Electronic Supplementary Information (ESI)

Single excitable dual emissive novel luminescent pigment to generate advanced security features for anti-counterfeiting applications

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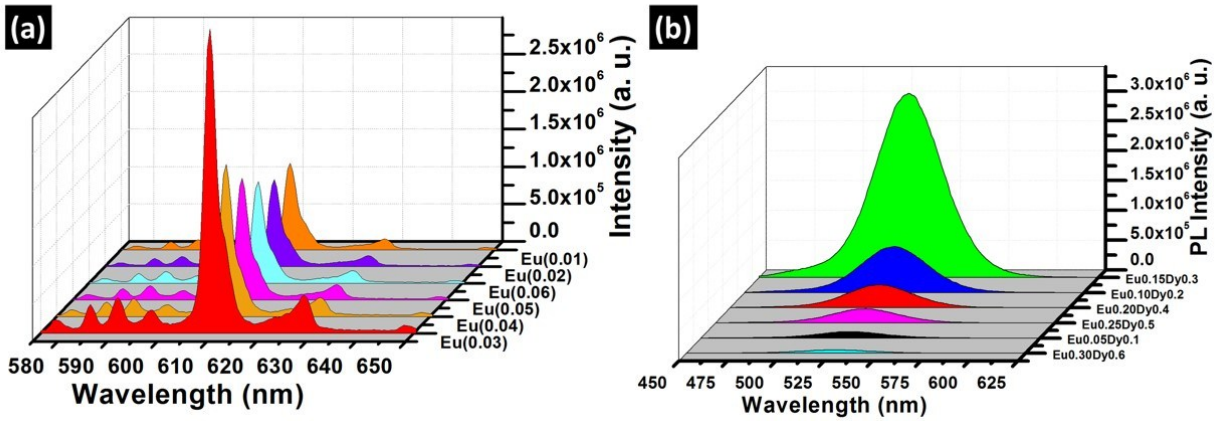
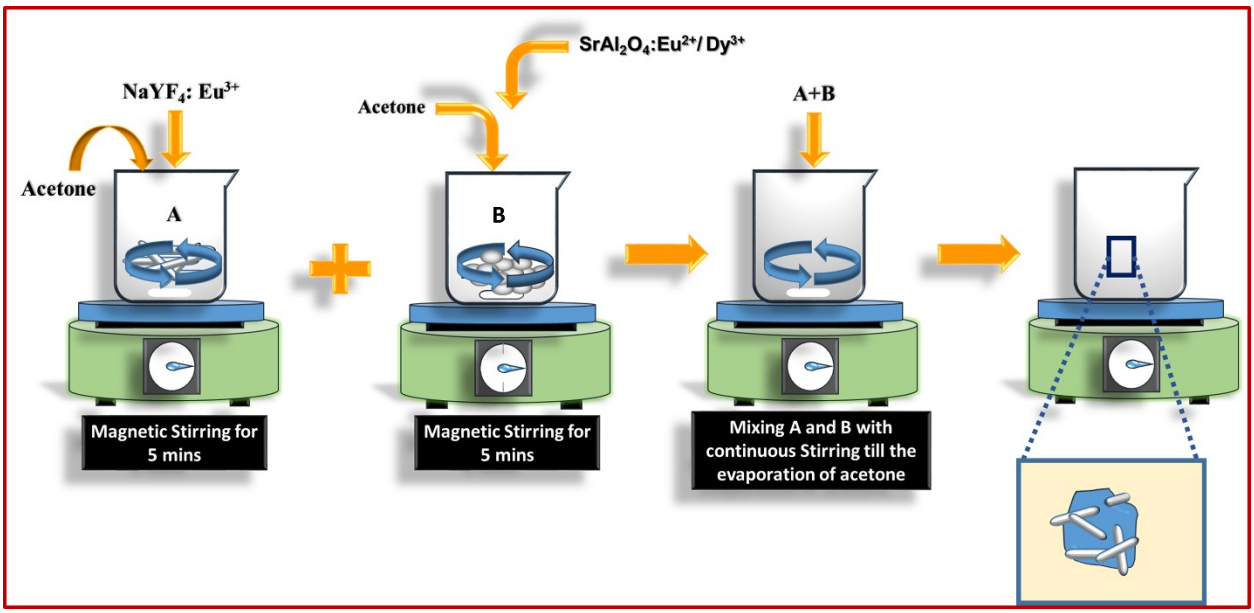
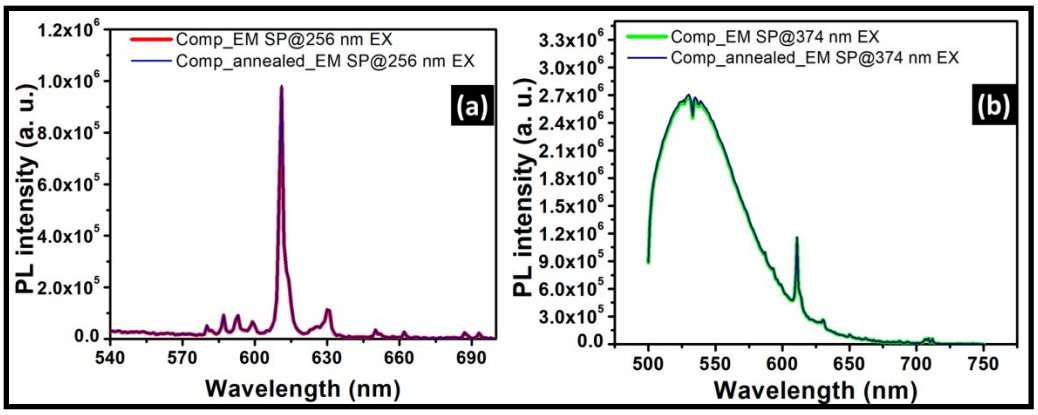
Table of contents:



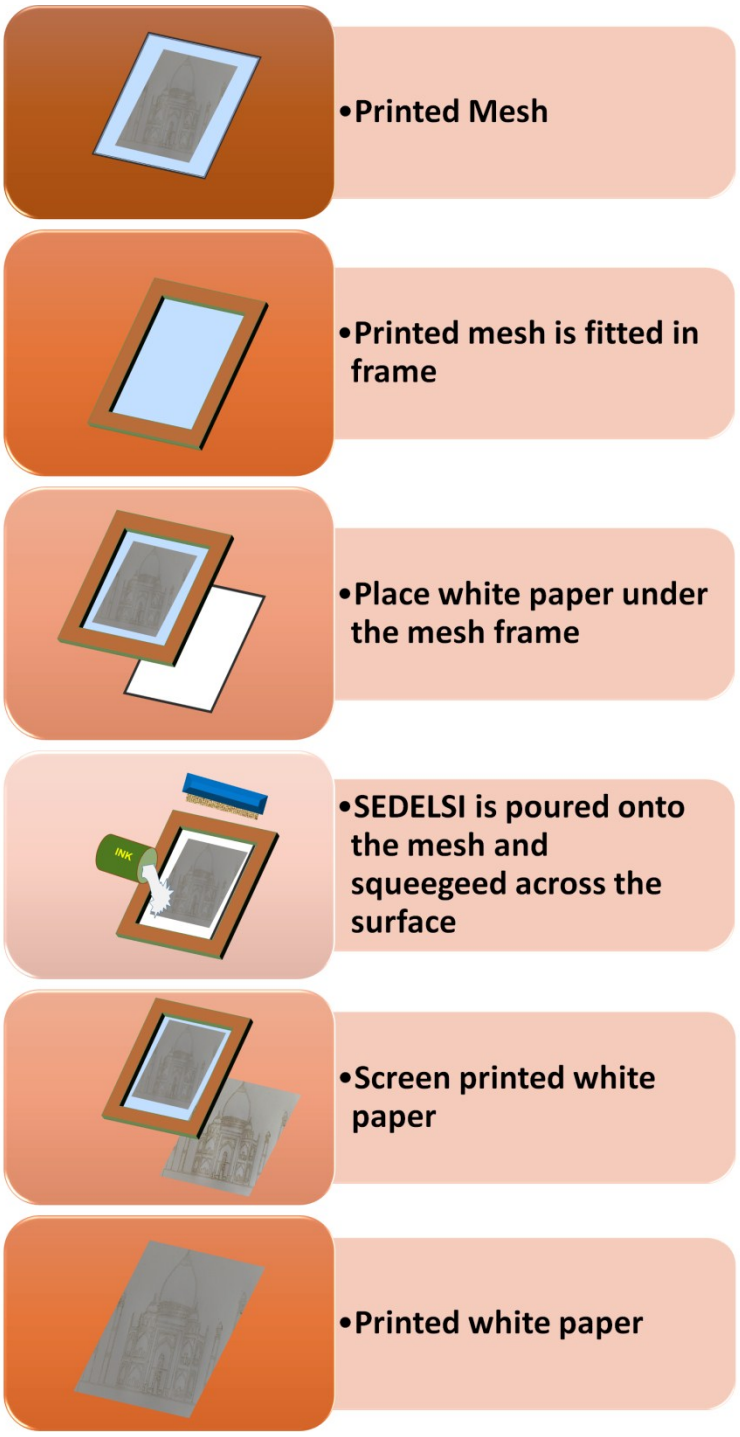
Supplementary Figure S1. PL intensity variation of a) $NaY_{1-x}F_4:Eu_x^{3+}$ phosphor at different concentration of Eu^{3+} atoms, b) $Sr_{1-x-y}Al_2O_4:Eu_x^{2+}/Dy_y^{3+}$ phosphor at different concentration of Eu^{2+} and Dy^{3+} atoms.



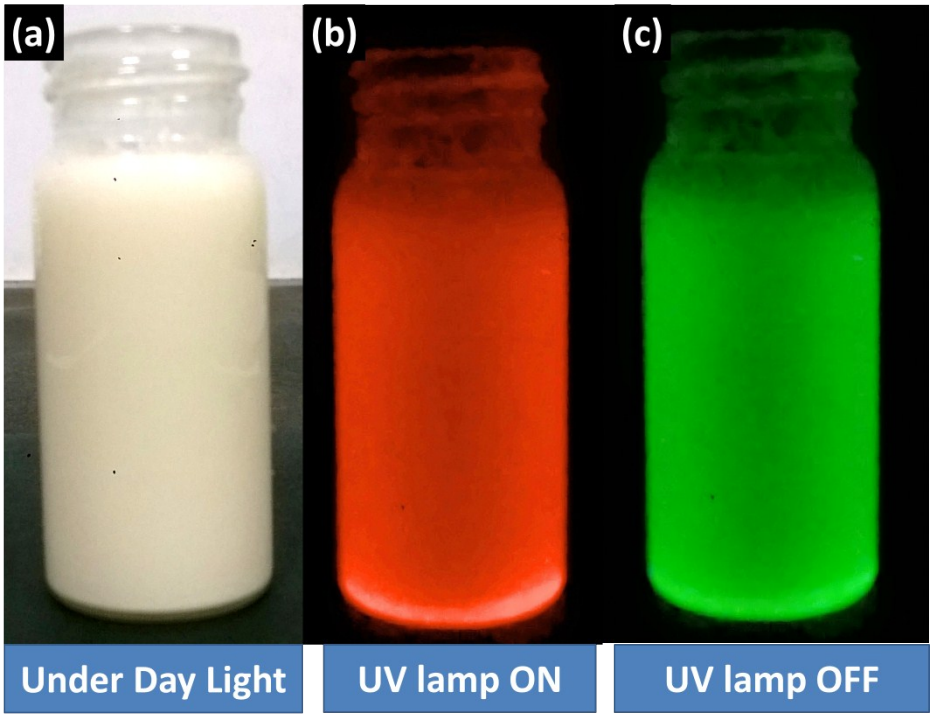
Supplementary Figure S2. Schematic for the synthesis of single excitable dual emissive luminescent pigment by facile combinatory admixing of $NaYF_4:Eu^{3+}$ and $SrAl_2O_4:Eu^{2+}/Dy^{3+}$ phosphors.



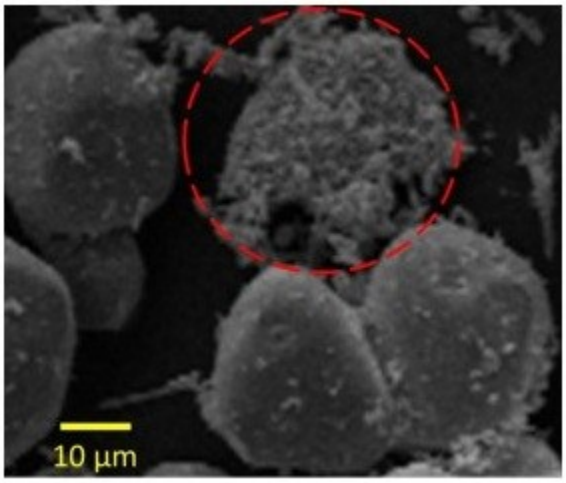
Supplementary Figure S3. Comparative PL emission spectra of (a) annealed and unannealed luminescent composite pigment of $NaYF_4:Eu^{3+}$@ $SrAl_2O_4:Eu^{2+},Dy^{3+}$ at 256 nm excitation (xenon lamp) wavelength and (b) annealed and unannealed luminescent composite pigment of $NaYF_4:Eu^{3+}$@ $SrAl_2O_4:Eu^{2+},Dy^{3+}$ at 374 nm excitation (xenon lamp) wavelength.



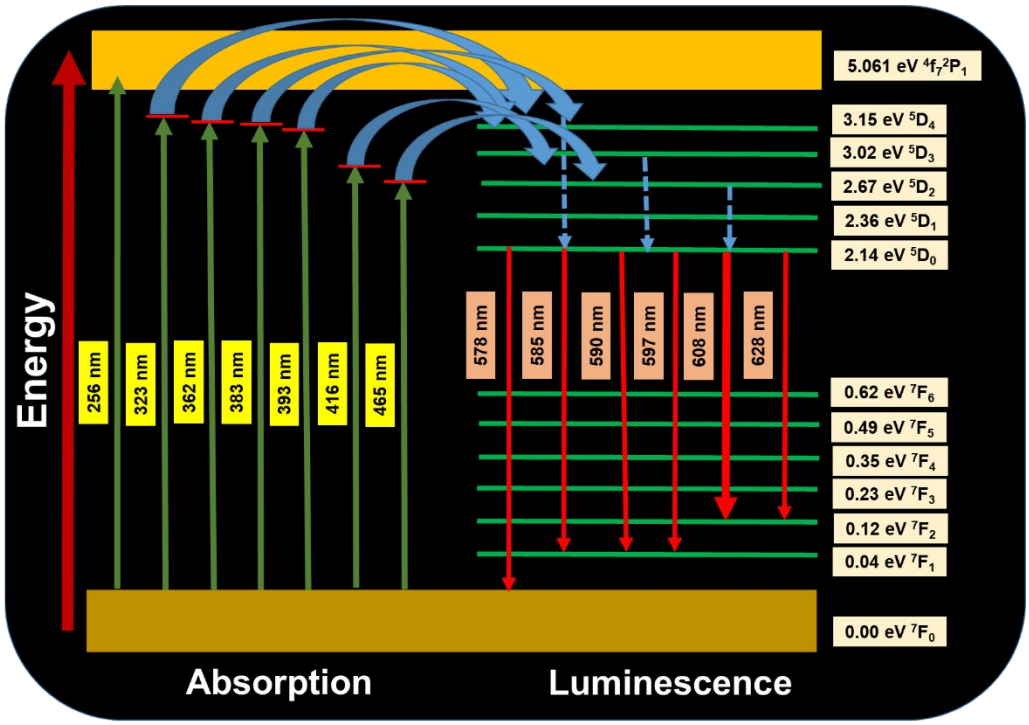
Supplementary Figure S4. Schematic illustration procedure of screen printing process on non-fluorescent white bond paper.



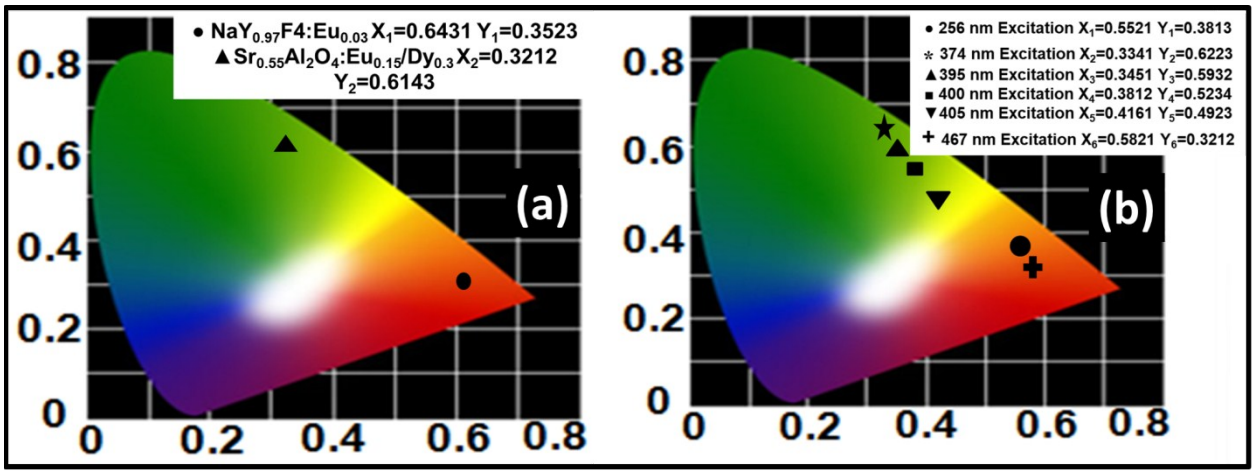
Supplementary Figure S5. Optical photographs of single excitable dual emissive luminescent security ink under a), b) and c) daylight, 254 nm UV lamp ON and OFF, respectively.



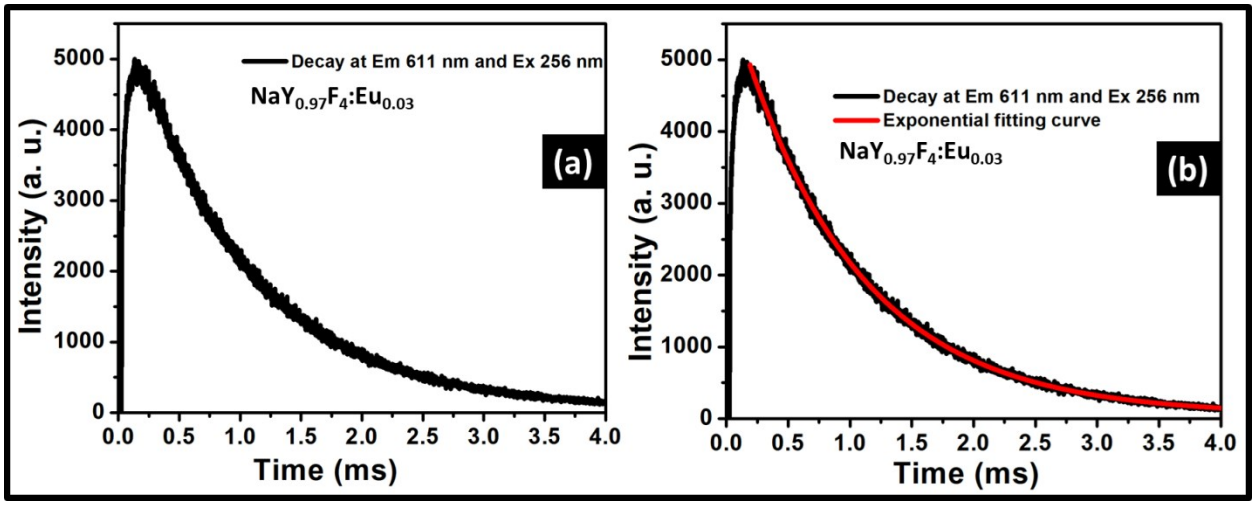
Supplementary Figure S6. SEM image of single excitable dual emissive unannealed luminescent pigment. The red marked encircled area shows the agglomerated rods of $NaYF_4$: Eu^{3+} phosphor which are not stuck with spherical $SrAl_2O_4$:Eu^{2+},Dy^{3+} phosphor.



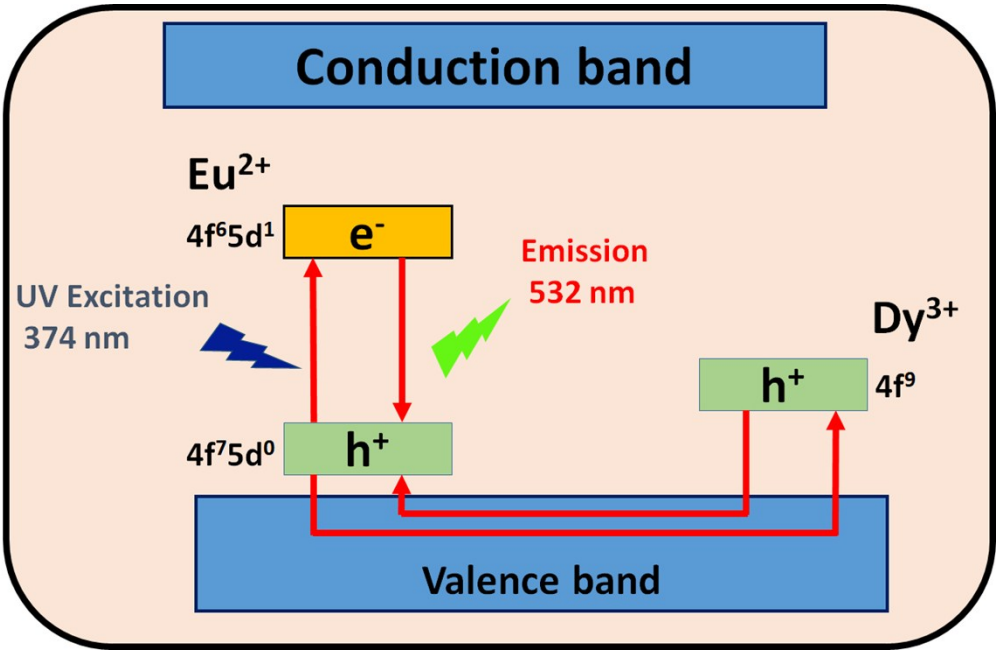
Supplementary Figure S7. Energy level diagram of $NaYF_4:Eu^{3+}$ phosphor.



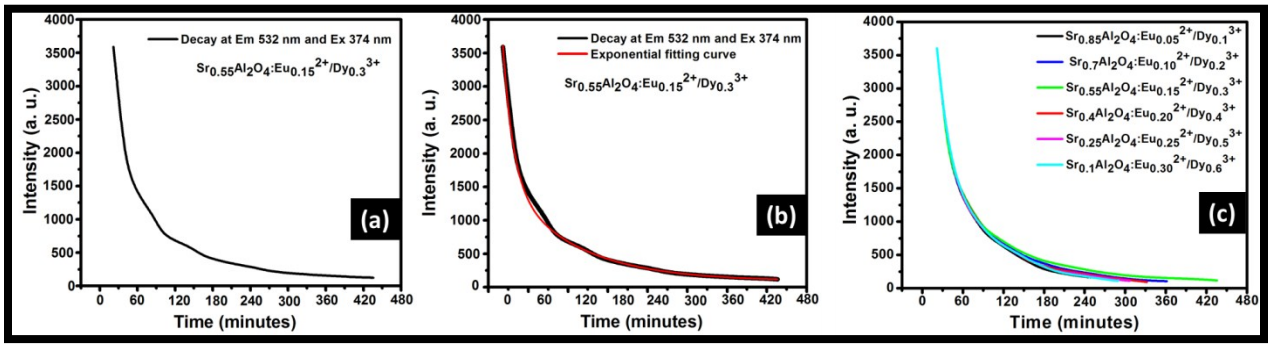
Supplementary Figure S8. CIE color coordinates of a) $NaY_{0.97}F_4:Eu_{0.03}^{3+}$ phosphor (red emission) and $Sr_{0.55}Al_2O_4:Eu_{0.15}^{2+}/Dy_{0.3}^{3+}$ phosphor (green emission) at the excitation wavelengths 256 (xenon lamp) and 374 nm (xenon lamp), respectively and b) single excitable dual emissive annealed luminescent pigment at the different excitation wavelengths of 256, 374, 395, 400, 405 and 467 nm.



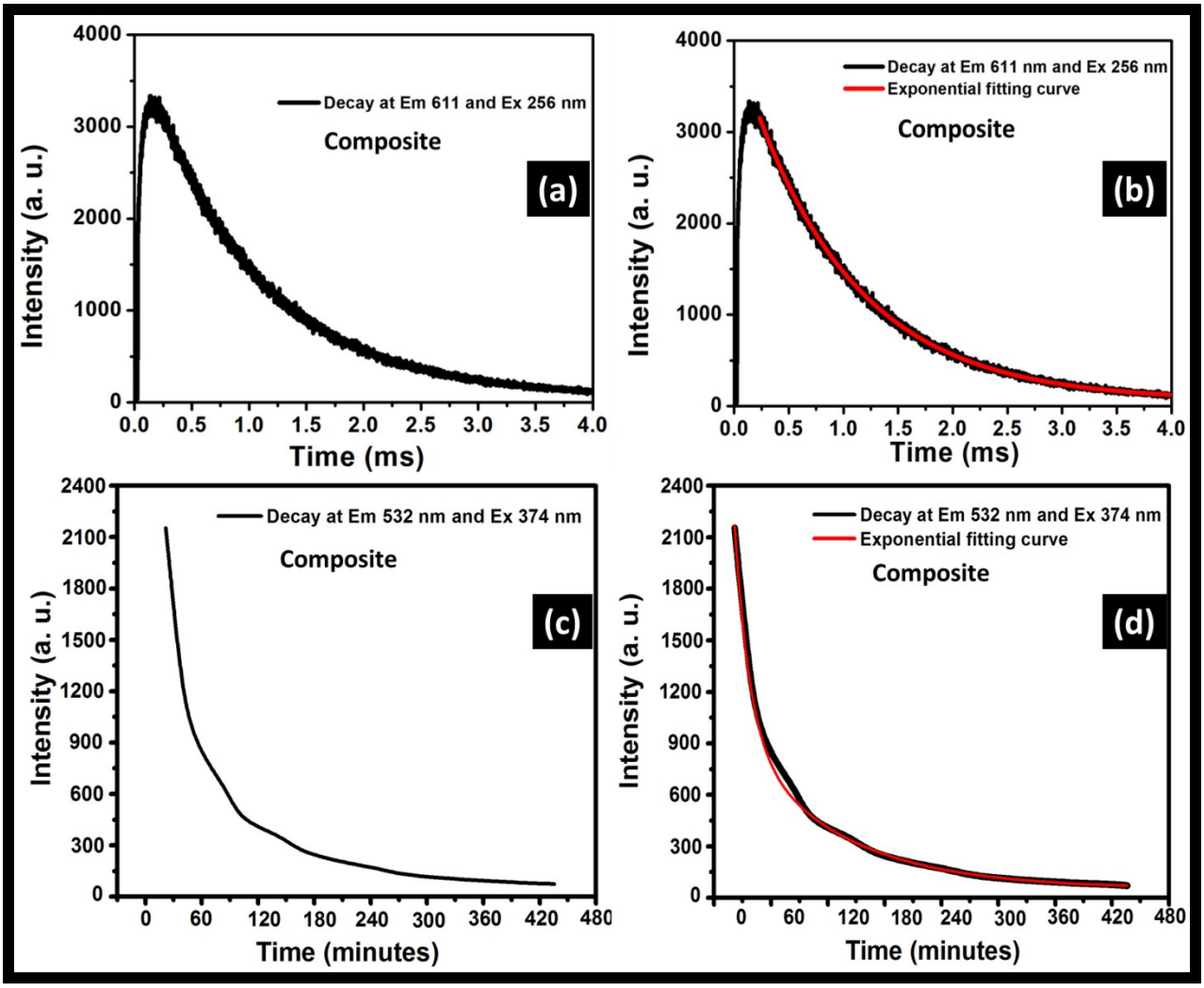
Supplementary Figure S9. a) TRPL decay profile of $NaY_{0.97}F_4$: $Eu_{0.03}^{3+}$ phosphor @ 611 nm emission wavelength upon an excitation wavelength of 256 nm (xenon lamp) and b) exponential fitting of the decay profile.



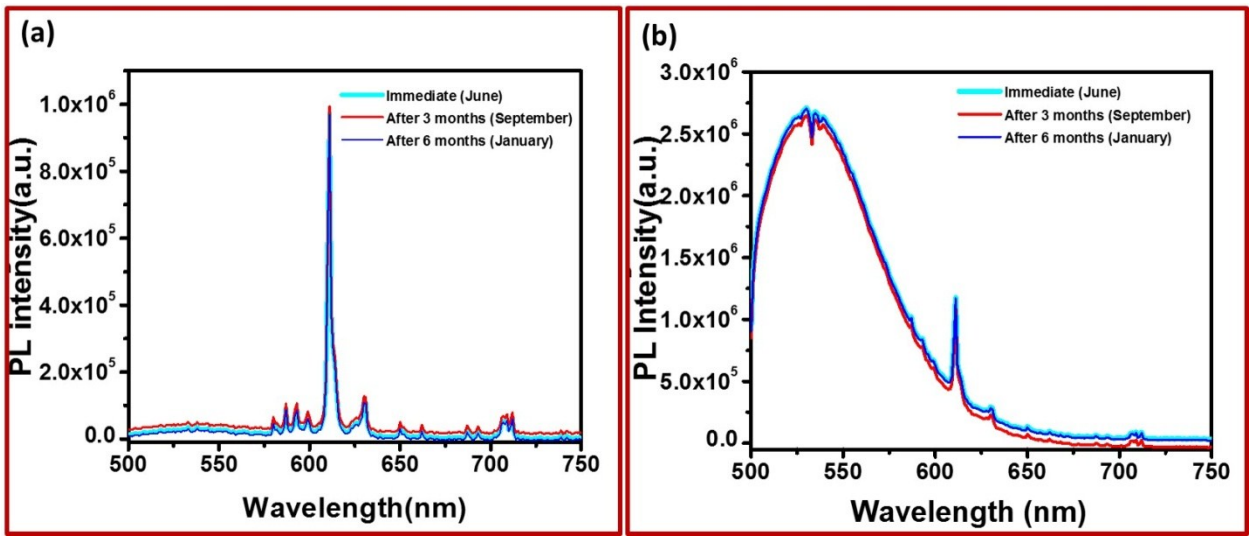
Supplementary Figure S10. Mechanism of long decay phosphorescence in $SrAl_2O_4:Eu^{2+}/Dy^{3+}$ phosphor.



Supplementary Figure S11. a) TRPL afterglow decay curve of the $Sr_{0.55}Al_2O_4:Eu_{0.15}^{2+}/Dy_{0.3}^{3+}$ phosphor after 15 min excitation with a 374 nm wavelength xenon flash lamp, it reveals a very broad time framed emission for more than 4 hours and b) decay curve with exponential fitting and c) TRPL decay profile of $SrAl_2O_4:Eu^{2+}/Dy^{3+}$ phosphor at the different concentrations of Eu and Dy atoms under the excitation wavelength 374 nm (xenon lamp) and 532 nm emission wavelength.

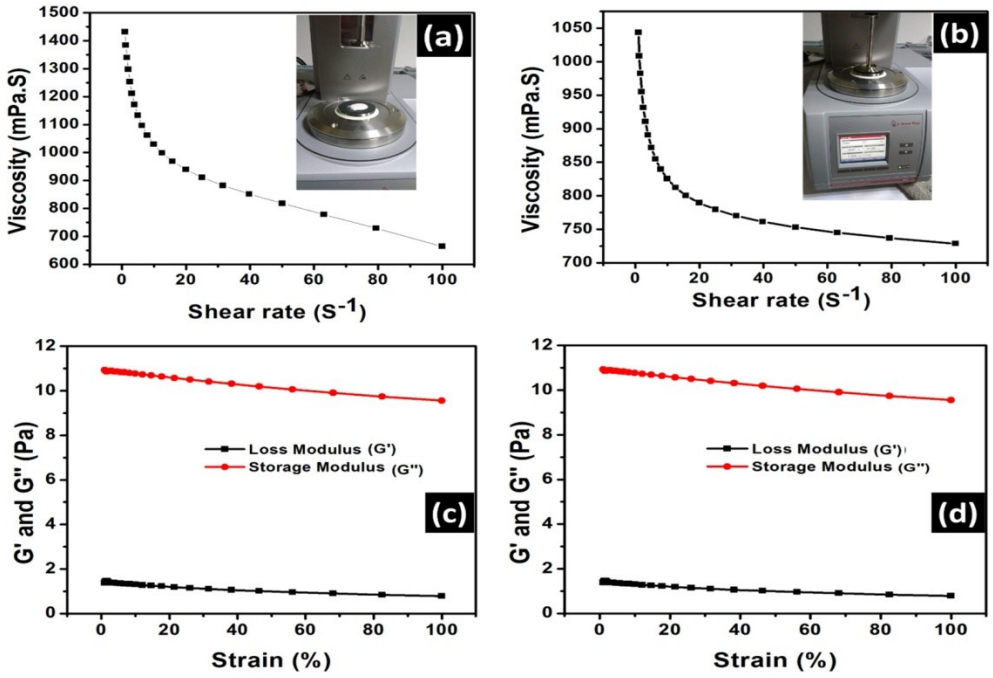


Supplementary Figure S12. a) TRPL decay profile of single excitable dual emissive luminescent pigment recorded at 611 nm emission wavelength upon an excitation wavelength of 256 nm (xenon lamp), b) exponential fitting of the decay profile of single excitable dual emissive annealed luminescent pigment upon 611 nm emission and 256 nm excitation (xenon lamp) wavelength, c) TRPL decay profile of single excitable dual emissive annealed luminescent pigment recorded at 532 nm emission wavelength upon an excitation wavelength of 374 nm (xenon lamp) and d) exponential fitting of the decay profile of single excitable dual emissive annealed luminescent pigment upon 532 nm emission and 374 nm(xenon lamp) excitation wavelength.

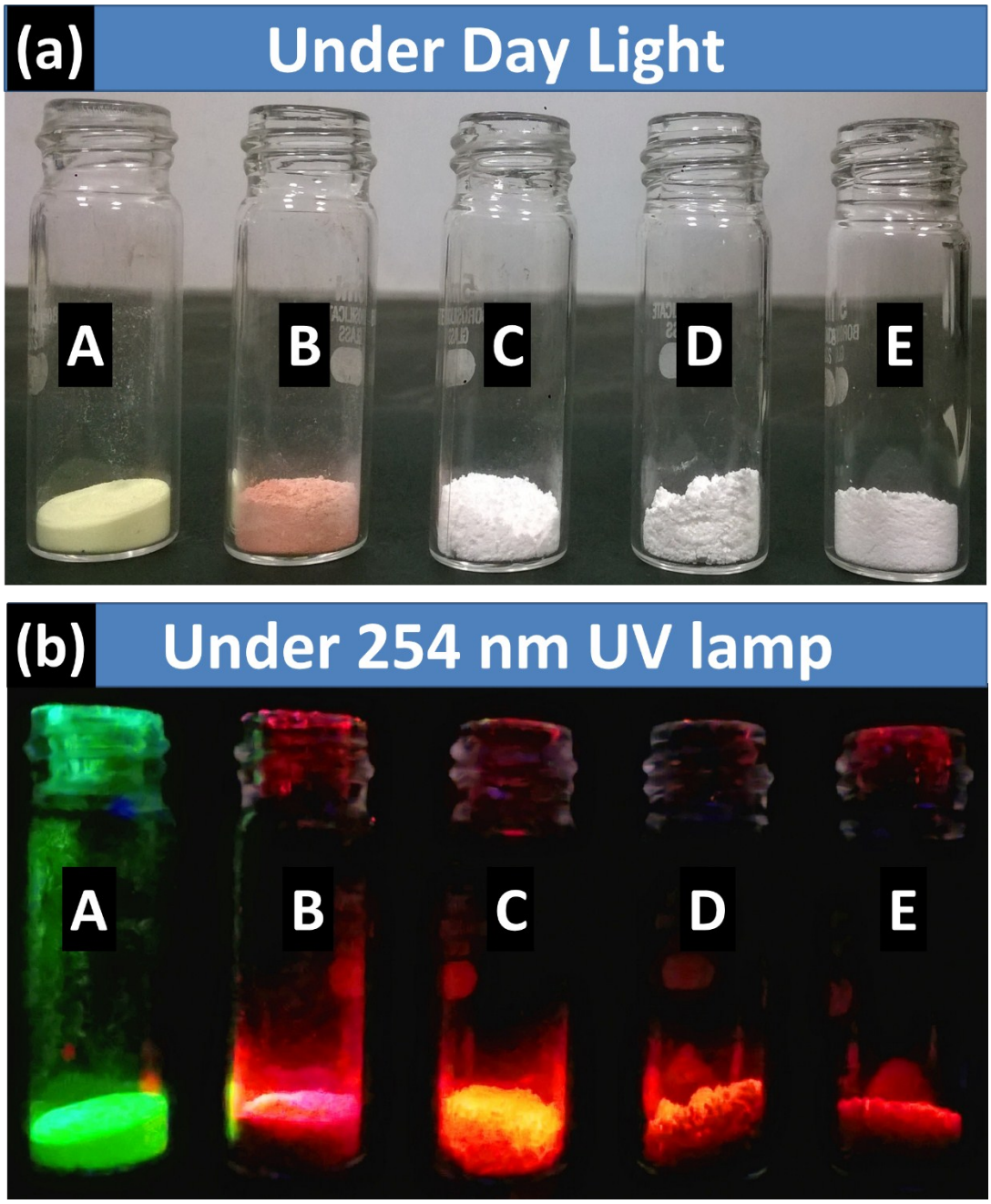


Supplementary Figure S13. PL emission spectra of printed image using single excitable dual emissive luminescent security ink under different weather conditions in the presence of 254 nm UV lamp a) ON and b) OFF.

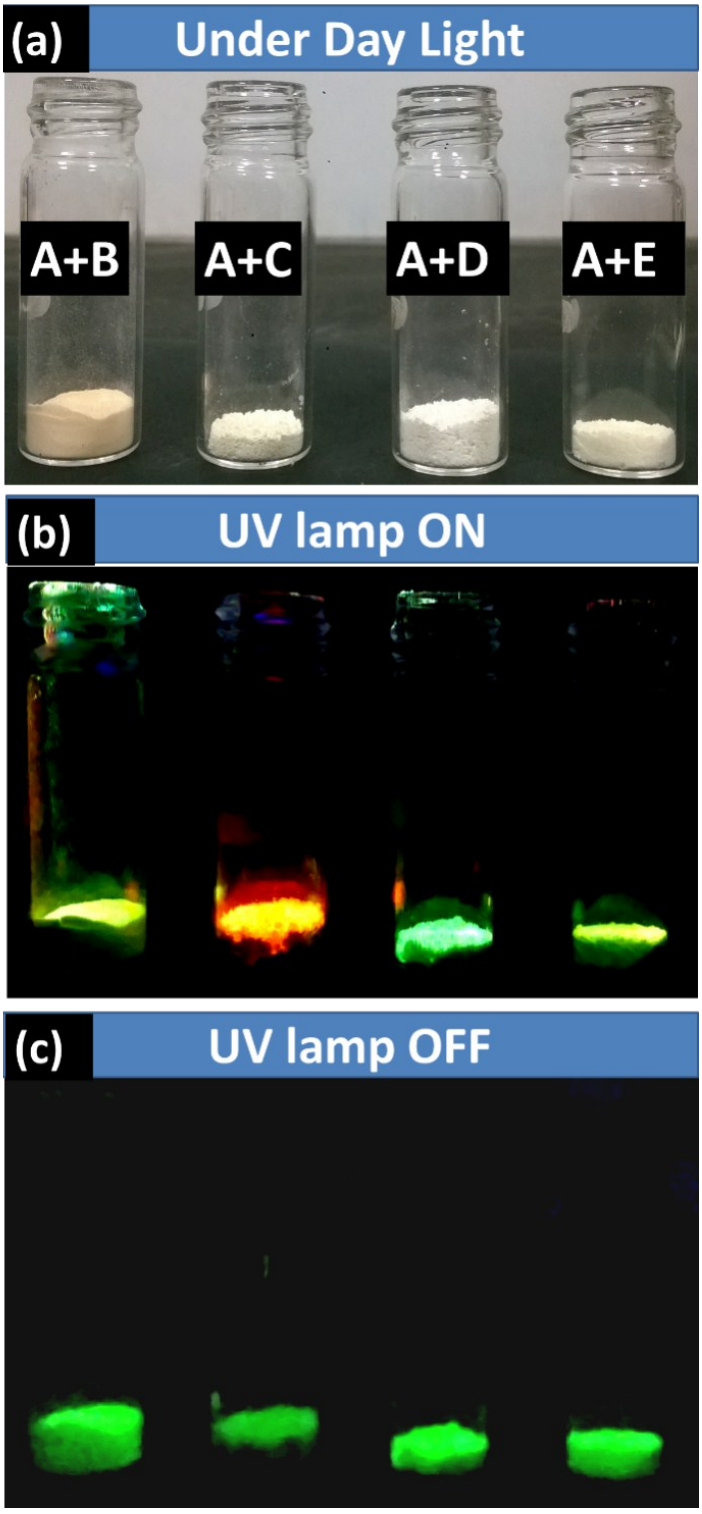
We have taken the PL spectra from same height and area in all three cases including all conditions similar for comparative study to confirm the stability of PL. We have also calibrated the equipment using standard quinine sulfate as reference material for PL before performing PL measurement.



Supplementary Figure S14. a) and b) viscosity at different shear stress rate of single excitable dual emissive luminescent security ink at immediately synthesized ink formation time and after 6 months duration, respectively; the inset of a) and b) shows the optical photographs of sample holder of rheometer on which single excitable dual emissive luminescent security ink is placed, c) and d) shows the dynamic viscoelastic properties of the single excitable dual emissive luminescent security ink at immediately synthesized ink formation time and after 6 months duration, respectively.



Supplementary Figure S15. Optical photographs of (A) $SrAl_2O_4:Eu^{2+}/Dy^{3+}$ phosphor, (B) $Eu(TTA)_3Phen$, (C) $NaYF_4:Eu^{3+}$ phosphor, (D) $YBO_3:Eu^{3+}$ phosphor and (E) $Y_2O_3:Eu^{3+}$ phosphor under a) daylight and b) 254 nm UV lamp, respectively.



Supplementary Figure S16. Optical photographs of A+B, A+C, A+D, A+E composite pigments; a), b) and c) under daylight, 254 nm UV lamp ON and OFF, respectively.

Table. 1: Synthesis of $NaY_{0.97}F_4$: $Eu^{3+}_{0.03}$ by taking different amounts of raw materials.

For 3 mol % doping concentration of Eu in $NaYF_4$ ($NaY_{0.97}F_4$:$Eu^{3+}_{0.03}$)			
NaF (amount in g)	**Y_2O_3** (amount in g)	**Eu_2O_3**(amount in g)	**$NaYF_4$:Eu^{3+}** (amount in g)
0.4198	1.095	0.0527	1.254
41.98	109.5	5.27	125.4
167.92	438	21.08	501.6
335.84	876	42.16	1003.2

Table. 2: Synthesis of $Sr_{0.55}Al_2O_4$:$Eu^{2+}_{0.15}$/$Dy^{3+}_{0.30}$ by taking different amounts of raw materials.

For 15 mol % and 30 mol % doping concentration of Eu and Dy, respectively in $SrAl_2O_4$ ($Sr_{0.55}Al_2O_4$:$Eu^{2+}_{0.15}$/$Dy^{3+}_{0.30}$)				
$SrCO_3$ (amount in g)	**Al_2O_3** (amount in g)	**Eu_2O_3** (amount in g)	**Dy_2O_3** (amount in g)	**$SrAl_2O_4$:Eu^{2+}/Dy^{3+}** (amount in g)
0.8119	0.5098	0.2639	0.559	1.93
81.19	50.98	26.39	55.947	193.05
324.76	203.92	105.56	223.78	772.28
649.52	407.84	211.12	447.57	1544.44

Table. 3: Synthesis of $NaY_{0.97}F_4$: $Eu^{3+}_{0.03}$ @ $Sr_{0.55}Al_2O_4:Eu^{2+}_{0.15}/Dy^{3+}_{0.30}$ annealed luminescent composite pigment by taking different amounts of $NaY_{0.97}F_4:Eu^{3+}_{0.03}$ and $Sr_{0.55}Al_2O_4:Eu^{2+}_{0.15}/Dy^{3+}_{0.30}$ in 3:1 Weight ratio .

3:1 ratio of $NaY_{0.97}F_4:Eu^{3+}_{0.03}$ and $Sr_{0.55}Al_2O_4:Eu^{2+}_{0.15}/Dy^{3+}_{0.30}$ phosphor		
$NaY_{0.97}F_4:Eu^{3+}_{0.03}$ (amount in g)	**$Sr_{0.55}Al_2O_4:Eu^{2+}_{0.15}/Dy^{3+}_{0.30}$** (amount in g)	**SEDELP** (amount in g)
1.254	1.930	3.184
125.4	193.05	318.45
501.6	772.218	1273.81
1003.2	1544.44	2547.64

Table. 4: Ratio of intensities at 532 and 611 nm wavelengths.

Excitation Wavelength (nm)	**Intensity I_1 at 532 nm wavelength (a. u.)**	**Intensity I_2 at 611 nm wavelength (a. u.)**	**I_2/ I_1**
256	35552.64	973745.09	27.388
374	2678774.61	1148310.89	0.428
395	2415494.25	3103914.25	1.285
400	2290614.19	3163964.37	1.381
405	2187527.31	1825939.16	0.834
467	124003.614	3970348.85	32.018

Table S5: Ratio of PL intensities of individual phosphor and annealed luminescent composite pigments.

Materials	**PL Intensity (a. u.)** $NaYF_4:Eu^{3+}$ (256 nm)	**PL Intensity (a. u.)** $SrAl_2O_4:Eu^{2+}/Dy^{3+}$ (374 nm)
Individual phosphors	$I_1=2.7*10^6$	$I_3= 2.7*10^6$
single excitable dual emissive luminescent pigment	$I_2= 1.7*10^6$	$I_4= 2.3*10^6$
	$I_1/I_2 = 1.6$	$I_3/I_4 = 1.1$