

## Oxygen-Induced Downshifting and Lanthanide Upconversion Luminescence in $\text{Sr}_2\text{YbF}_7$

### Nanoparticles for Dual-Mode Security Applications

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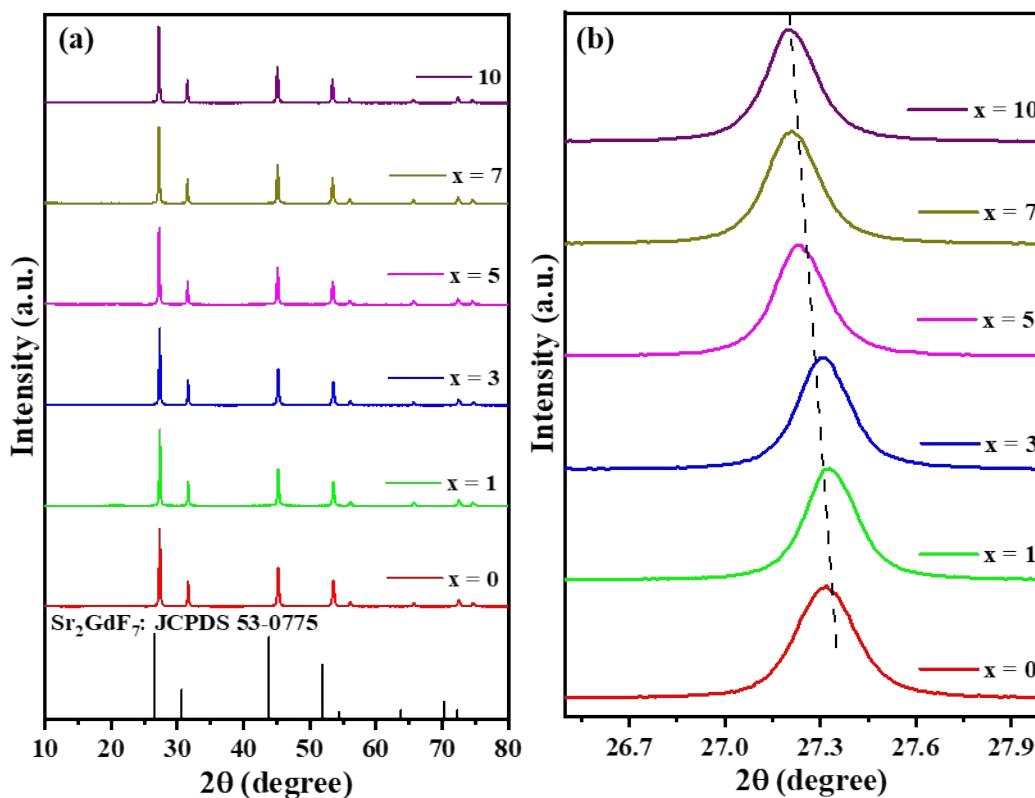
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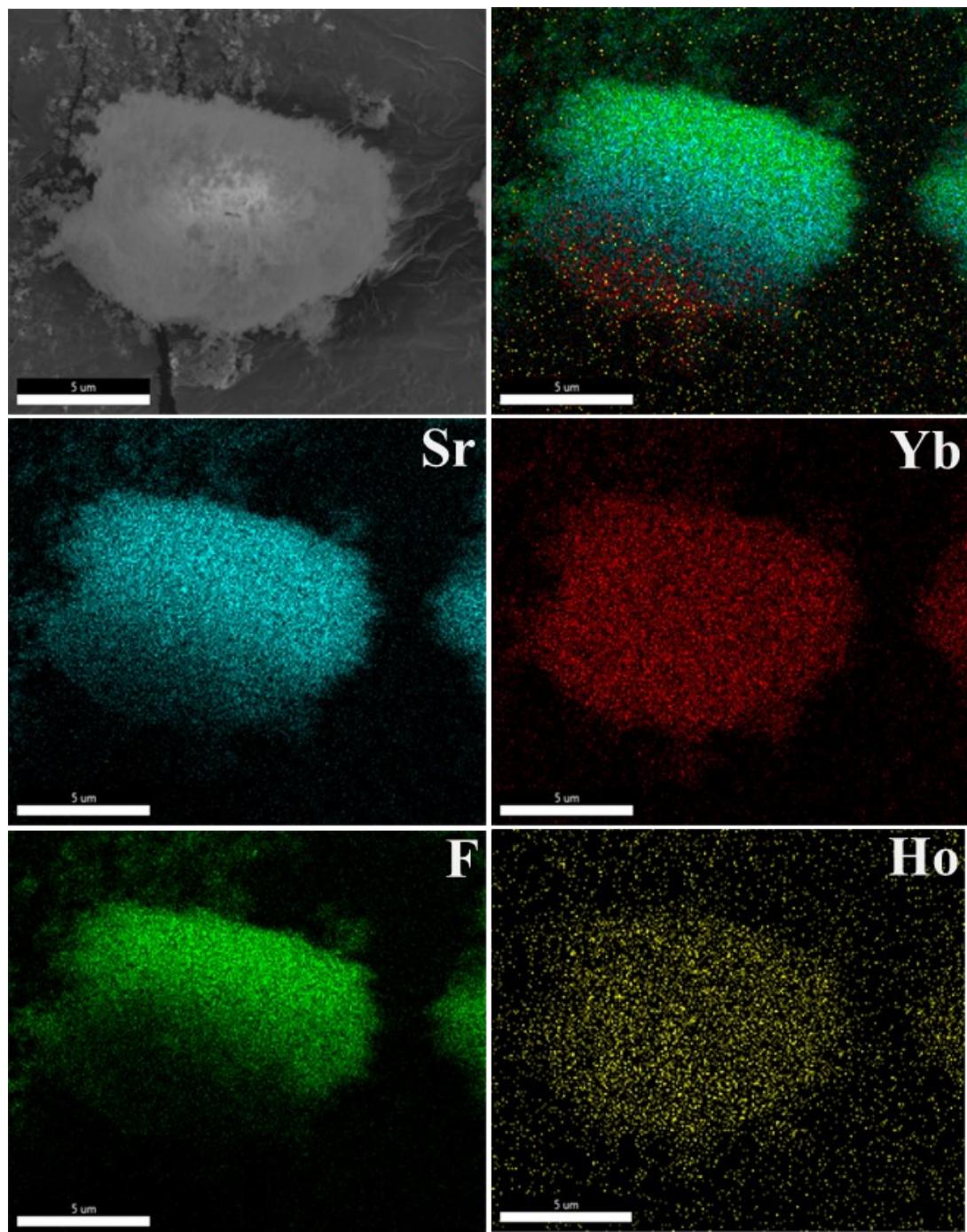
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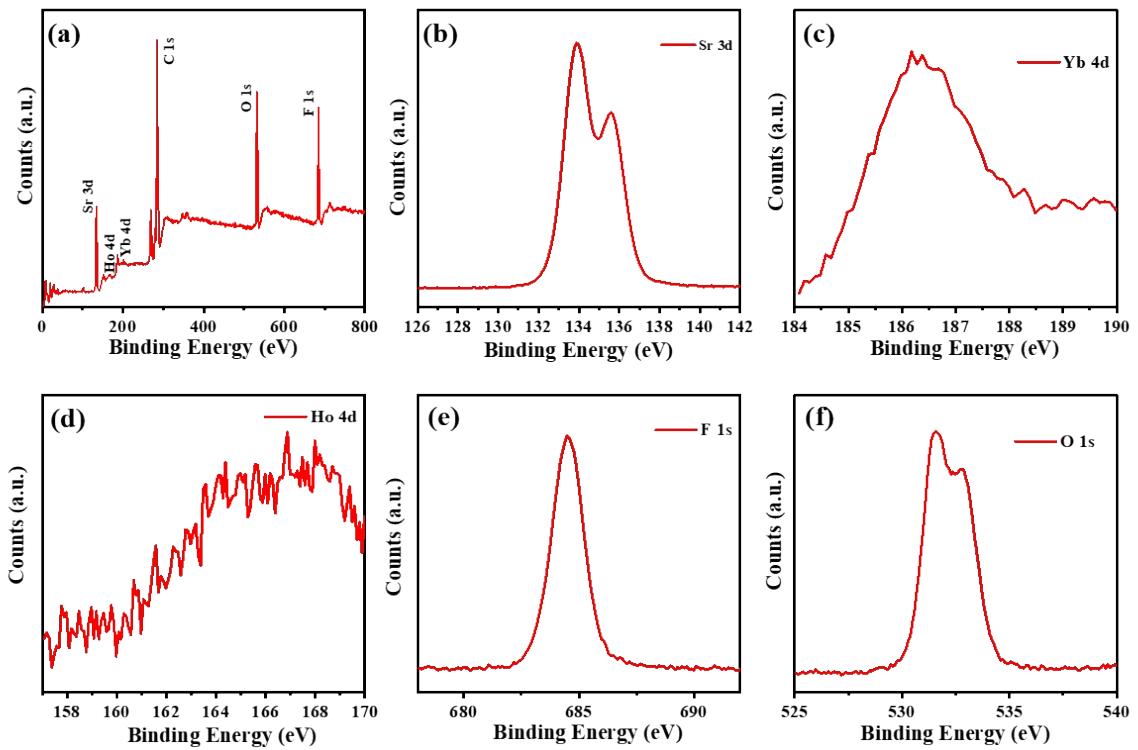
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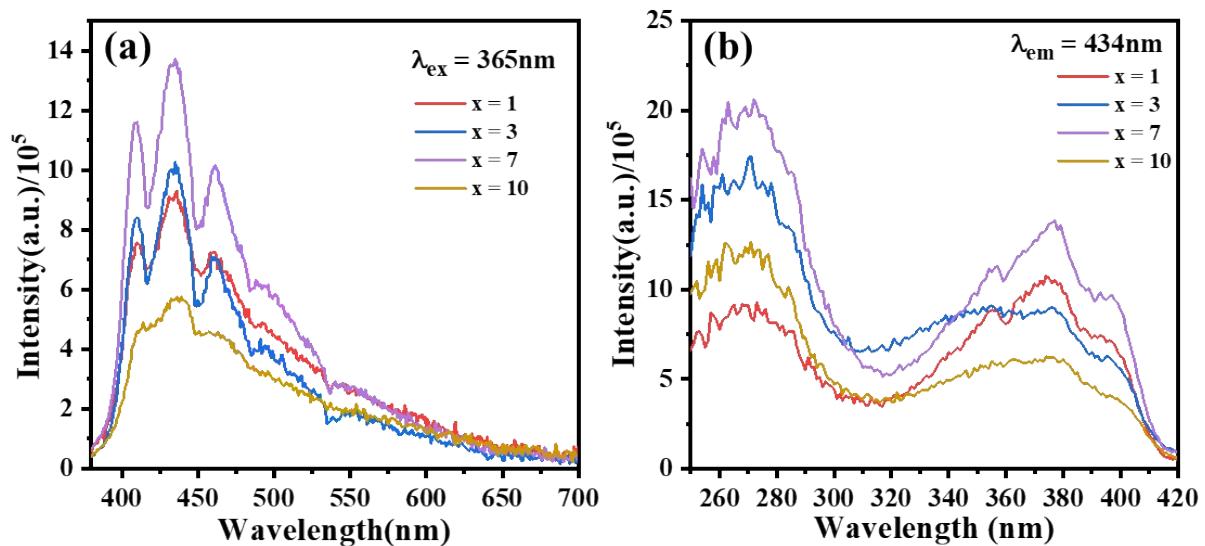
**Figure S1:** (a) XRD patterns of  $\text{Sr}_2\text{YbF}_7$ :  $x\%$   $\text{Ho}^{3+}$  nanoparticles, (b) Zoomed XRD patterns within the  $26.5$ – $28^\circ$   $2\theta$  range.



**Figure S2:** FESEM (field emission scanning electron microscopy) image and elemental mapping of the SYF: 7%  $\text{Ho}^{3+}$  by using FESEM-EDX (energy-dispersive X-ray analysis).

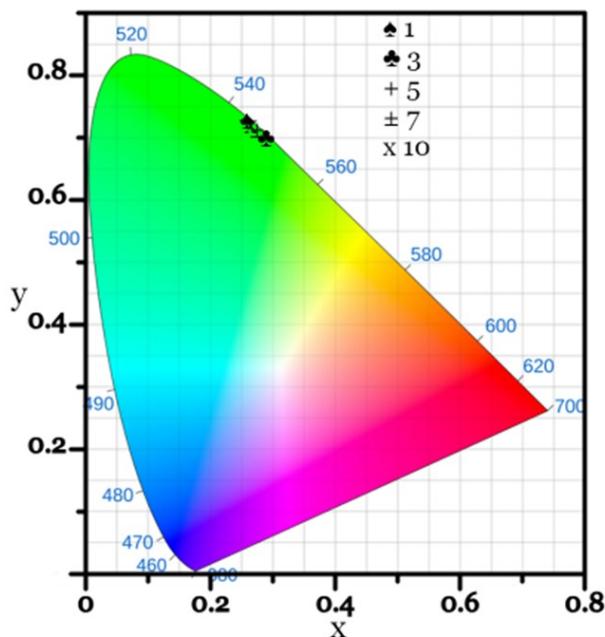


**Figure S3:** (a) Survey scan and High-resolution XPS spectra for (b) Sr 3d, (c) Yb 4d, (d) Ho 4d, (e), F 1s and (f) O 1s region of the  $\text{Sr}_2\text{YbF}_7$ : 7%  $\text{Ho}^{3+}$  sample.



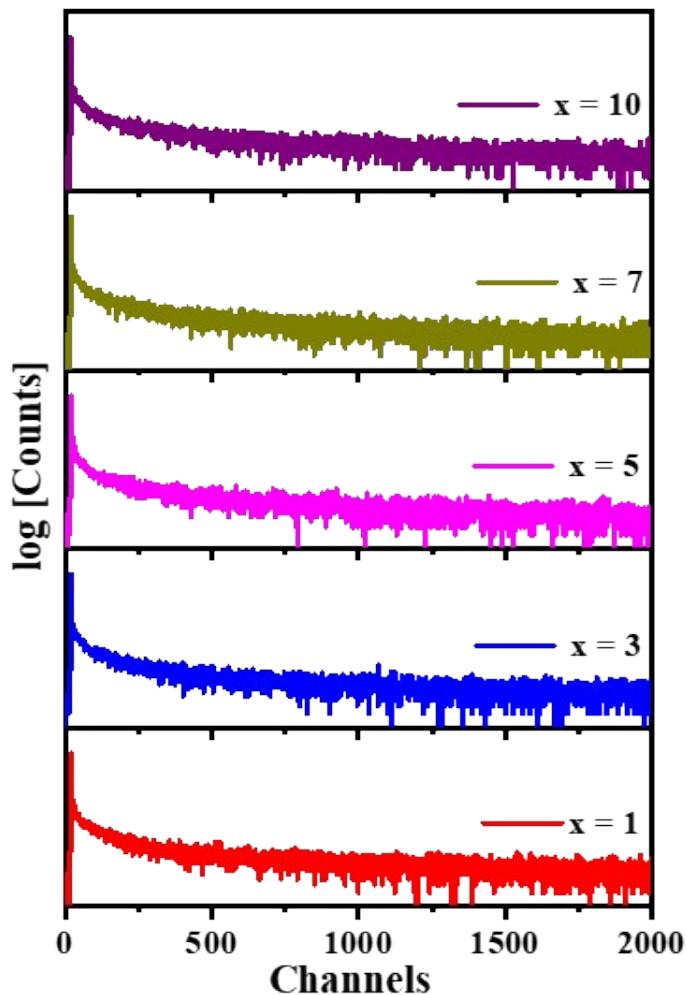
**Figure S4:** The room temperature solid-state excitation and emission spectra of the SYF:  $x\%$   $\text{Ho}^{3+}$  (each plot shows the wavelengths used for excitation and emission): **(a)** Emission spectra at 365 nm, **(b)** 434 nm excitation spectra.

## CIE chromaticity diagram 1931



S.No.	Con. of $\text{Ho}^{3+}$ (%)	x	y
1.	1	0.26	0.73
2.	3	0.29	0.70
3.	5	0.26	0.73
4.	7	0.27	0.71
5.	10	0.27	0.72

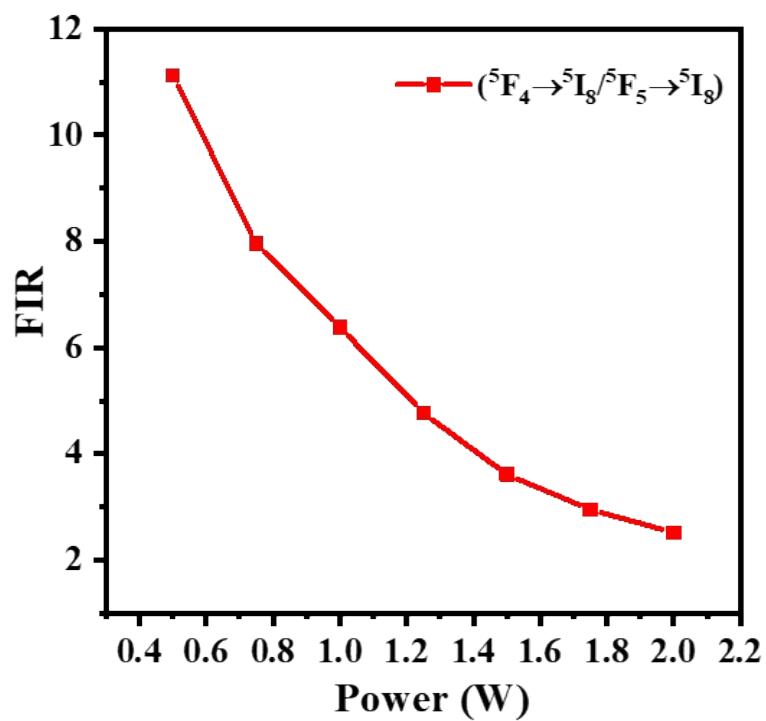
**Figure S5:** CIE 1931 chromaticity diagram and colour coordinates (x, y) of SYF: x% Ho nanomaterials at 980 nm excitation.



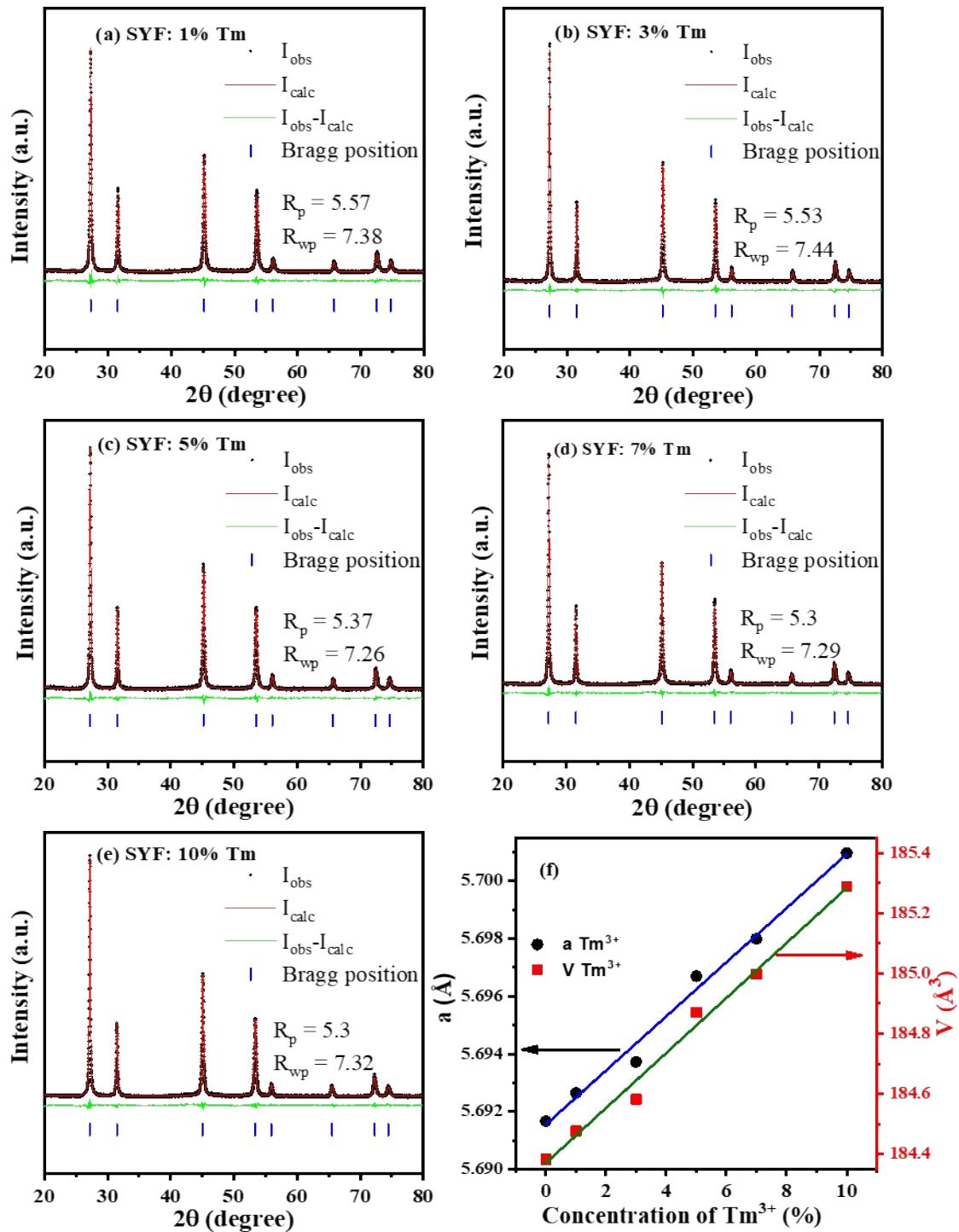
**Figure S6:** Decay curves of the  $\text{Ho}^{3+}$  excited state at 365 nm wavelength of the SYF:  $x\%$   $\text{Ho}^{3+}$ .

**Table S1:** PL decay curves of SYF as a function of  $\text{Ho}^{3+}$  concentration ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ,  $\lambda_{\text{em}} = 434 \text{ nm}$ ).

Con. of $\text{Ho}^{3+}$	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	Avg. $\tau$ (ns)
1	23.75	16.4	76.25	171	166
3	25.43	16.4	74.57	161	155
5	25.64	16.9	74.36	156	150
7	25.17	16.3	74.83	151	145
10	25.25	11.6	74.75	146	142



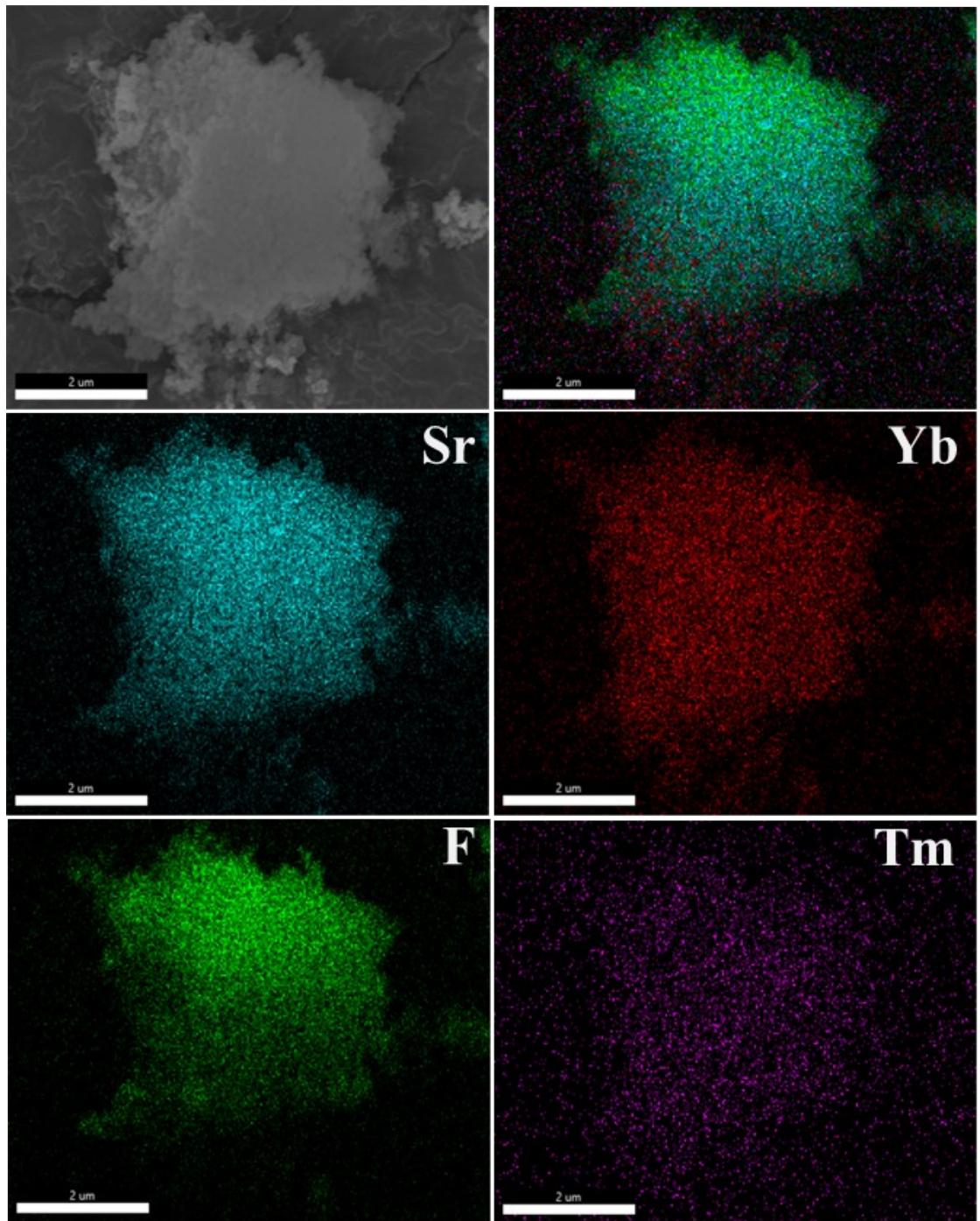
**Figure S7:** FIR of SYF: 7% Ho<sup>3+</sup> nanomaterial as a function of pump power.



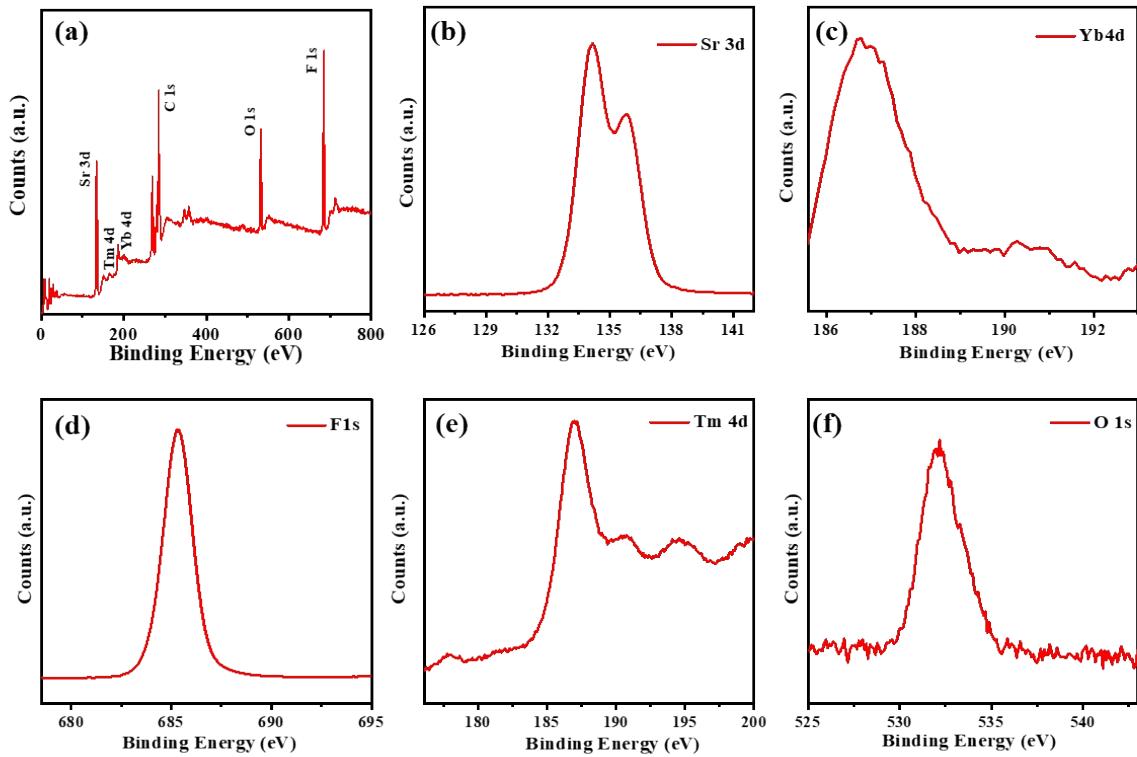
**Figure S8:** Rietveld refinement plot of the powder XRD data of sample  $\text{Sr}_2\text{Yb}_{1-y}\text{Tm}_y\text{F}_7$ .

**Table S2:** Refined structural parameters of the  $\text{Sr}_2\text{Yb}_{1-y}\text{Tm}_y\text{F}_7$  samples.

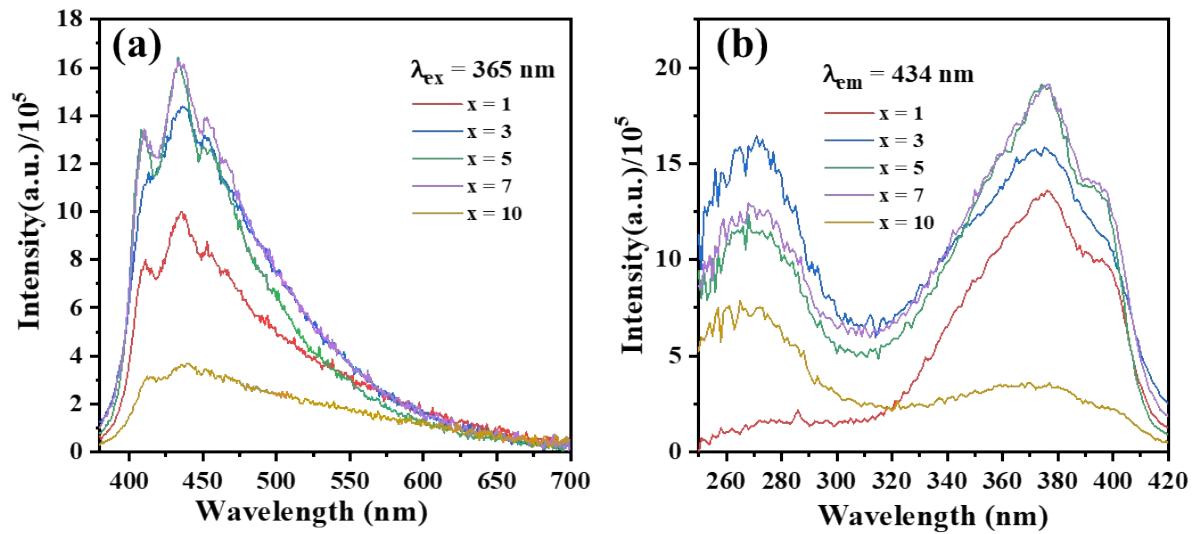
Nominal composition	$\text{Sr}_2\text{Yb}_{0.99}\text{Tm}_{0.01}\text{F}_7$	$\text{Sr}_2\text{Yb}_{0.97}\text{Tm}_{0.03}\text{F}_7$	$\text{Sr}_2\text{Yb}_{0.95}\text{Tm}_{0.05}\text{F}_7$	$\text{Sr}_2\text{Yb}_{0.93}\text{Tm}_{0.07}\text{F}_7$	$\text{Sr}_2\text{Yb}_{0.90}\text{Tm}_{0.10}\text{F}_7$
x (%)	1	3	5	7	10
a (Å)	5.6926(1)	5.6937(1)	5.6967(1)	5.6980(1)	5.7010(1)
V (Å) <sup>3</sup>	184.477(6)	184.582(5)	184.871(5)	184.998(5)	185.287(5)
FU	$\text{Sr}_{0.667}\text{Yb}_{0.330}\text{Tm}_{0.003}\text{F}_{2.333}$	$\text{Sr}_{0.667}\text{Yb}_{0.323}\text{Tm}_{0.010}\text{F}_{2.333}$	$\text{Sr}_{0.667}\text{Yb}_{0.317}\text{Tm}_{0.017}\text{F}_{2.333}$	$\text{Sr}_{0.667}\text{Yb}_{0.310}\text{Tm}_{0.023}\text{F}_{2.333}$	$\text{Sr}_{0.667}\text{Yb}_{0.300}\text{Tm}_{0.033}\text{F}_{2.333}$
Z	4	4	4	4	4
<b>M: 4c (0,0,0)</b>					
Occ					
Sr	0.667	0.667	0.667	0.667	0.667
Yb	0.330	0.323	0.317	0.310	0.300
Ho/Tm	0.003	0.010	0.017	0.023	0.033
<b>F1: 8f (1/4, 1/4, 1/4)</b>					
occ.	0.676(4)	0.695(4)	0.692(4)	0.721(4)	0.756(4)
<b>F2: 32f (x,x,x) x</b>	0.4029(10)	0.4049(10)	0.4042(11)	0.4042(10)	0.4040(11)
Occ.	0.0844(22)	0.0865(21)	0.0800(21)	0.0873(20)	0.0744(21)
<b>U<sub>iso</sub> (Å)<sup>2</sup></b>	0.0262(4)	0.0254(4)	0.0274(4)	0.0224(4)	0.0241(4)
wR (%)	7.38	7.44	7.26	7.29	7.32
R (%)	5.57	5.53	5.37	5.3	5.3
GOF	2.18	2.16	2.16	2.06	2.08
FU estimated	$\text{Sr}_{0.667}\text{Yb}_{0.333}\text{Tm}_{0.003}\text{F}_{1.721}\text{O}_{0.306}$	$\text{Sr}_{0.667}\text{Yb}_{0.323}\text{Tm}_{0.010}\text{F}_{1.721}\text{O}_{0.306}$	$\text{Sr}_{0.667}\text{Yb}_{0.317}\text{Tm}_{0.017}\text{F}_{1.715}\text{O}_{0.309}$	$\text{Sr}_{0.667}\text{Yb}_{0.310}\text{Tm}_{0.023}\text{F}_{1.948}\text{O}_{0.193}$	$\text{Sr}_{0.667}\text{Yb}_{0.300}\text{Tm}_{0.033}\text{F}_{1.881}\text{O}_{0.226}$



**Figure S9:** FESEM image and elemental mapping of the SYF: 5%  $\text{Tm}^{3+}$  by using FESEM-EDX.

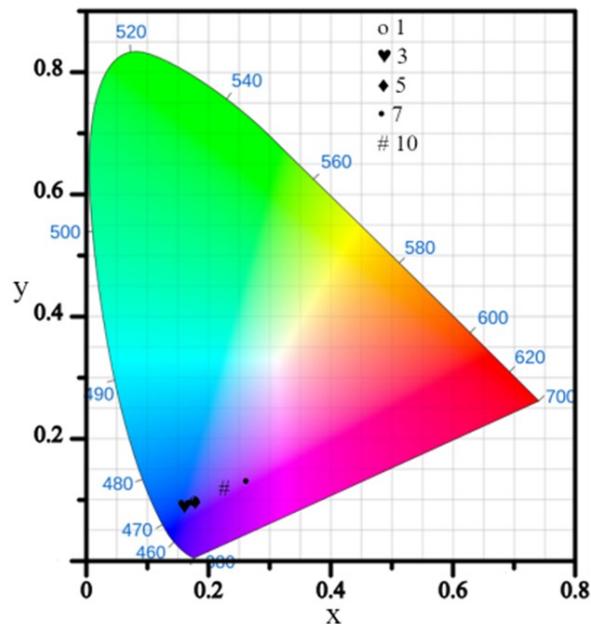


**Figure S10:** (a) Survey scan and High-resolution XPS spectra for (b) Sr 3d, (c) Yb 4d, (d) F 1s, (e) Tm 4d and (f) O 1s region of the  $\text{Sr}_2\text{YbF}_7$ : 5%  $\text{Tm}^{3+}$  sample.



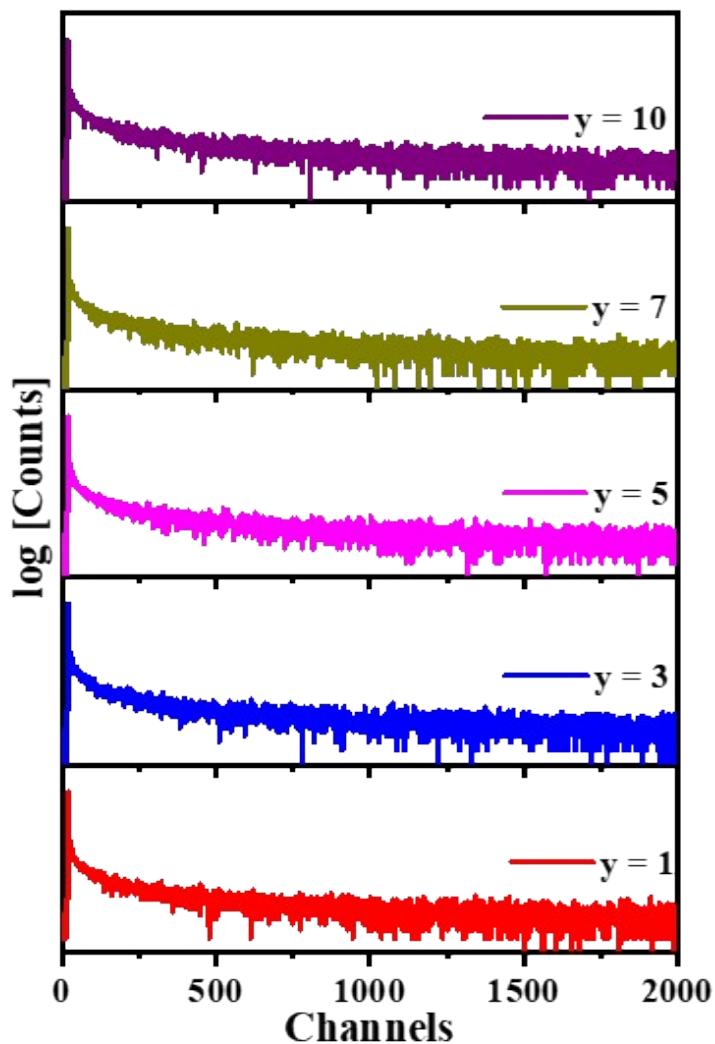
**Figure S11:** Emission and excitation spectra of the SYF doped with  $\text{Tm}^{3+}$ . With excitation wavelengths of **(a)** 365 nm the emission spectra was captured, **(b)** At 434 nm, the excitation spectra was tracked.

## CIE chromaticity diagram 1931



S.No.	Con. of $Tm^{3+}$ (%)	x	y
1.	1	0.178	0.1
2.	3	0.16	0.088
3.	5	0.175	0.095
4.	7	0.265	0.129
5.	10	0.227	0.118

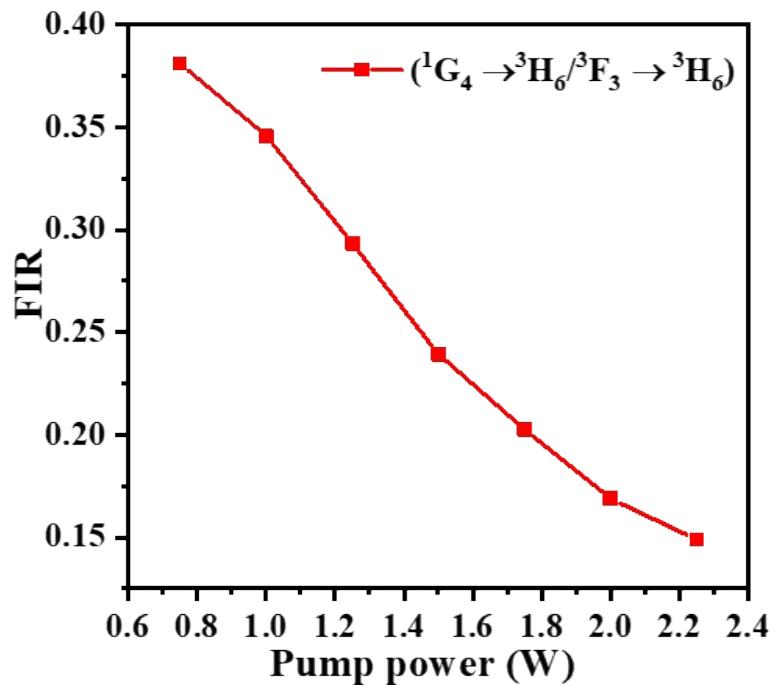
**Figure S12:** CIE 1931 chromaticity diagram and colour coordinates (x, y) of SYF: y% Tm nanomaterials at 980 nm excitation.



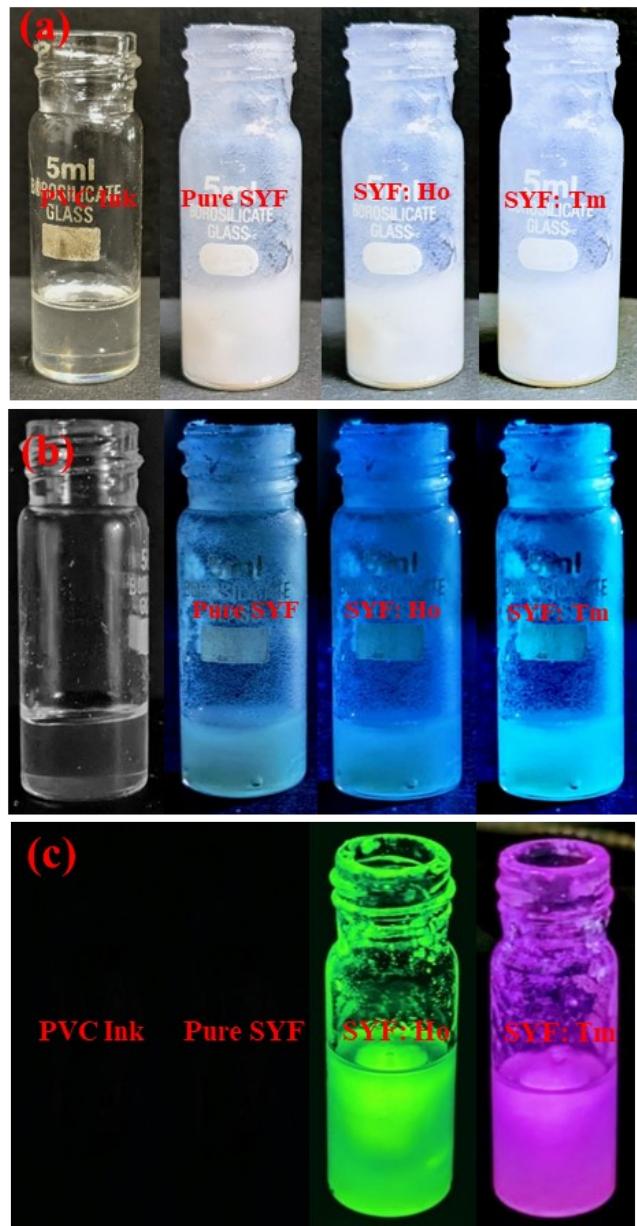
**Figure S13:** Decay curves of the Tm<sup>3+</sup> excited state at 365 nm wavelength of the SYF: y% Tm<sup>3+</sup>.

**Table S3:** PL decay curves of SYF as a function of Tm<sup>3+</sup> concentration ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ,  $\lambda_{\text{em}} = 434 \text{ nm}$ ).

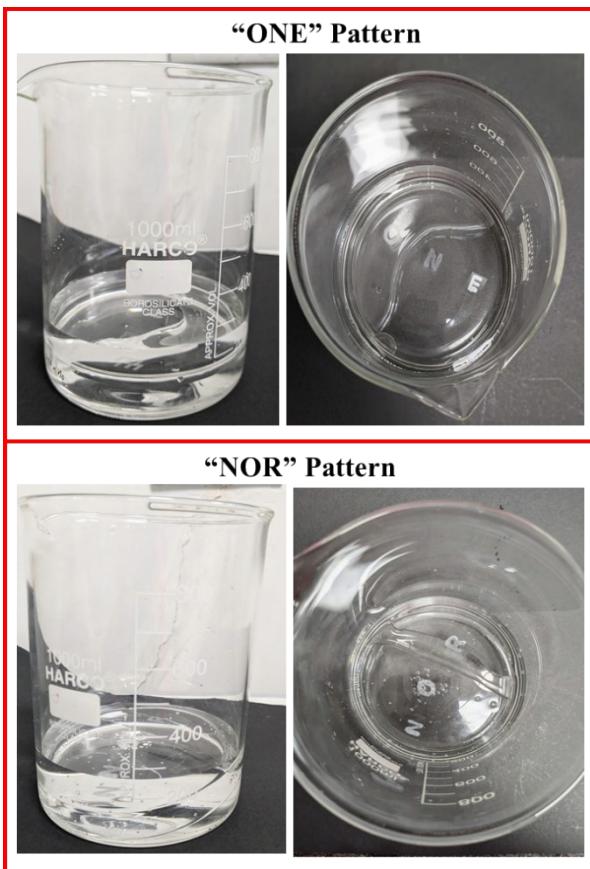
Con. of Tm <sup>3+</sup>	A <sub>1</sub>	$\tau_1$ (ns)	A <sub>2</sub>	$\tau_2$	Avg. $\tau$ (ns)
1	21.87	18.0	78.13	172	167
3	24.52	18.2	75.48	169	164
5	25.37	15.0	74.63	166	162
7	24.91	15.3	75.09	166	161
10	25.33	16.6	74.67	165	160



**Figure S14:** FIR of SYF: 5% Tm<sup>3+</sup> nanomaterial as a function of pump power.



**Figure S15:** Photograph of PVC ink, ink prepared with undoped sample, SYF: 7%  $\text{Ho}^{3+}$  and SYF: 5 %  $\text{Tm}^{3+}$  (a) under daylight, (b) under 365 nm UV light, (b) under 980 nm NIR light.



**Figure S16:** Five hours of stability testing of printed patterns in water