

Supplementary Information for

Red emitting Sm(II) phosphors: Thermally switchable Luminescence in Sm(AlX₄)₂ (X = Cl, Br) by 5d-4f and intra-4f transitions

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Experimental section

Materials and methods

SCXRD Analysis:

Single crystal X-ray determinations were performed with a BRUKER AXS Smart Apex 1 diffractometer with graphite monochromator (Mo-K_α radiation; λ = 0.71073 Å) and a Bruker CRYOFLEX low-temperature system at 100 K. The structure was solved using direct methods, refined with the least-squares method as implemented in ShelXL^{1,2} and expanded using Fourier techniques, all within the OLEX2³ software suite. All non-hydrogen atoms were refined anisotropically. Depictions of the crystal structures were created using the program DIAMOND.⁴ The crystallographic data of Sm(AlBr₄)₂ has been deposited at the Cambridge Crystallographic Data Centre as CSD 2084707.

PXRD Analysis:

PXRD analyses were carried out with a Bruker D8 Discover diffractometer with Da Vinci design, focusing Göbel mirror and linear LynxEye detector. Powder samples were prepared in Lindemann glass capillaries with 0.5 mm diameter under inert gas atmosphere. The samples were measured in transmission geometry using Cu-K_α radiation (λ = 1.54056 Å). It is noteworthy that Sm(AlCl₄)₂ and Sm(AlBr₄)₂ are regularly decomposing during the measurements (20 min) even in argon filled and picein sealed capillaries, preventing the collection of high-quality PXRD data. Furthermore, the measurements were performed stepwise over 2Theta, therefore higher angles were measured after longer time and should be considered with caution. In addition, samples of Sm(AlBr₄)₂ fully absorb the Cu-K_α radiation. As a result, PXRD data for Sm(AlBr₄)₂ cannot be provided and PXRD data on Sm(AlCl₄)₂ shows slight deviations to data simulated from SC-XRD regarding influences of different measurement temperature, orientation of crystals and starting of decomposition.

Photoluminescence

Photoluminescence excitation and emission spectra were recorded with a Horiba Jobin Yvon Fluorolog 3 photoluminescence spectrometer equipped with a 450 W Xe lamp, Czerny-Turner double grating (1200 grooves per mm) excitation and emission monochromators and an FL-1073 PMT detector. Excitation spectra were recorded from 250 to 700 nm and corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. Emission spectra were recorded from 550 to 850 nm and corrected for the spherical response of the monochromators and the detector using typical correction spectra provided by the manufacturer. Additionally, the 1st and 2nd harmonic oscillations of the excitation source were blocked by an edge filter (475 nm). The luminescence lifetimes were obtained by determination of the overall process decay times with an Edinburgh Instruments (FLS920) spectrometer. The samples were prepared in quartz glass cuvettes under inert gas. The decay times were recorded by time-correlated single-photon counting (TCSPC) with a microsecond flashlamp for an excitation wavelength of 299 nm, 363 nm or 365 nm. The luminescence emission was collected at right angles to the excitation source, and the emission wavelength was selected with a monochromator and detected by a single-photon avalanche diode (SPAD). The resulting intensity decays were calculated through tail-fit analysis (Edinburgh F900 analysis software). The fit qualities were evidenced by the χ² values (χ² ≤ 1.30).

Photoluminescence quantum yields were determined with the above-mentioned HORIBA Jobin Yvon Spex Fluorolog 3 spectrometer equipped with a HORIBA Quanta-j F-3029 Integrating Sphere using a FluoroEssence™ software. For the measurements, solid samples were filled into Starna Micro Cell cuvettes 18-F/ST/C/Q/10 (fluorescence with ST/C closed-cap, material UV quartz glass Spectrosil Q, pathlength 10 mm, matched). Dry barium sulphate was used as a reference material. For determining the quantum yield of Sm(AlCl₄)₂ a solid solution of Sm(AlCl₄)₂ (20 mg) with barium sulphate (1100 mg) was used, whereas for determining the quantum yield of Sm(AlBr₄)₂ the pure substance was used. The photoluminescence completely vanishes upon grinding Sm(AlBr₄)₂ with barium sulphate.

General procedures

Because of the moisture- and air- sensitivity of anhydrous AlCl_3 and AlBr_3 , Sm and of the reaction products, all manipulations were carried out under inert gas atmosphere in Duran® glass ampoules, using vacuum line, Schlenk and glovebox (MBraun, Labmaster SP and Innovative Technology, Pure Lab) techniques. The reactions in Duran® glass ampoules were performed in heating furnaces based on Al_2O_3 tubes with Kanthal wire resistance and NiCr/Ni temperature elements. For temperature control, heating programs were applied with Eurotherm 2416 control units. The starting material AlCl_3 (anhydrous, 99 %, Sigma–Aldrich) was purified by sublimation prior to use and Sm (99.99 %, smart elements) was filed to a powder prior to reactions. AlBr_3 (anhydrous, 99.999 %, Sigma–Aldrich) was used as purchased. 1,2-difluorobenzene was dried by dynamical drying over 4 Å molecular sieves, degassed by three freeze-pump-thaw cycles and stored over 4 Å molecular sieves.

Synthesis of $\text{Sm}(\text{AlCl}_4)_2$

$\text{Sm}(\text{AlCl}_4)_2$ was achieved by a solvothermal redox reaction of Sm (50 mg, 3 eq., 330 μmol) with AlCl_3 (118 mg, 8 eq., 885 μmol). AlCl_3 was grinded in a mortar to a fine powder and sealed together with the Sm-powder and 0.5 ml 1,2-difluorobenzene in a Duran® glass ampoule under reduced pressure ($p = 1 \times 10^{-3}$ mbar). The solvent was frozen using liquid nitrogen before evacuating and sealing of the ampoule. Subsequently, the ampoule was placed in a tubular furnace and heated to 120 °C within 24 h. This temperature was kept for 48 h until the oven was finally cooled to room temperature in 48 h. For purification, the solvent was removed using a syringe and the obtained raw-product was washed three times with 1 ml boiling 1,2-difluorobenzene. This procedure leads to a red and crystalline reaction product. Yield: 126 mg. The product is highly air and moisture sensitive.

Synthesis of $\text{Sm}(\text{AlBr}_4)_2$

$\text{Sm}(\text{AlBr}_4)_2$ was achieved by a solvothermal redox reaction of Sm (50 mg, 3 equiv., 330 μmol) with AlBr_3 (236 mg, 8 equiv., 885 μmol). AlBr_3 was grinded in a mortar to a fine powder and sealed together with the Sm-powder and 0.5 ml 1,2-difluorobenzene in a Duran® glass ampoule under reduced pressure ($p = 1 \times 10^{-3}$ mbar). The solvent was frozen using liquid nitrogen before evacuating and sealing of the ampoule. Subsequently, the ampoule was placed in a tubular furnace and heated to 120 °C within 12 h. This temperature was kept for 48 h until the oven was finally cooled to room temperature in 12 h. For purification, the solvent was removed using a syringe and the obtained raw-product was washed three times with 1 ml boiling 1,2-difluorobenzene. This procedure leads to a deep red and crystalline reaction product from which a suitable single-crystal for SCXRD was picked. Yield: 164 mg. The product is highly air and moisture sensitive.

Modified Synthesis of $\text{Sm}(\text{AlCl}_4)_2$ to proof the formation of elemental aluminium

This modified reaction was carried out by a solvent-free melt-synthesis of Sm (200 mg, 3 equiv., 1.33 mmol) with AlCl_3 (452 mg, 8 equiv., 3.39 mmol). AlCl_3 was grinded in a mortar to a fine powder and sealed together with the Sm-powder in a quartz glass ampoule under reduced ($p = 1 \times 10^{-3}$ mbar). Subsequently, the ampoule was placed in a tubular furnace and heated to 700 °C within 3 h. This temperature was kept for 12 h and it was finally cooled to room temperature in 8 h. This procedure leads to a red-brownish bulk product containing small metal-balls. A metal ball was picked and washed three times with 5 ml benzene using an ultrasonic bath. The metal ball was investigated by REM/EDX. Yield 18 mg. The metal ball also contains impurities of elemental silicon.

Characterisation

X-ray Crystallography

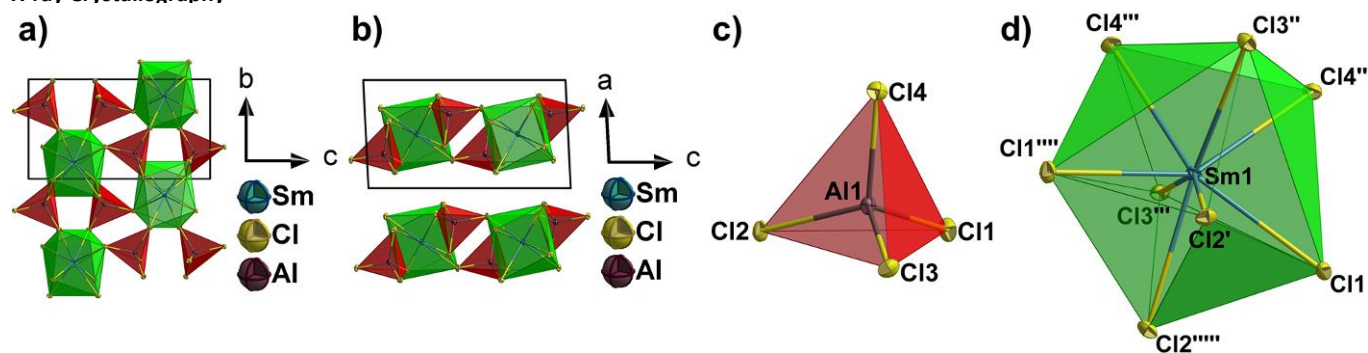


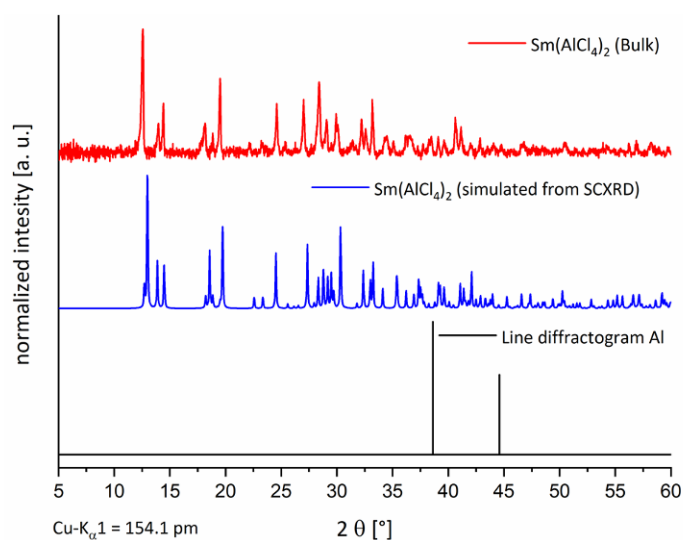
Figure S1: a) Crystal structure of the literature known $\text{Sm}(\text{AlCl}_4)_2$ with a view along $[100]$ and b) with a view along $[0-10]$. c) Extended coordination of Al^{3+} by four chlorido-ligands and d) extended coordination of Sm^{3+} by eight chlorido ligands. The SmCl_8 -dodecahedra are represented in green and the AlCl_4 -tetrahedra are depicted in red. Thermal ellipsoids depict a 50 % probability level of the atoms. Symmetry operations: I = $1-x, 1-y, 1-z$; II = $1-x, -y, 1-z$; III: $x, -y, -0.5+z$, IIII = $1-x, y, 0.5-z$; IIIII = $x, 1-y, -0.5+z$.⁵

Table S1: Crystallographic data of $\text{Sm}(\text{AlBr}_4)_2$. Deviations are given in brackets.

	$\text{Sm}(\text{AlBr}_4)_2$
Empirical formula	$\text{Al}_2\text{Br}_8\text{Sm}$
Formula weight [$\text{g}\cdot\text{mol}^{-1}$]	843.59
Crystal colour and shape	clear blackish red block
Crystal size [mm]	$0.283 \times 0.279 \times 0.214$
Crystal system	orthorhombic
Space group	$Pbca$
a [pm]	1204.4(1)
b [pm]	1195.9(1)
c [pm]	2084.2(2)
α [°]	90
β [°]	90
γ [°]	90
V [pm^3]	$3001.9(6)\cdot 10^6$
Z	8
ρ_{calc} [$\text{g}\cdot\text{cm}^{-3}$]	3.733
$\mu(\text{MoK}\alpha)$ [mm^{-1}]	25.279
Measurement temperature [K]	100
Absorption correction type	multi-scan
2θ range [°]	5.17 to 61.306
No. of measured reflections	46871
No. of independent reflections ($I > 2\sigma(I)$)	4633 [$R_{\text{int}} = 0.0984, R_{\text{sigma}} = 0.0519$]
Data/restraints/parameters	4633/0/100
Goodness-of-fit on F^2	1.028
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0352, \omega R_2 = 0.0647$
Final R indices (all data)	$R_1 = 0.0639, \omega R_2 = 0.0727$
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ [$e\cdot\text{\AA}^{-3}$]	1.19/-0.99

Table S2: Interatomic distances of $\text{Sm}(\text{AlBr}_4)_2$. Deviations are given in brackets.

Atoms	Distance [pm]	Atoms	Distance [pm]
Sm1 – Br1	318.93(4)	Al1 – Br1	229.54(2)
Sm1 – Br2	319.90(3)	Al1 – Br2	229.82(3)
Sm1 – Br3	321.34(2)	Al1 – Br3	229.49(2)
Sm1 – Br4	321.72(3)	Al1 – Br4	229.52(2)
Sm1 – Br5	316.89(4)	Al2 – Br5	229.78(2)
Sm1 – Br6	322.01(3)	Al2 – Br6	229.63(2)
Sm1 – Br7	317.79(3)	Al2 – Br7	229.58(2)
Sm1 – Br8	320.14(2)	Al2 – Br8	229.50(2)

PXRD-Analysis of $\text{Sm}(\text{AlCl}_4)_2$ **Figure S2:** Comparison of the experimental (red, top), simulated (blue, middle) PXRD pattern of $\text{Sm}(\text{AlCl}_4)_2$ and the literature known line diffractogram of aluminium (black, bottom).

SEM/EDX

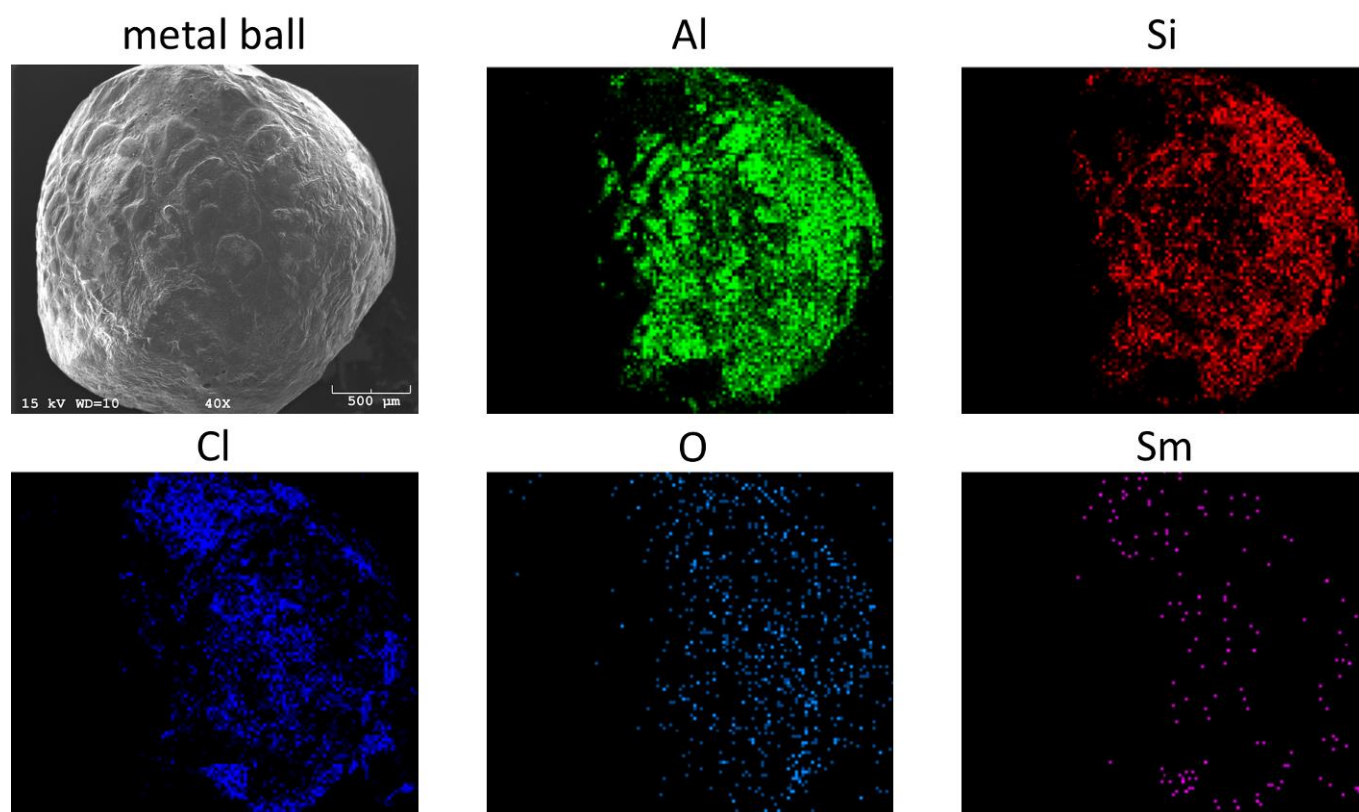


Figure S3: Element mapping of the metal ball. The experimental data reveals aluminium (green, top) and silicon (red, top) as the main components of the metal balls surface. Oxygen (blue, bottom) was only observed as traces on the surface.

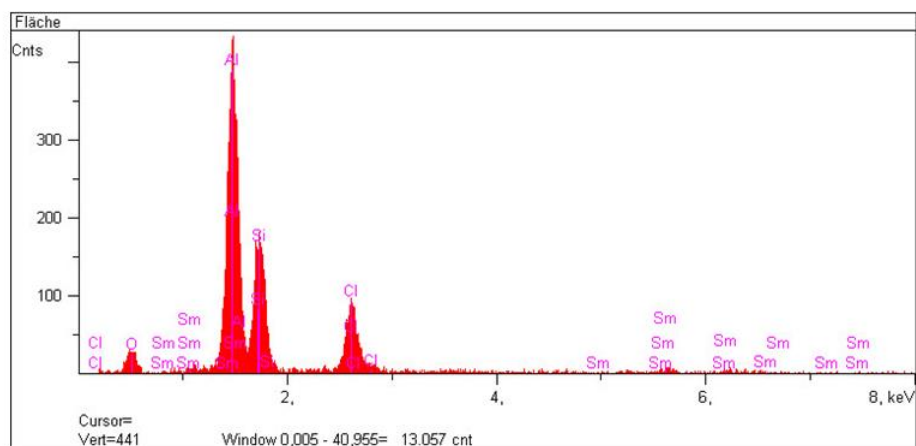


Figure S4: EDX spectra of the metal ball. The evaluation of the experimental data reveals aluminium as the main component of the metal-balls surface.

Photoluminescence Spectroscopy

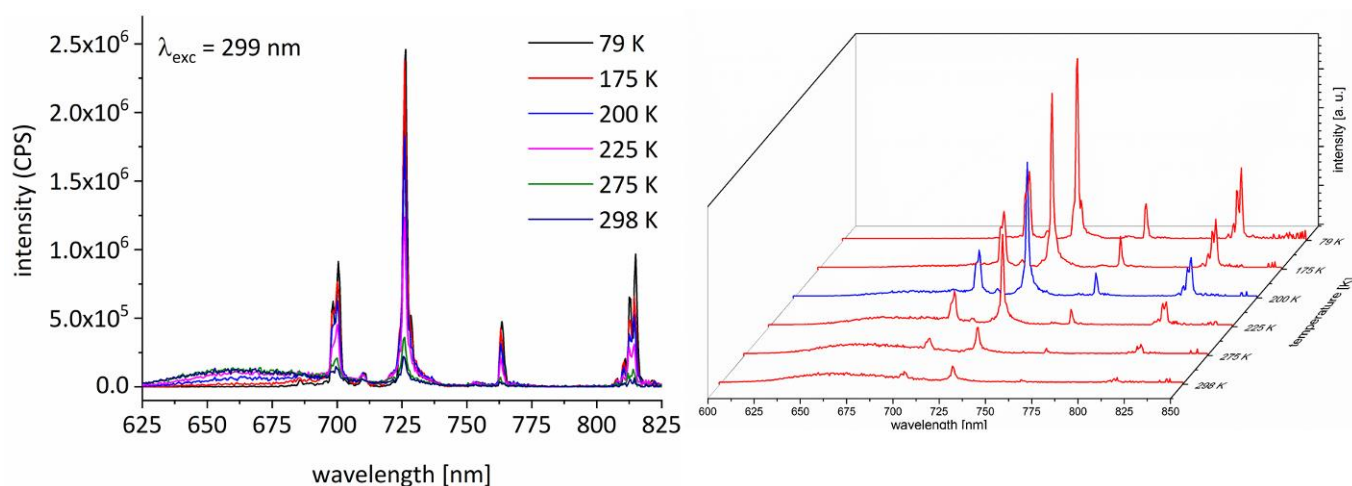


Figure S5: Temperature dependency of the photoluminescence of $\text{Sm}(\text{AlCl}_4)_2$.

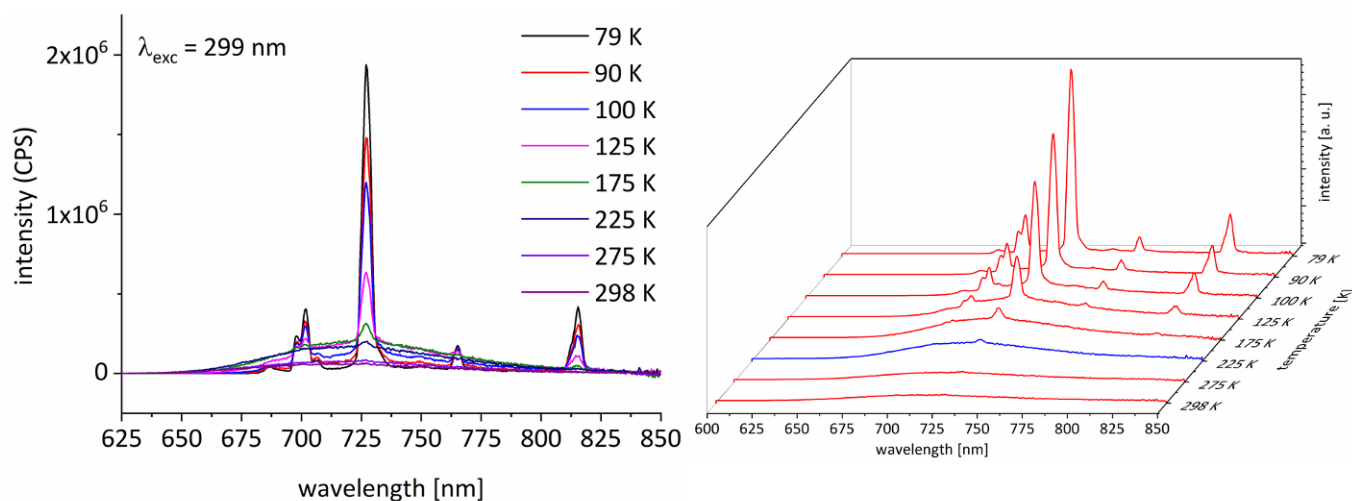


Figure S6: Temperature dependency of the photoluminescence of $\text{Sm}(\text{AlBr}_4)_2$.

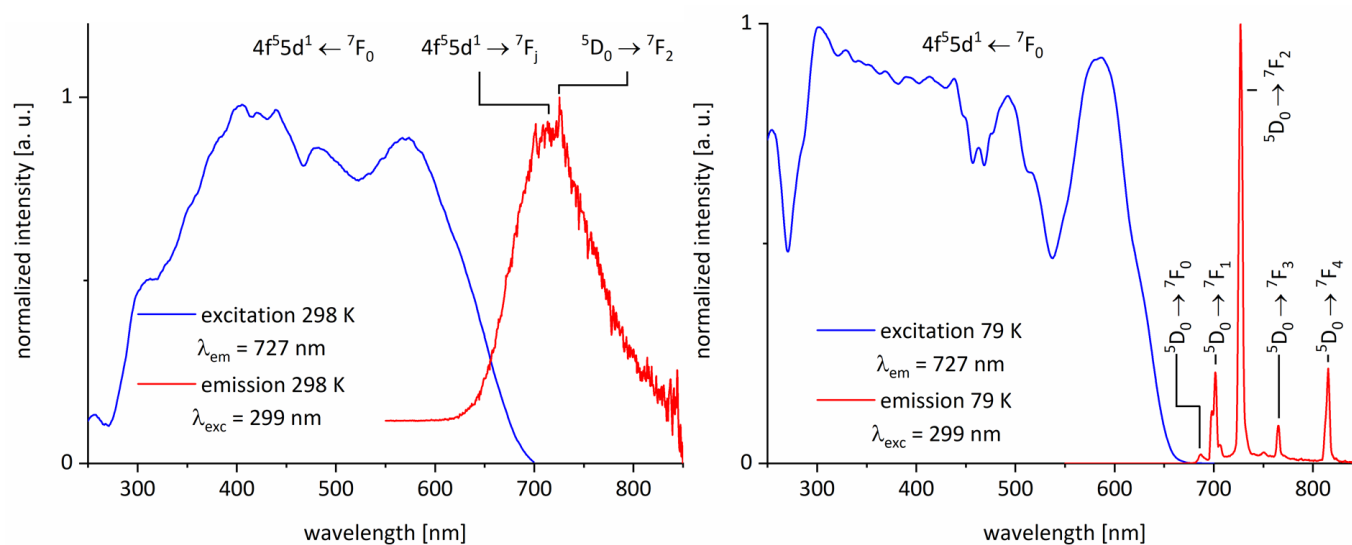
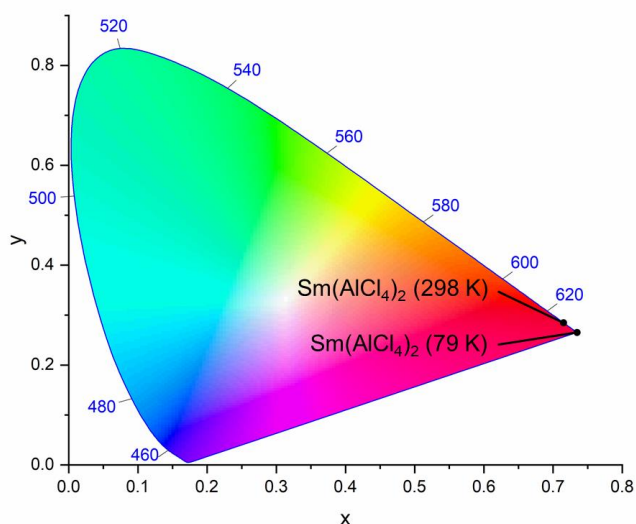


Figure S7: Excitation (blue) and emission (red) spectra of $\text{Sm}(\text{AlBr}_4)_2$ (left: 298 K, right: 79 K, ($\lambda_{\text{exc}} = 400 \text{ nm}$)).

CIE 1931



CIE 1931

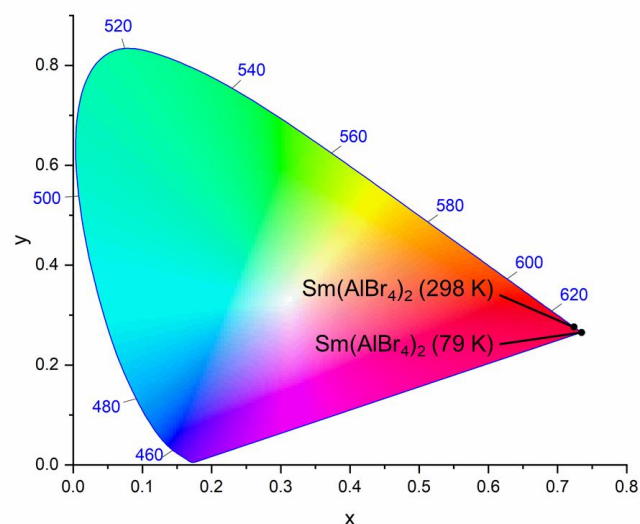


Figure S8: CIE 1931 color space chromaticity diagram of $\text{Sm}(\text{AlCl}_4)_2$ (left) and $\text{Sm}(\text{AlBr}_4)_2$ (right), illustrating the colour dots of the respective Sm-salt at 298 K and 79 K. For determination of the CIE x, y chromaticities, the recorded background with no emissive processes was excluded and only the emission data in the range of 595–840 nm (298 K) and 675 nm–825 nm (79 K) was used.

Table S3: CIE x, y chromaticities of $\text{Sm}(\text{AlCl}_4)_2$ and $\text{Sm}(\text{AlBr}_4)_2$.

Compound	Temperature [K]	λ_{exc} [nm]	CIE x, y chromaticities
$\text{Sm}(\text{AlCl}_4)_2$	298	370	0.715, 0.285
	79	370	0.735, 0.265
$\text{Sm}(\text{AlBr}_4)_2$	298	299	0.724, 0.276
	79	299	0.735, 0.265

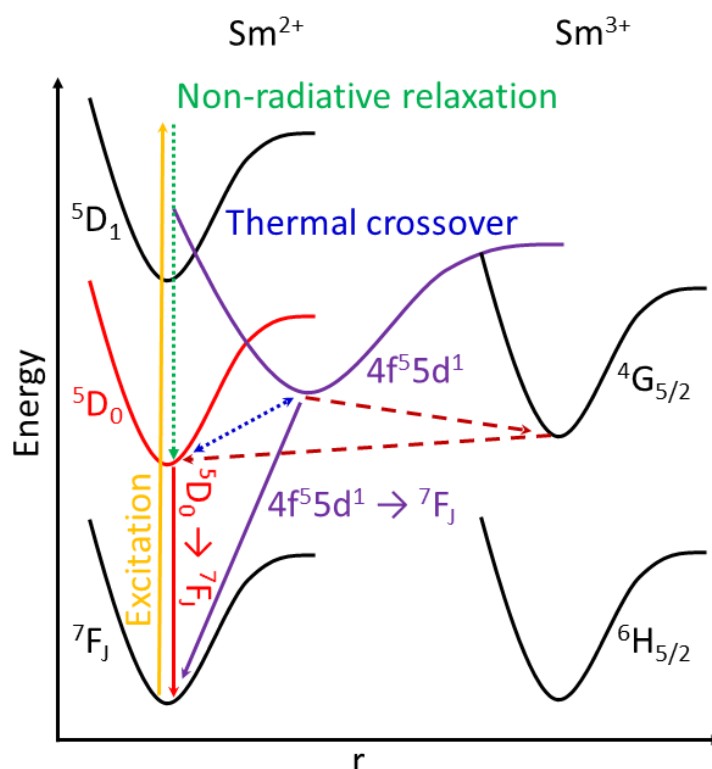


Figure S9: Proposed energy migration path in $\text{Sm}(\text{AlX}_4)_2:\text{Sm}^{3+}$ ($X = \text{Cl}, \text{Br}$), illustrating the additional, non-radiative energy transfer process between Sm^{3+} and Sm^{2+} (dashed line). Dotted lines illustrate non-radiative processes.

Table S4: Details of decay time and quantum efficiencies of Sm(AlCl₄)₂ and Sm(AlBr₄)₂. Deviations are given in brackets.

	T [K]	λ_{em} [nm]	λ_{exc} [nm]	τ	Standard deviation	B	Standard deviation	χ^2	ϕ [%]
Sm(AlCl ₄) ₂	298	660	363	274.60 μ s (29 %) 715.40 μ s (71 %)	2.84 μ s 2.32 μ s	3532.998 3324.161	30.7922 33.8135	1.090	24 % (λ_{exc} = 550 nm)
		700	363	259.12 μ s (29 %) 727.21 μ s (71 %)	2.35 μ s 2.11 μ s	3989.680 3466.075	27.3973 29.6247	1.245	
	79	726	299	1852.21 μ s (22 %) 4697.96 μ s (78 %)	22.74 μ s 12.96 μ s	4188.008 5759.092	46.2198 50.7803	1.007	-
Sm(AlBr ₄) ₂	298	715	365	35.17 μ s	0.03 μ s	8235.441	9.8174	1.057	4 % (λ_{exc} = 550 nm)
	79	727	299	1400.71 μ s (17 %) 3069.93 μ s (83 %)	22.92 8.14	3157.161 6919.912	62.3199 67.6471	0.940	-

Literature

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