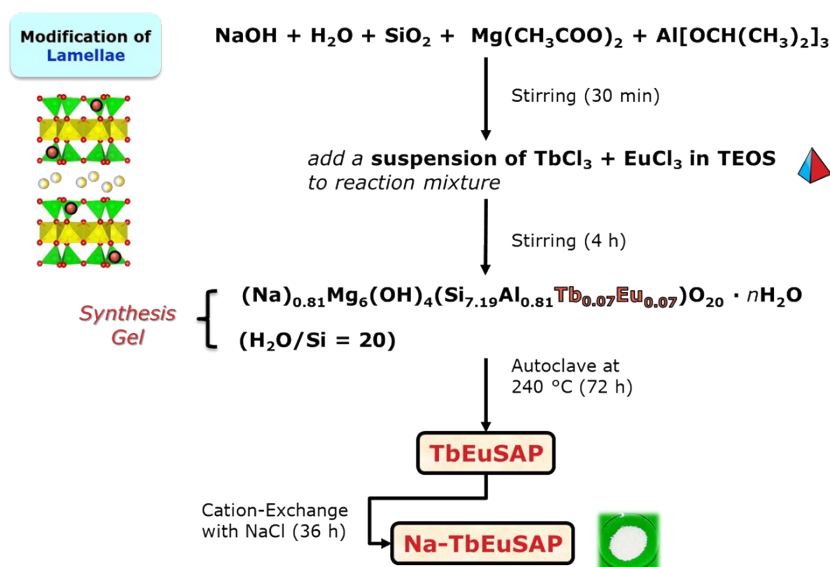
Na-TbSAP and Na-TbEuSAP samples were then tested as follows: 20 mg of clay were dispersed in 2.5 mL of ultrapure water, and the mixture was sonicated for 10 min. The dispersion was transferred in a 3.0 mL quartz cuvette, placed in the spectrofluorometer and stirred continuously at RT during the test. The emission spectrum of each sample, collected at $\lambda_{\text{exc}} = 270$ nm (Na-TbSAP, Na-TbEuSAP) and 395 nm (Na-TbEuSAP) nm was recorded in the absence and after contact with different amount of CrO_4^{2-} . For each experiment, a specific aliquot was taken from sol. A, B, C, D or E and added to the cuvette.

2) Analytical Methods

- The elemental analyses were performed on a Thermo Fisher Scientific X5 Series Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Waltham, MA, USA). Prior to the analysis, the solid samples were mineralized by treatment with a mixture of nitric acid (HNO₃, 5 mL) and hydrofluoric acid (HF, 5 mL) at 100 °C for 6 h.
- X-ray powder (XRPD) diffractograms were collected on unoriented ground powders with a ThermoARL X'TRA-048 Powder Diffractometer with a Cu-K_{α1} ($\lambda = 1.54062 \text{ \AA}$) monochromatic radiation. Diffractograms were recorded at RT in the 2°-65° 2θ range, with a step size of 0.02° and a rate of 1.0°/min. The X-ray profiles at low angles (2-15° 2θ) were collected with narrower slits and a rate of 0.25°/min.
- The cationic exchange capacity (CEC) parameter was determined by UV-Visible spectroscopic method reported in the literature.⁵ In detail, 0.300 g of each Na⁺-exchanged sample (Na-SAP, Na-TbSAP and Na-TbEuSAP) were exchanged with Co³⁺ ions in 10 mL of 0.02 M solution of [Co(NH₃)₆]³⁺ at RT for 60 h. After separation by centrifugation (5000 rpm for 5 min, two times), the relative solutions were analysed by UV-Visible spectroscopy. UV-Visible spectra were recorded at RT in the range 300-600 nm with a resolution of 1 nm, using a double-beam Perkin Elmer Lambda 900 Spectrophotometer. The absorbance of the band at 475 nm (¹A_{1g} → ¹T_{1g}),⁶ associated to a *d-d* spin-allowed Laporte-forbidden transition of Co³⁺, was monitored in order to quantify the amount of Co³⁺ ions remained in solution and, thus, the CEC parameter of clays.
- Thermogravimetric analyses (TGA) were carried out with a Setaram SETSYS Evolution Thermobalance. The data were collected in the range 50-1100 °C with a heating rate of 10 °C/min under oxygen (O₂) flow (100 mL/min).
- Dynamic light scattering (DLS) experiments were carried out at 25 °C by using a Malvern Zetasizer NanoZS, operating in a particle size range 0.6-6 μm and equipped with a He-Ne laser ($\lambda = 633 \text{ nm}$). The samples were dispersed in ultrapure water (1 mg/mL) in the presence of xanthan gum (0.1 wt.%), to improve the particle dispersion, and then sonicated for 10 min before the analyses. No precipitation was observed after few hours. The pH of suspensions was 7.0.
- Photoexcitation and photoluminescence (PL) spectra were recorded on a Horiba Jobin-Yvon Model IBH FL-322 Fluorolog 3 Spectrometer equipped with a 450 W Xenon arc lamp, double grating excitation and emission monochromators (2.1 nm·mm⁻¹ dispersion; 1200 grooves per mm) and a Hamamatsu Model R928 photomultiplier tube. For Na-

TbSAP, the excitation spectrum was monitored at 545 nm, while the emission spectrum was recorded under irradiation at 270 nm. For Na-TbEuSAP, instead, excitation spectra were monitored at 545 and 615 nm, while the emission spectra were recorded under irradiation at 270 and 395 nm. Excitation and emission spectra were collected at solid state with bandpass of 2 nm. The samples were introduced as ground powder in a specific sample holder and the experiments are collected in the front-face geometry. Time-resolved measurements were performed at solid state by using the time-correlated single-photon counting (TCSPC) option. A 370 nm spectraLED laser was used to excite both Na-TbSAP and Na-TbEuSAP samples, monitoring the emission band of Tb³⁺ at 545 nm. Signals were collected using an IBH DataStation Hub photon counting module. Data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). For the PL sensing tests, the emission spectra in aqueous suspension of Na-TbSAP and Na-TbEuSAP samples were collected in the presence of progressive CrO₄²⁻ concentrations with excitation at 270 and 395 nm, under continuous stirring at RT and with bandpass of 3 nm.

3) Figures



Scheme S1. Schematic view of the preparation of the luminescent Na-TbEuSAP clay.

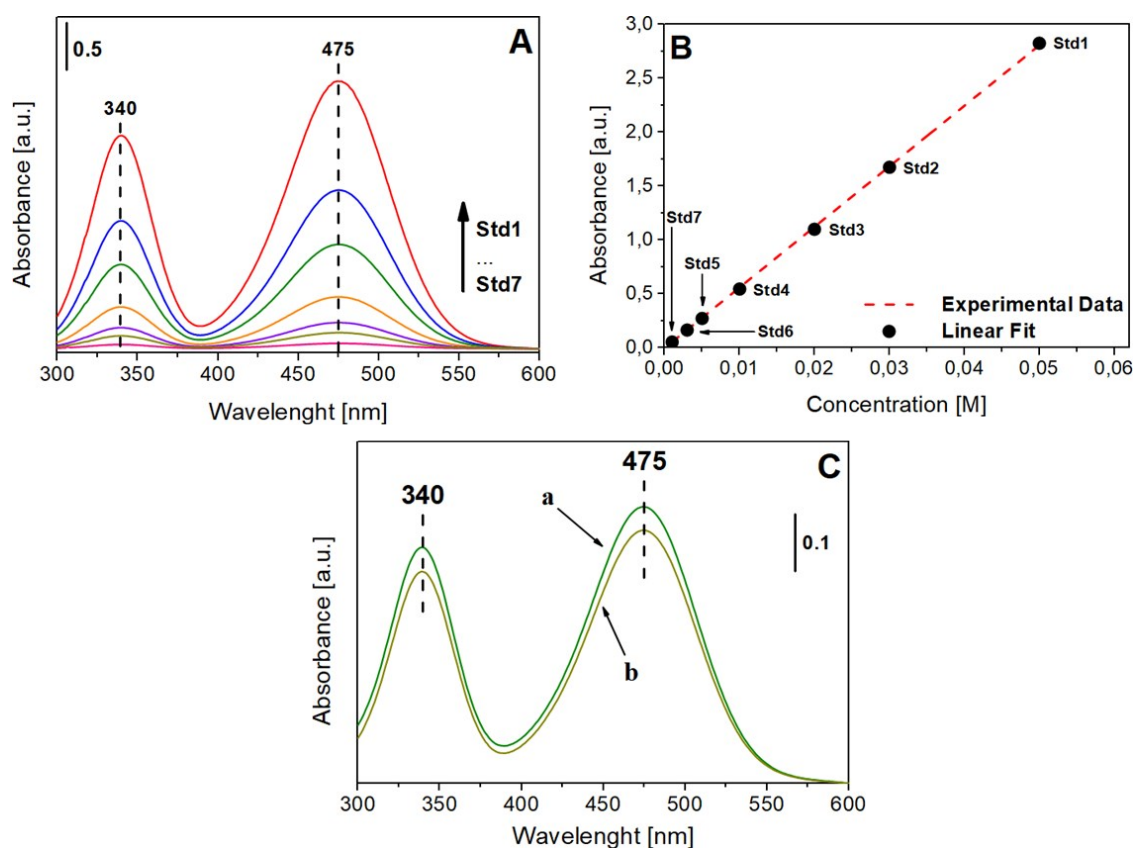


Fig. S1. A) UV-Visible spectra of standard aqueous solutions of $[\text{Co}(\text{NH}_3)_6]^{3+}$, from 0.001 mM to 0.05 mM. B) Calibration curve obtained by the UV-Visible spectra reported in A ($\lambda_{\text{abs}} = 475$ nm). C) UV-Visible spectra of the supernatant of Co-TbSAP (a) and Co-TbEuSAP (b) samples.

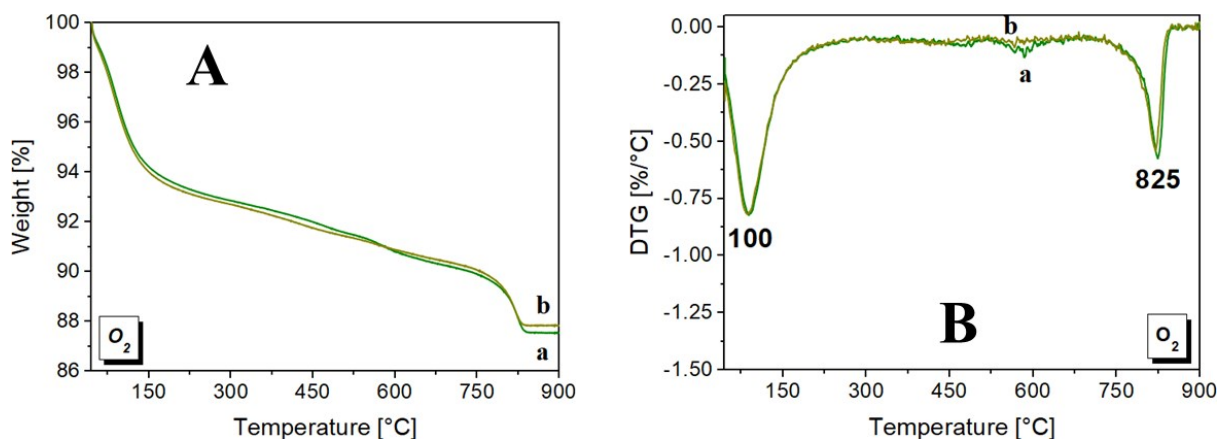


Fig. S2. TGA (A) and DTG (B) profiles of Na-TbSAP (a) and Na-TbEuSAP (b) samples. The analyses were carried out under O_2 flow.

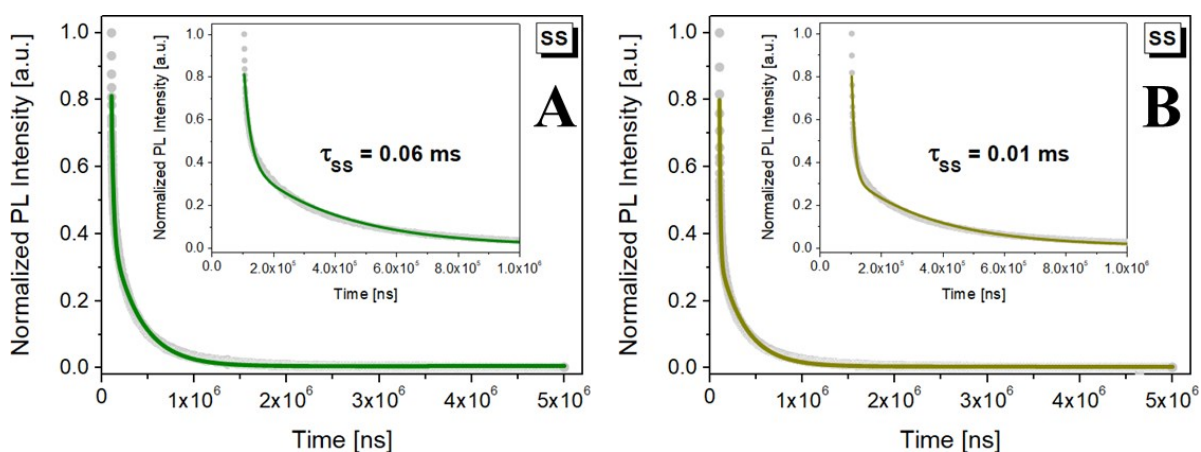


Fig. S3. Normalized PL intensity decay profiles at solid state of Na-TbSAP (A) and Na-TbEuSAP (B) samples. The decay curves were collected under irradiation at 370 nm with a SpectraLED laser source, by monitoring the intensity of the 5D_4 - 7F_5 transition (545 nm) over time. The curves fitting (a zoom of the short times is reported in the inset) was performed with a bi-exponential function (straight line). The χ^2 and RSS (residual sum of squares) values are reported in the table below:

Sample	χ^2	RSS
Na-TbSAP	3.0331E-5	0.29676
Na-TbEuSAP	2.9928E-5	0.29271

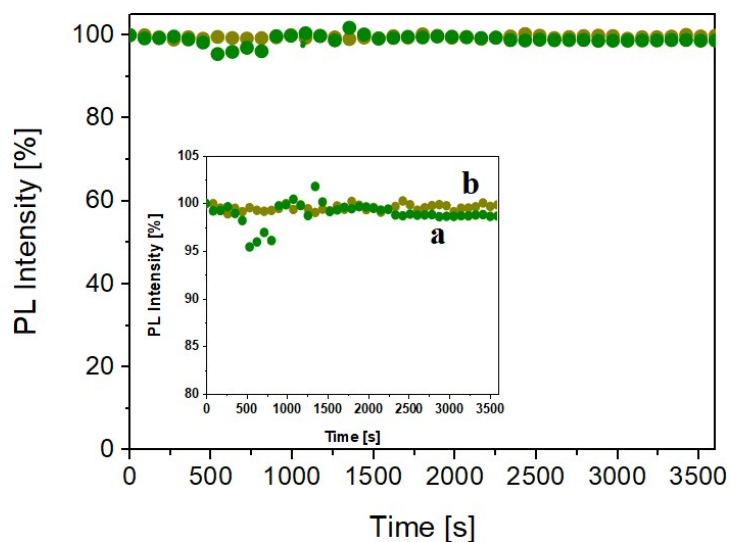


Fig. S4. Photobleaching tests at solid state of Na-TbSAP (a) and Na-TbEuSAP (b) samples, under irradiation at 270 nm. For Na-TbSAP (a), the intensity of 5D_4 - 7F_5 transition (545 nm) was monitored for 1 h. The intensity of 5D_0 - 7F_2 transition at 615 nm was analysed for Na-TbEuSAP sample (b).

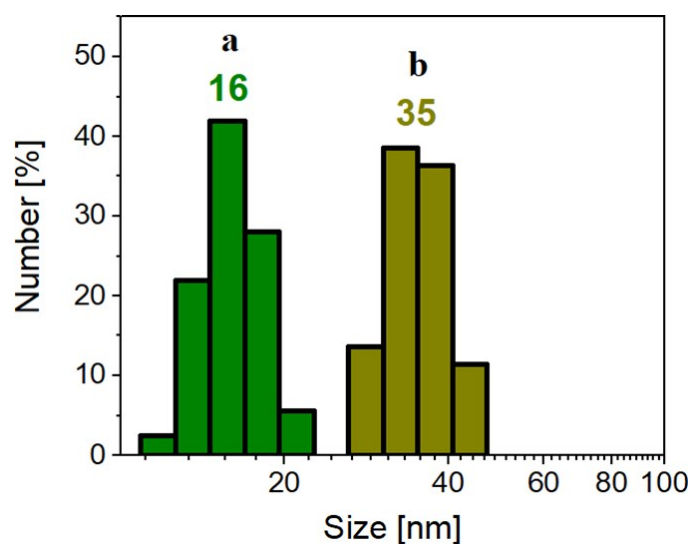


Fig. S5. Hydrodynamic diameters distribution in aqueous solution of Na-TbSAP (a) and Na-TbEuSAP (b) samples.

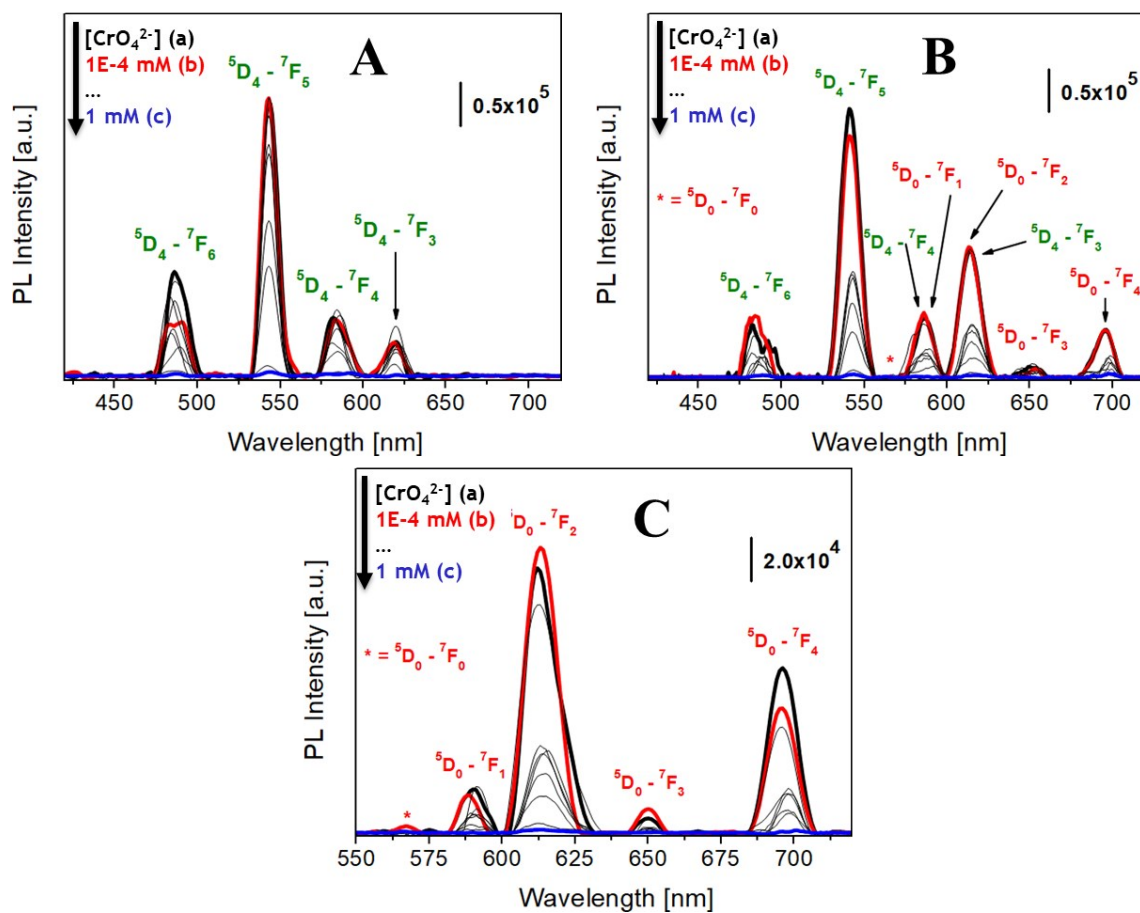


Fig. S6. Emission spectra of Na-TbSAP (A = λ_{exc} at 270 nm) and Na-TbEuSAP (B = 270 nm, C = 395 nm) samples, before (black curve (a)) and after addition of CrO_4^{2-} (red curve (b) = 0.0001 mM, blue curve (c) = 1 mM). The spectra were collected in aqueous suspensions, under continuous stirring at RT.






Fig. S7. Non-linear Stern-Volmer plots of F_0/F vs CrO_4^{2-} concentrations for: A) Na-TbSAP ($\lambda_{\text{exc}} = 270$ nm, $\lambda_{\text{em}} = 545$ nm), B) Na-TbEuSAP ($\lambda_{\text{exc}} = 270$ nm, $\lambda_{\text{em}} = 545$ nm), C) Na-TbEuSAP ($\lambda_{\text{exc}} = 270$ nm, $\lambda_{\text{em}} = 615$ nm) and D) Na-TbEuSAP ($\lambda_{\text{exc}} = 395$ nm, $\lambda_{\text{em}} = 615$ nm). The curves fitting is reported for each graph, together with their second-order polynomial (quadratic) equations and R^2 .

4) Tables

Tab. S1. Asymmetry factors (R) of Tb^{3+} and Eu^{3+} for Na-TbSAP and Na-TbEuSAP samples, under irradiation at 270 and 395 nm, extrapolated from emission spectra at solid state reported in Fig. 2B.

Sample	R 545/490 nm (5D_4 - 7F_5 / 5D_4 - 7F_6)	R 615/592 nm (5D_0 - 7F_2 / 5D_0 - 7F_1)
Na-TbSAP ($\lambda_{exc} = 270$ nm)	4.30	/
Na-TbEuSAP ($\lambda_{exc} = 270$ nm)	3.72	2.79
Na-TbEuSAP ($\lambda_{exc} = 395$ nm)	/	4.94

Tab. S2. Photometric data, in accordance to CIE 1931 colour spaces, for Na-TbSAP (D) and Na-TbEuSAP (DA) samples, under irradiation at 270 and 395 nm.

SAMPLE	λ_{exc} [nm]	x	y	R	G	B	Hex	Color	Color Purity [%]
Na-TbSAP	270	0,3362	0,5335	147	255	76	93FF4C		61.6%
Na-TbEuSAP	395	0,5080	0,3363	255	103	96	FF6760		53.3%
Na-TbEuSAP	270	0,3912	0,4500	255	249	121	FFF979		52.6%

Tab. S3. ($K_D * K_S$) and ($K_D + K_S$) parameters for Na-TbSAP and Na-TbEuSAP samples, under irradiation at 270 and 395 nm, obtained from the fit of the Stern-Volmer plots in Fig. S7 and applying the equations (S1-3). The main emission bands at 545 and 615 nm of Tb^{3+} and Eu^{3+} , respectively, were monitored.

Sample	($K_D * K_S$) [(mM) $^{-2}$]	($K_D + K_S$) [(mM) $^{-1}$]
Na-TbSAP (270,545)	4.345E+01	3.041E+01
Na-TbEuSAP (270,545)	3.447E+01	6.939E+01
Na-TbEuSAP (270,615)	6.505E+01	1.545E+01
Na-TbEuSAP (395,615)	7.119E+01	1.660E+01

$$SQE: \frac{F_0}{F} = 1 + K_S \cdot [Q] \quad (S1)$$

$$DQE: \frac{F_0}{F} = 1 + (k_q \cdot \tau_0) \cdot [Q] = 1 + K_D \cdot [Q] \quad (S2)$$

$$SQE + DQE: \frac{F_0}{F} = [(K_S \cdot K_D) \cdot [Q]^2] + [(K_S + K_D) \cdot [Q]] + 1 \quad (S3)$$

where F_0 and F are the fluorescence intensities in the absence and in presence of the quencher, respectively (measured at 545 or 615 nm), K_S and K_D are the static (SQE) and dynamic (DQE) quenching constants [mM^{-1}] and $[Q]$ is the quencher concentration.

5) References

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