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

Supporting Information

Eu^{3+}/Tb^{3+} and Dy^{3+} POM@MOFs and 2D coordination polymers based on pyridine-2,6-dicarboxylic acid for ratiometric optical temperature sensing

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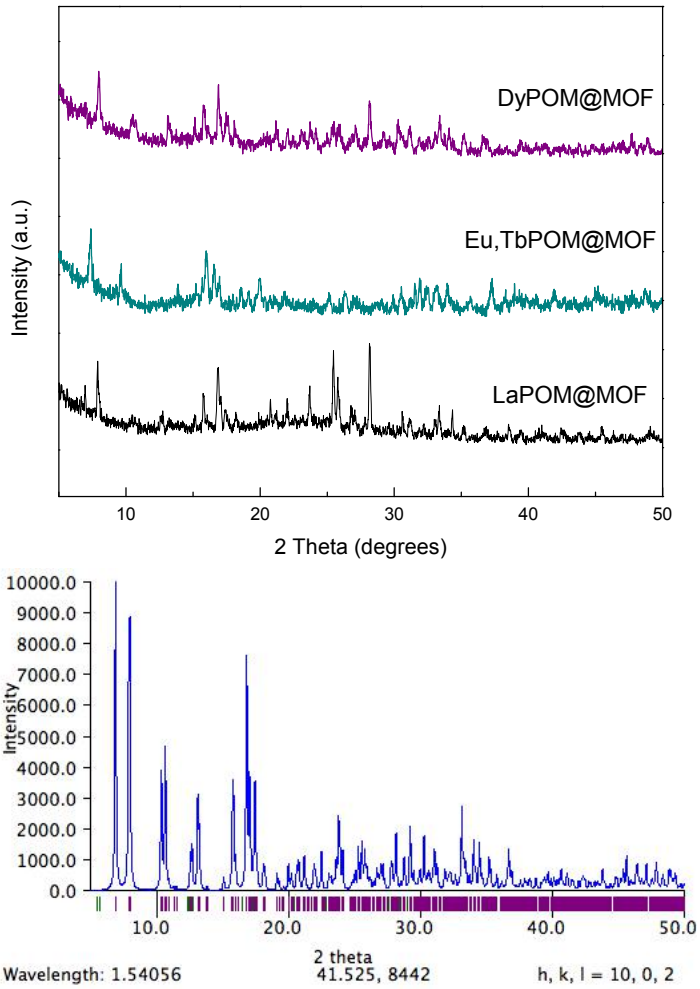

Fig. S1 Top: powder XRD diffractograms of POM@MOF samples (**LaPOM@MOF**, **Eu,TbPOM@MOF**, **DyPOM@MOF**), bottom: powder XRD diffractogram simulated based on single crystal **LaPOM@MOF**.

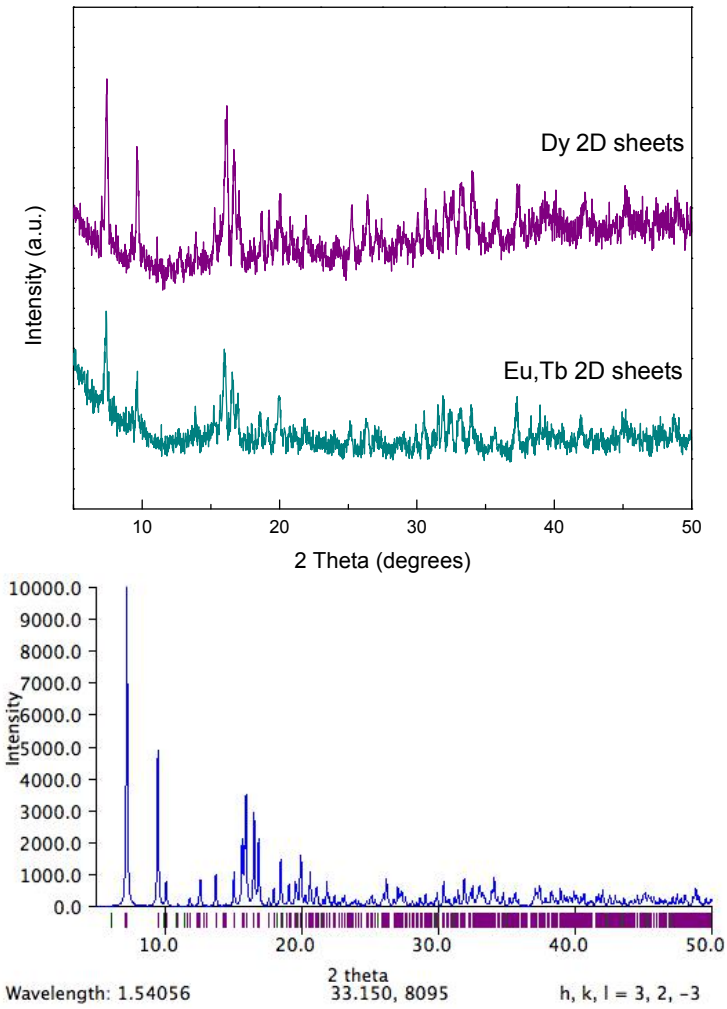

Fig. S2 Top: powder XRD diffractograms of 2D sheet samples (**Eu,Tb 2D Sheets**, **Dy 2D sheets**), bottom: powder XRD diffractogram simulated based on single crystal **Eu,Tb 2D sheets**.

Table S1. Relative Ln^{3+} contents for the LnPOM@MOF and Ln 2D sheets samples during synthesis (calcd.) and as determined by XRF.

Sample	Molar amount used in synthesis [mmol]				La^{3+} ion		Eu^{3+} ion		Tb^{3+} ion		Dy^{3+} ion	
	$La(NO_3)_3$	$Eu(NO_3)_3$	$Tb(NO_3)_3$	$Dy(NO_3)_3$	Calcd.	XRF	Calcd.	XRF	Calcd.	XRF	Calcd.	XRF
Eu,Tb POM@MOF	0.90	0.05	0.05	x	90%	89.9%	5%	7.1%	5%	3.0%	x	x
Dy POM@MOF	0.90	x	x	0.10	90%	99.2%	x	x	x	x	10%	0.8%
Eu,Tb 2D sheets	x	0.50	0.50	x	x	x	50%	43.9%	50%	56.1%	x	x

Table S2 Assignment of peaks labeled in Fig. 3 (**Eu,TbPOM@MOF**).

Peak	Wavelength (nm)	Wavenumber (cm^{-1})	Transition
		Excitation	
a	278.8	35868	$\pi \rightarrow \pi^*$
		Emission	
b	488.7	20462	$^5D_4 \rightarrow {}^7F_6$ (Tb)
c	542.5	18433	$^5D_4 \rightarrow {}^7F_5$ (Tb)
d	591.7	16900	$^5D_0 \rightarrow {}^7F_1$ (Eu)
e	614.4	16276	$^5D_0 \rightarrow {}^7F_2$ (Eu)
f	648.8	15413	$^5D_0 \rightarrow {}^7F_3$ (Eu)
g	694.3	14403	$^5D_0 \rightarrow {}^7F_4$ (Eu)

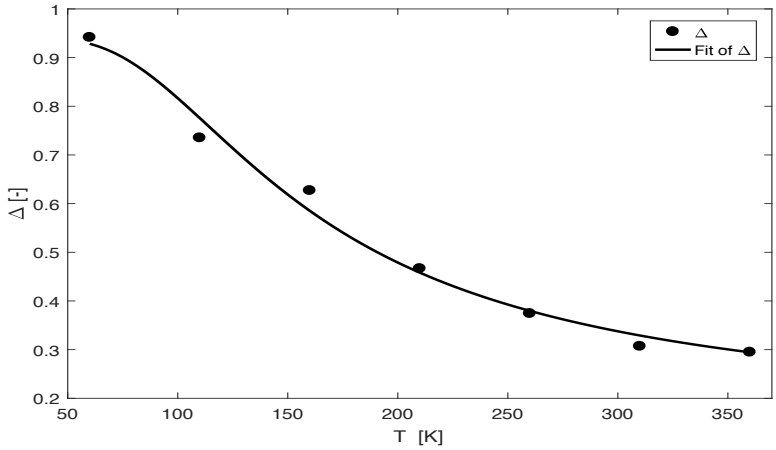

Fig. S3 Plot presenting the calibration curve for compound **Eu,TbPOM@MOF** when equation 2 (Δ_2) is employed. The points represent the experimental Δ_2 parameters and the solid line shows the best fit of the experimental points using equation 2. The calculated integrated areas were: 530.0 – 560.0 nm for Tb^{3+} and 603.0 – 635.0 nm for Eu^{3+}. When fitting the data points with equation 2 R^2 = 0.94033.

Table S3. CIE color coordinates (x, y) and CCT calculated at different temperatures for **Eu,TbPOM@MOF** compound.

Temperature [K]	x coordinate	y coordinate	CCT [K]
60K	0.281	0.258	12575
110K	0.285	0.256	12109
160K	0.321	0.283	6390
210K	0.432	0.359	2685
260K	0.490	0.383	2133
310K	0.522	0.388	1880
360K	0.519	0.384	1875

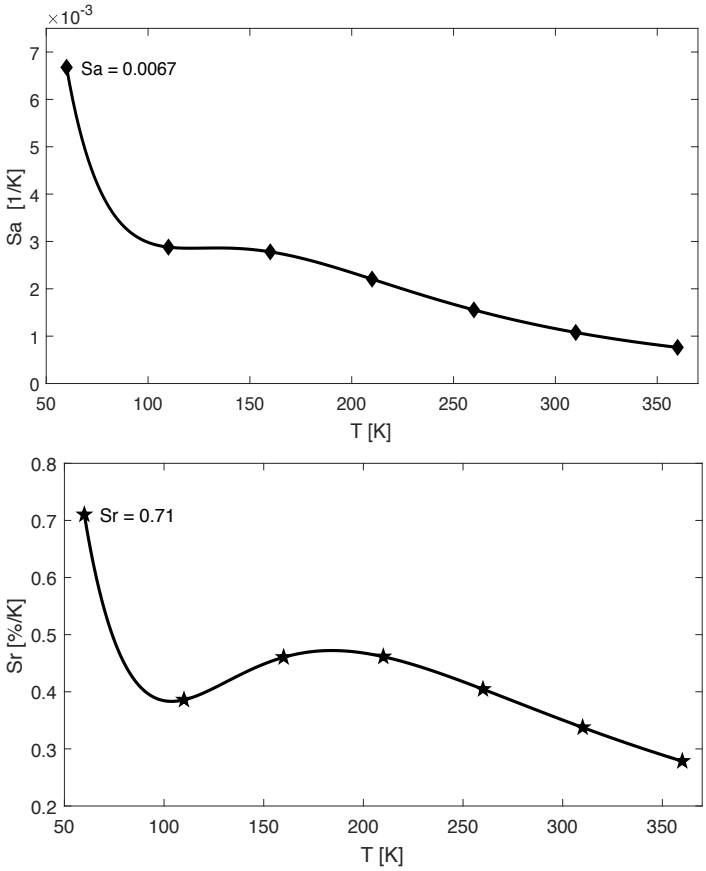

Fig. S4 Top: plot presenting the absolute sensitivity Sa values at varied temperatures (60K – 360K); bottom: plot presenting the relative sensitivity Sr values at varied temperatures (60K – 360K) for **Eu,TbPOM@MOF** compound. The solid lines are guides for eyes. Sa and Sr were calculated based on results obtained from Δ_3 (see Fig. 5 in paper).

Table S4 Decay times recorded for **Eu,TbPOM@MOF** compound.

Temp. [K]	T_1 decay Eu^{3+} [µs]	T_2 decay Eu^{3+} [µs]	Average decay Eu^{3+} [µs]	R^2	T_1 decay Tb^{3+} [µs]	T_2 decay Tb^{3+} [µs]	Average decay Tb^{3+} [µs]	R^2
60	1484	422	1235	0.998	679	161	436	0.998
160	1445	527	1129	0.998	489	94	312	0.996
260	1447	428	1122	0.998	1143	106	684	0.996
298	1346	321	1094	0.997	1244	50	647	0.990
360	1064	166	904	0.996	1091	38	375	0.974

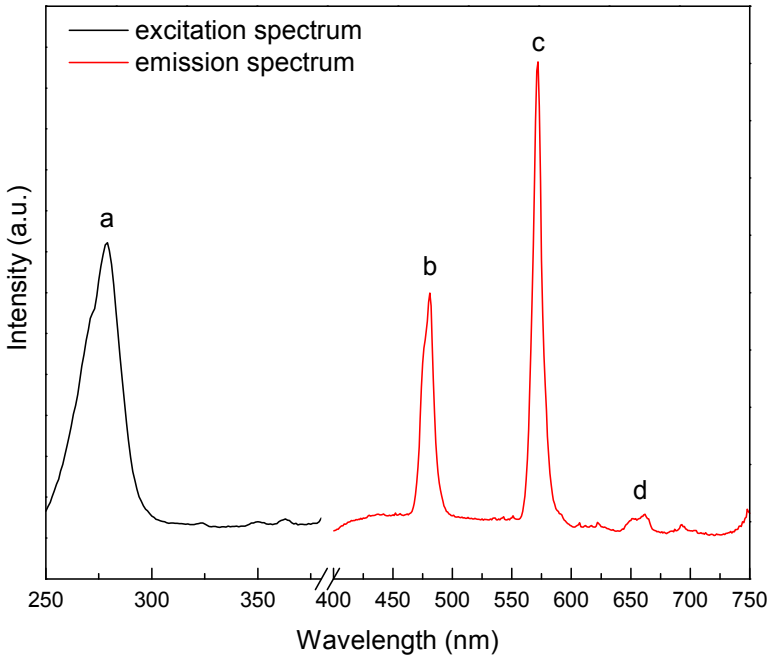

Fig. S5 Combined emission-excitation spectrum of **DyPOM@MOF** recorded at RT.

Table S5 Assignment of peaks labeled in Fig. S5 (**DyPOM@MOF**).

Peak	Wavelength (nm)	Wavenumber (cm^{-1})	Transition
		Excitation	
a	278.8	35868	$\pi \rightarrow \pi^*$
		Emission	
b	480.0	20833	$^4F_{9/2} \rightarrow {}^6H_{15/2}$
c	571.4	17501	$^4F_{9/2} \rightarrow {}^6H_{13/2}$
d	661.5	15117	$^4F_{9/2} \rightarrow {}^6H_{11/2}$

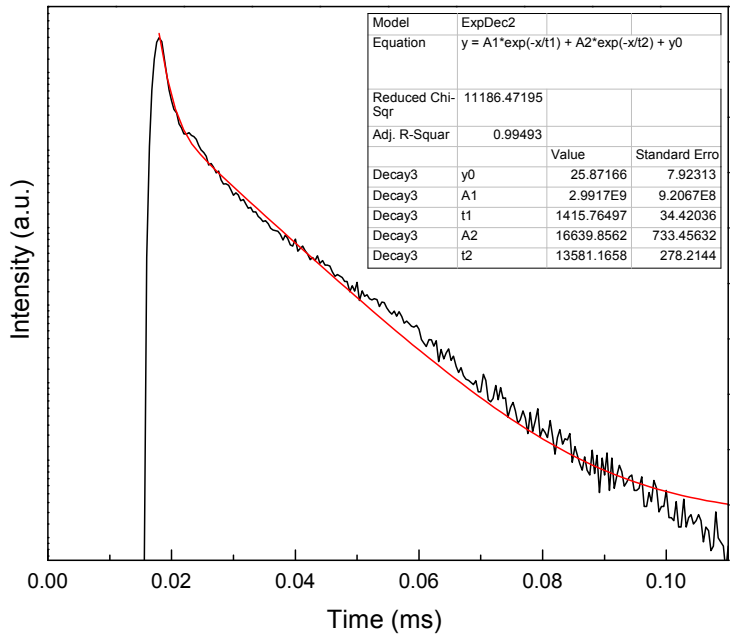

Fig. S6 Decay profile of **DyPOM@MOF**.

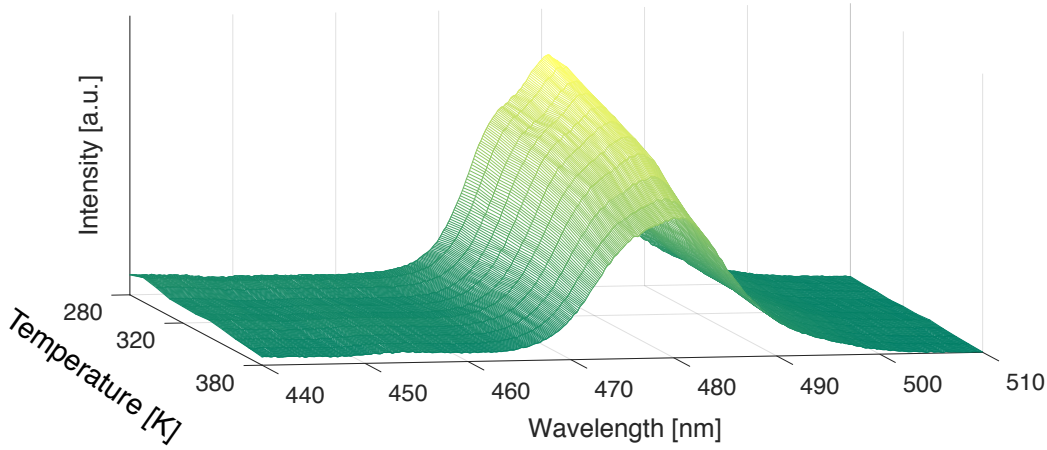

Fig. S7 Emission map of spectra recorded at 280 – 380K for **Dy POM@MOF**.

Table S6 Assignment of peaks labeled in Fig. 7 (**Eu,Tb 2D sheets**).

Peak	Wavelength (nm)	Wavenumber (cm^{-1})	Transition
		Excitation	
a	287.0	34843	$\pi \rightarrow \pi^*$
b	390.9	25582	$^5L_6 \leftarrow {}^7F_0$ (Eu)
c	462.1	21640	$^5D_2 \leftarrow {}^7F_0$ (Eu)
		Emission	
d	489.4	20433	$^5D_4 \rightarrow {}^7F_6$ (Tb)
e	541.6	18464	$^5D_4 \rightarrow {}^7F_5$ (Tb)
f	594.0	16835	$^5D_0 \rightarrow {}^7F_1$ (Eu)
g	614.4	16276	$^5D_0 \rightarrow {}^7F_2$ (Eu)
h	647.8	15437	$^5D_0 \rightarrow {}^7F_3$ (Eu)
i	695.6	14376	$^5D_0 \rightarrow {}^7F_4$ (Eu)

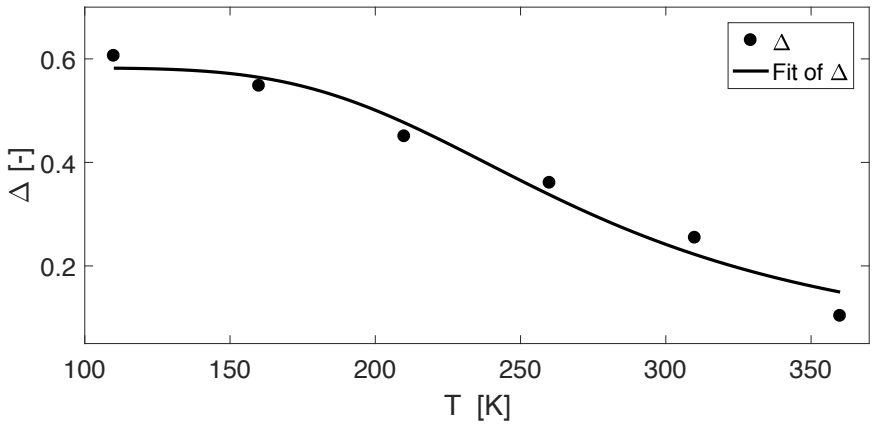

Fig. S8 Plot presenting the calibration curve for compound **Eu,Tb 2D sheets** when equation 2 (Δ_2) is employed. The points represent the experimental Δ_2 parameters and the solid line shows the best fit of the experimental points using equation 2. The calculated integrated areas were: 530.0 – 560.0 nm for Tb^{3+} and 604.0 – 630.0 nm for Eu^{3+}. When fitting the data points with equation 2 $R^2 = 0.97042$.

Table S7. CIE color coordinates (x, y) and CCT calculated at different temperatures for **Eu,Tb 2D sheets** compound.

Temperature [K]	x coordinate	y coordinate	CCT [K]
110K	0.503	0.450	2460
160K	0.514	0.444	2303
210K	0.531	0.433	2082
260K	0.549	0.419	1863
310K	0.573	0.403	1623
360K	0.617	0.370	1247

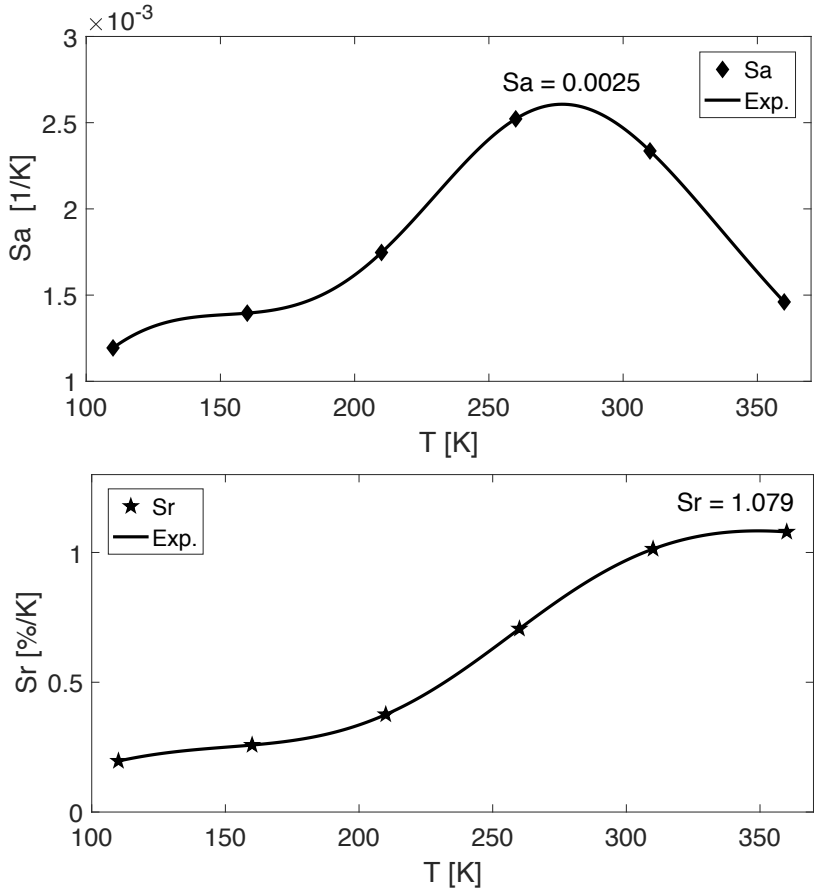

Fig. S9 Top: plot presenting the absolute sensitivity Sa values at varied temperatures (60K – 360K); bottom: plot presenting the relative sensitivity Sr values at varied temperatures (60K – 360K) for **Eu,Tb 2D sheets** compound. The solid lines are guides for eyes. Sa and Sr were calculated based on results obtained from Δ_3 (see Fig. 9).

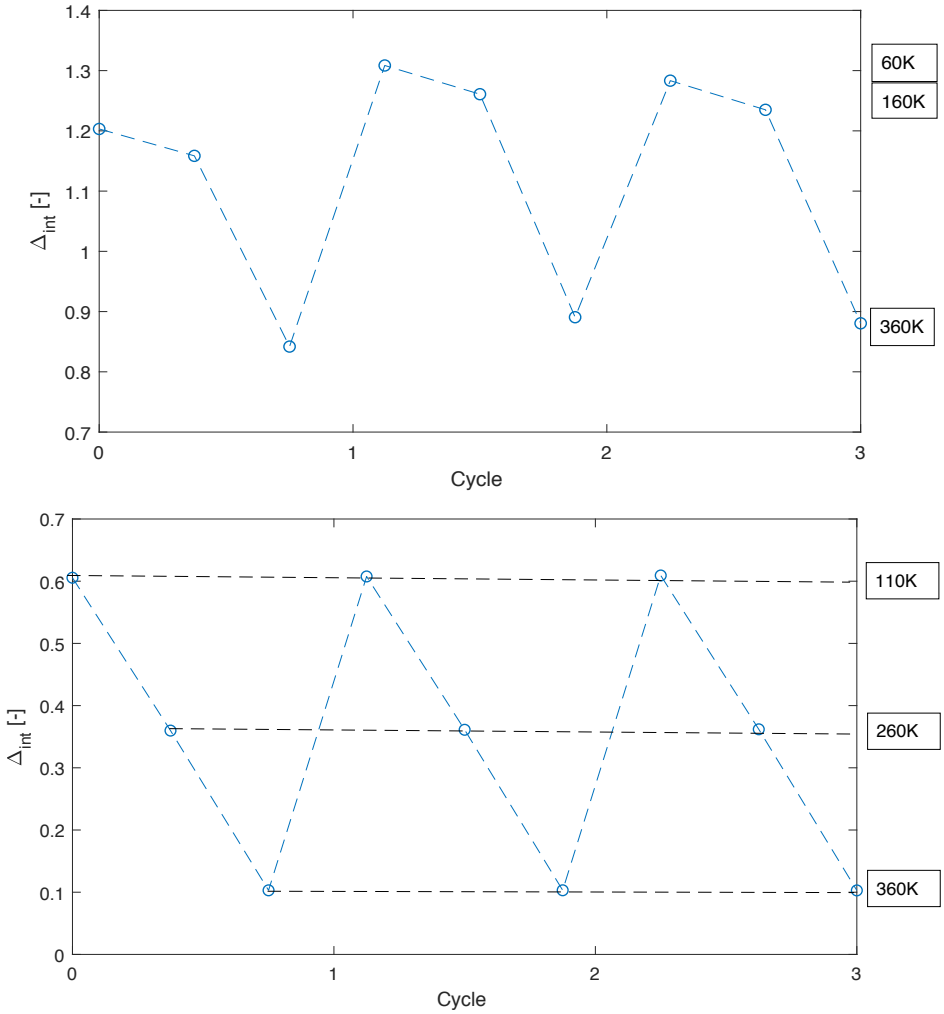

Fig. S10 Plots showing heating, cooling and reheating tests of **Eu,Tb POM@MOF** (top) and **Eu,Tb 2D sheets** (bottom). The **Eu,Tb POM@MOF** material shows lower repeatability (around 95% repeatability) and stability than the **Eu,Tb 2D sheets** material. In the **Eu,Tb 2D sheets** material Δ parameter remains stable throughout the recycle tests.

Table S8 Decay times recorded for **Eu,Tb 2D sheets** compound.

Temp. [K]	Decay Eu^{3+} [μs]	R^2	Decay Tb^{3+} [μs]	R^2
110	722	0.999	109	0.997
210	651	0.999	86	0.997
298	611	0.999	73	0.996
310	587	0.999	61	0.995

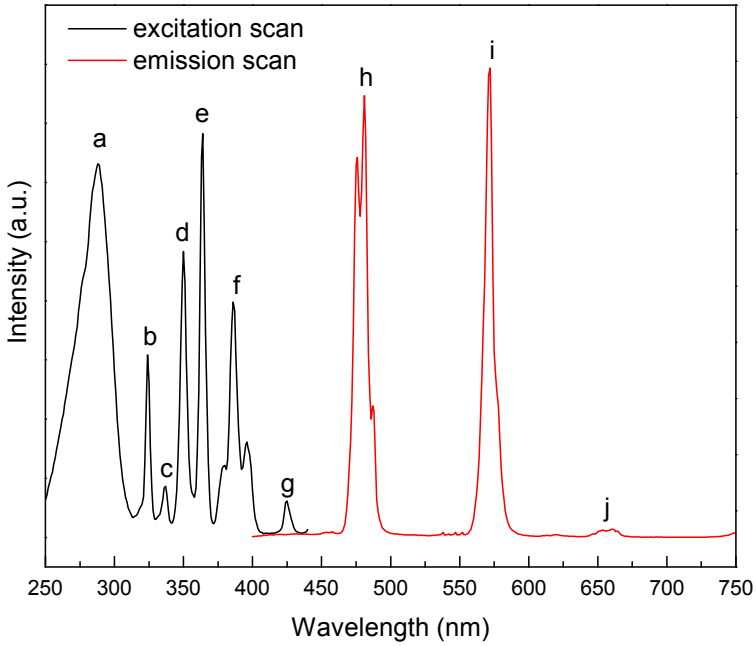

Fig. S11 Combined emission-excitation of **Dy 2D sheets** recorded at RT.

Table S9 Assignment of labeled peaks in Fig. S10 (**Dy 2D sheets**).

Peak	Wavelength (nm)	Wavenumber (cm^{-1})	Transition
		Excitation	
a	288.4	34674	$\pi \rightarrow \pi^*$
b	323.5	30912	$^6P_{3/2} \leftarrow {}^6H_{15/2}$
c	336.1	29753	$^4F_{5/2}$, $^4D_{5/2} \leftarrow {}^6H_{15/2}$
d	349.3	28629	$^6P_{7/2} \leftarrow {}^6H_{15/2}$
e	363.1	27541	$^6P_{5/2} \leftarrow {}^6H_{15/2}$
f	385.8	25920	$^4F_{7/2} \leftarrow {}^6H_{15/2}$
g	424.5	23557	$^4G_{11/2} \leftarrow {}^6H_{15/2}$
		Emission	
h	481.3	20777	$^4F_{9/2} \rightarrow {}^6H_{15/2}$
i	572.1	17479	$^4F_{9/2} \rightarrow {}^6H_{13/2}$
j	659.0	15175	$^4F_{9/2} \rightarrow {}^6H_{11/2}$

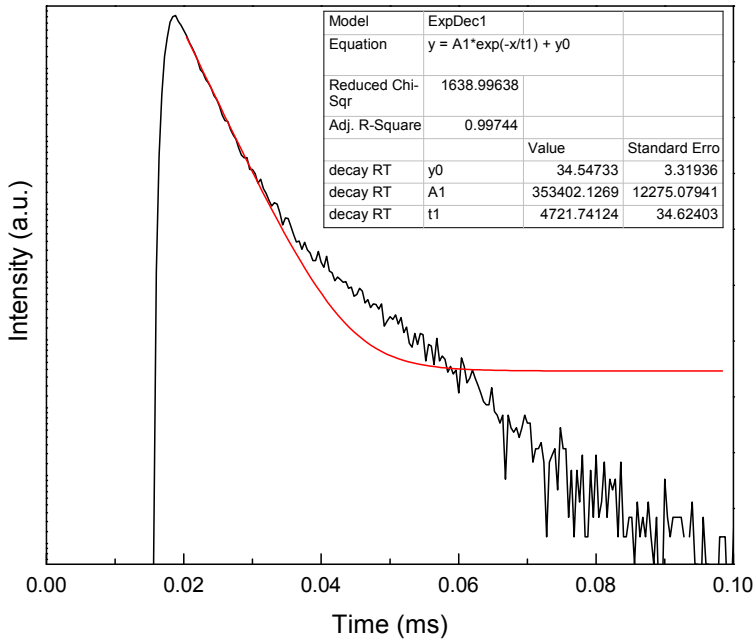

Fig. S12 Decay profile of **Dy 2D sheets**.

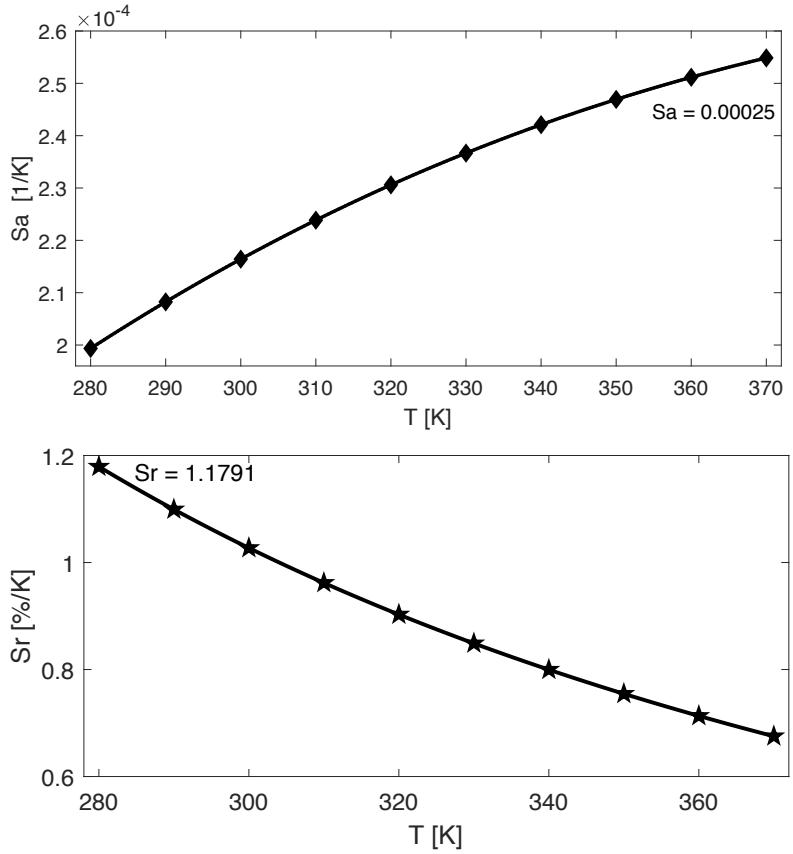

Fig. S13 Top: plot presenting the absolute sensitivity Sa values at varied temperatures (280K – 370K); bottom: plot presenting the relative sensitivity Sr values at varied temperatures (280K – 370K) for **Dy 2D sheets** compound. The solid lines are guides for eyes. Sa and Sr were calculated based on results obtained from Δ_1 using the peak maxima (see Fig. 11).