

Supporting Information

Color Tunable Upconversion Luminescent Perovskite Fluoride with Long-/Short-Lived Emissions toward Multiple Anti-counterfeiting

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Table S1 CIE chromaticity coordinates for $\text{KCdF}_3:2\% \text{Yb}^{3+}, 5\% \text{Mn}^{2+}, x\text{Ln}^{3+}$ ($x=0-2\%$)

Serial number	Ln^{3+} content (x)	CIE(X,Y)- $\text{KCdF}_3:2\% \text{Yb}^{3+}, 5\% \text{Mn}^{2+}, x\text{Ln}^{3+}$,		
		Er^{3+}	Ho^{3+}	Tm^{3+}
1	0%	(0.4438,0.5488)	(0.4716,0.5240)	(0.4712,0.5241)
2	0.001%	(0.4598,0.5346)	(0.4546,0.5399)	(0.4628,0.5201)
3	0.01%	(0.4786,0.5143)	(0.3744,0.6455)	(0.4449,0.5043)
4	0.1%	(0.5259,0.4667)	(0.3228,0.6641)	(0.3881,0.4280)
5	0.5%	-	-	(0.3629,0.4025)
6	1%	(0.5832,0.4100)	(0.3006,0.6855)	(0.3057,0.3221)
7	2%	(0.6289,0.3654)	(0.3182,0.6672)	(0.3896,0.4397)

Table S2 CIE chromaticity coordinates for $\text{KCdF}_3:2\% \text{Yb}^{3+}, \text{Ln}^{3+}, y\text{Mn}^{2+}$ ($y=0-97.95\%$)

Serial number	Mn^{2+} content (y)	CIE(X,Y)- $\text{KCdF}_3:2\% \text{Yb}^{3+}, \text{Ln}^{3+}, y\text{Mn}^{2+}$		
		1% Er^{3+}	0.1% Ho^{3+}	0.05% Tm^{3+}
1	0%	(0.4533,0.5314)	(0.2592,0.7242)	(0.1602,0.1137)
2	1%	(0.4779,0.5110)	(0.2668,0.7179)	(0.2893,0.2910)
3	5%	(0.5551,0.4372)	(0.3085,0.6781)	(0.4139,0.4666)
4	15%	(0.6504,0.3451)	(0.3446,0.6420)	(0.2913,0.2900)
5	30%	(0.6913,0.3053)	(0.4431,0.5468)	(0.1959,0.1581)
6	50%	(0.7134,0.2828)	(0.6227,0.3682)	(0.2187,0.1740)
7	70%	(0.7200,0.2767)	(0.6968,0.2957)	(0.2492,0.1837)
8	97/97.9/97.95%	(0.7168,0.2799)	(0.7118,0.2811)	(0.4278,0.3218)

Table S3 Pump power dependent CIE chromaticity coordinates for $\text{KCdF}_3:2\% \text{Yb}^{3+}, 5\% \text{Mn}^{2+}, \text{Ln}^{3+}$

2% $\text{Yb}^{3+}, 5\% \text{Mn}^{2+}, 0.01\% \text{Er}^{3+}$		2% $\text{Yb}^{3+}, 5\% \text{Mn}^{2+}, 0.01\% \text{Ho}^{3+}$		2% $\text{Yb}^{3+}, 5\% \text{Mn}^{2+}, 0.05\% \text{Tm}^{3+}$	
Power(mW)	CIE(X,Y)	Power(mW)	CIE(X,Y)	Power(mW)	0.05% Tm^{3+}
36	(0.5163,0.4792)	94	(0.3618,0.6266)	151	(0.4578,0.5027)
94	(0.5028,0.4929)	212	(0.3648,0.6250)	510	(0.4531,0.4998)
153	(0.4978,0.4976)	329	(0.3658,0.6241)	910	(0.4472,0.4940)
212	(0.4893,0.5053)	446	(0.3668,0.6230)	1300	(0.4433,0.4892)
270	(0.4814,0.5125)	563	(0.3677,0.6219)	1700	(0.4378,0.4858)
329	(0.4772,0.5160)	681	(0.3689,0.6207)	2100	(0.4340,0.4845)
387	(0.4706,0.5219)	798	(0.3705,0.6189)	2510	(0.4323,0.4845)
446	(0.4639,0.5277)	915	(0.3726,0.6167)	-	-
-	-	1033	(0.3748,0.6143)	-	-

Table S4 Temperature dependent CIE chromaticity coordinates for $\text{KCaF}_3:2\% \text{Yb}^{3+}, 5\% \text{Mn}^{2+}, \text{Ln}^{3+}$

Serial number	Temperature (K)	CIE(X,Y)- $\text{KCaF}_3:2\% \text{Yb}^{3+}, 5\% \text{Mn}^{2+}, \text{Ln}^{3+}$		
		0.01% Er^{3+}	0.01% Ho^{3+}	0.05% Tm^{3+}
1	RT	(0.4975,0.4982)	(0.4122,0.5803)	(0.4255,0.4680)
2	348	(0.4895,0.5045)	(0.4000,0.5915)	(0.4087,0.4725)
3	398	(0.4779,0.5140)	(0.3869,0.6031)	(0.4045,0.4827)
4	448	(0.4681,0.5212)	(0.3836,0.6048)	(0.3996,0.4894)
5	498	(0.4634,0.5227)	(0.3854,0.6008)	(0.3946,0.4981)
6	548	(0.4604,0.5145)	(0.3904,0.5896)	(0.3903,0.4996)
7	573	(0.4579,0.5181)	(0.3908,0.5811)	(0.3819,0.4651)

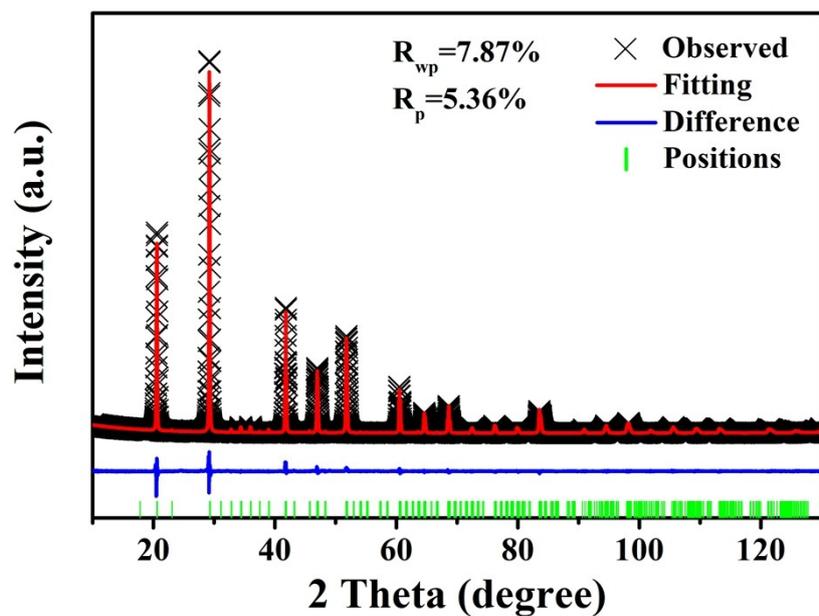


Fig. S1 XRD Rietveld refinement for the host KCdF_3 . (The structure model is based on the crystallographic data of KCdF_3 with space group Pbnm)

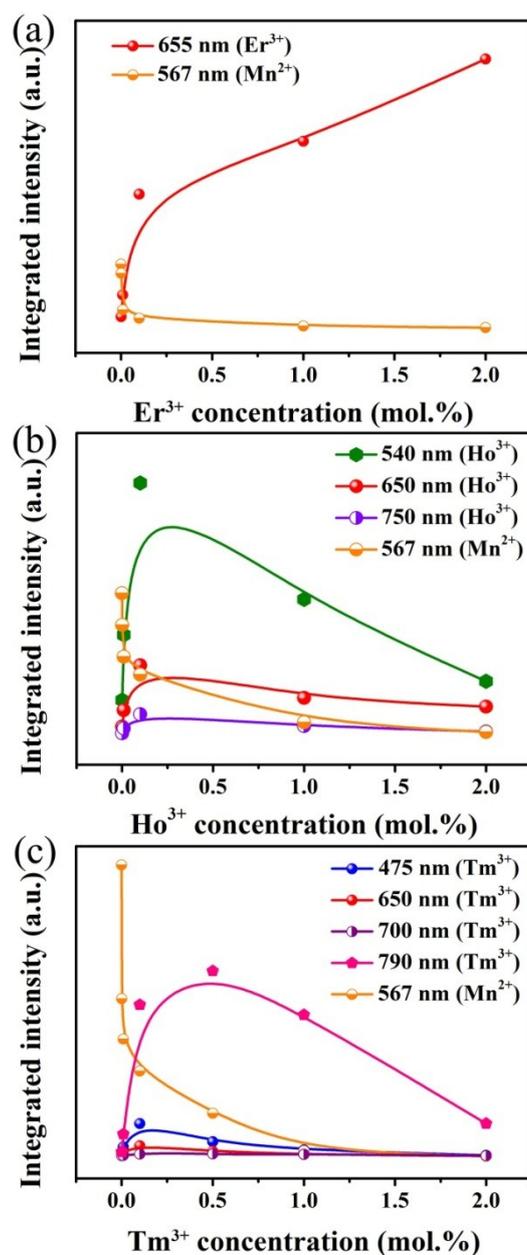


Fig. S2 Integrated intensity for different UC emission peaks of UCNPs (a) $\text{KCdF}_3:2\% \text{Yb}^{3+}, 5\% \text{Mn}^{2+}, x\text{Er}^{3+}$, (b) $\text{KCdF}_3:2\% \text{Yb}^{3+}, 5\% \text{Mn}^{2+}, x\text{Ho}^{3+}$, (c) $\text{KCdF}_3:2\% \text{Yb}^{3+}, 5\% \text{Mn}^{2+}, x\text{Tm}^{3+}$ ($x=0-2\%$).

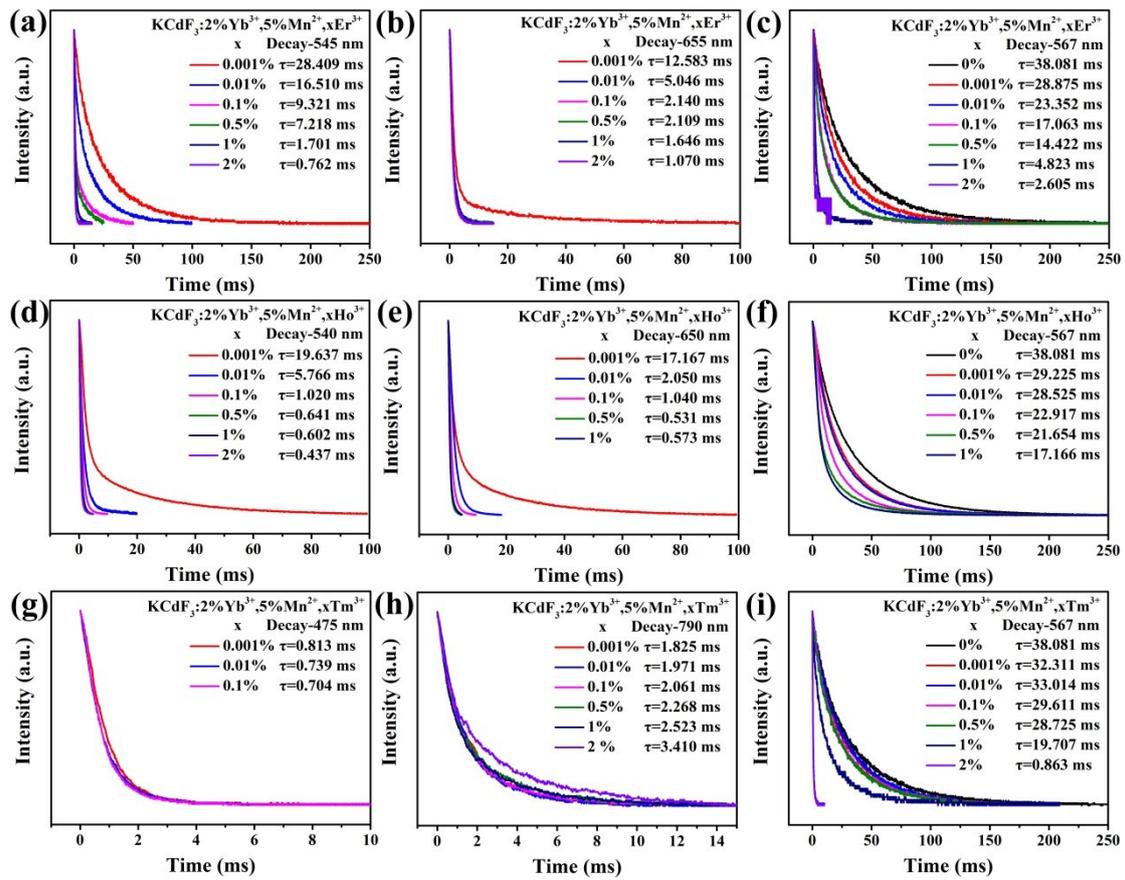


Fig. S3 UC luminescence decay curves for different emission peaks in $\text{KCdF}_3:2\% \text{Yb}^{3+}, 5\% \text{Mn}^{2+}, x \text{Ln}^{3+}$ ($\text{Ln}=\text{Er}, \text{Ho}, \text{Tm}, x=0-2\%$).

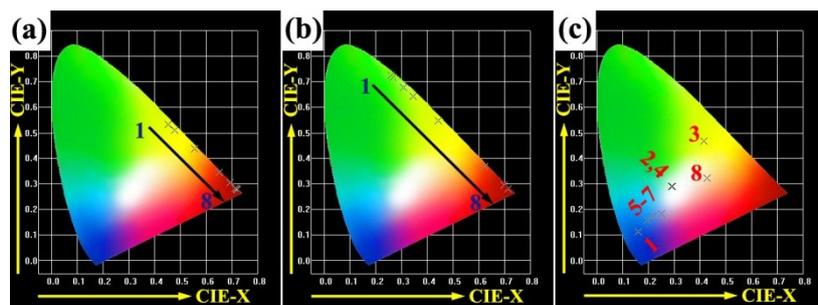


Fig. S4 CIE chromaticity diagram for UCNPs (a) $\text{KCdF}_3:2\% \text{Yb}^{3+}$, $1\% \text{Er}^{3+}$, γMn^{2+} , (b) $\text{KCdF}_3:2\% \text{Yb}^{3+}$, $0.1\% \text{Ho}^{3+}$, γMn^{2+} , (c) $\text{KCdF}_3:2\% \text{Yb}^{3+}$, $0.05\% \text{Tm}^{3+}$, γMn^{2+} ($\gamma=0-97.95\%$). The serial number “1-8” represents the samples with increasing doping concentration of Mn^{2+} . The corresponding compositions and CIE chromaticity coordinates can be seen in Table S2.

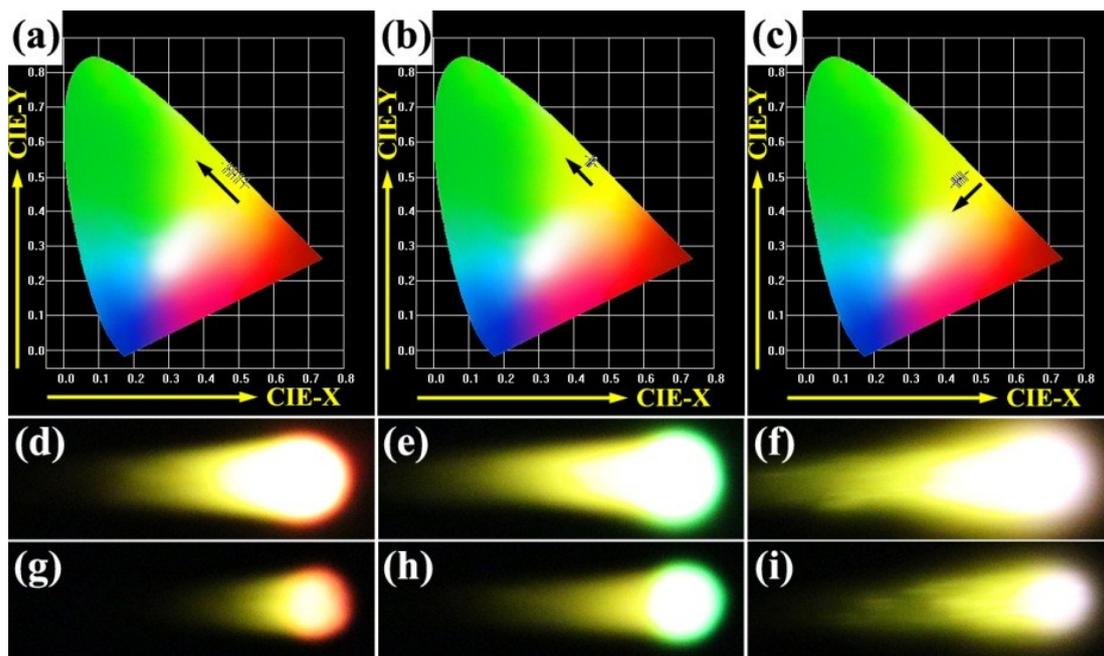


Fig. S5 Pump power dependent CIE chromaticity diagram for UCNPs (a) $\text{KCdF}_3:2\%\text{Yb}^{3+}$, $5\%\text{Mn}^{2+}$, $0.01\%\text{Er}^{3+}$, (b) $\text{KCdF}_3:2\%\text{Yb}^{3+}$, $5\%\text{Mn}^{2+}$, $0.01\%\text{Ho}^{3+}$, (c) $\text{KCdF}_3:2\%\text{Yb}^{3+}$, $5\%\text{Mn}^{2+}$, $0.05\%\text{Tm}^{3+}$; and the corresponding luminescent photographs excited under different power density (d-f) $\sim 13.41 \text{ W/cm}^2$, (g-i) $\sim 4.68 \text{ W/cm}^2$. The spot size is about 3.5 mm and the average speed of the 980 nm LD is about 2.57 cm/s.

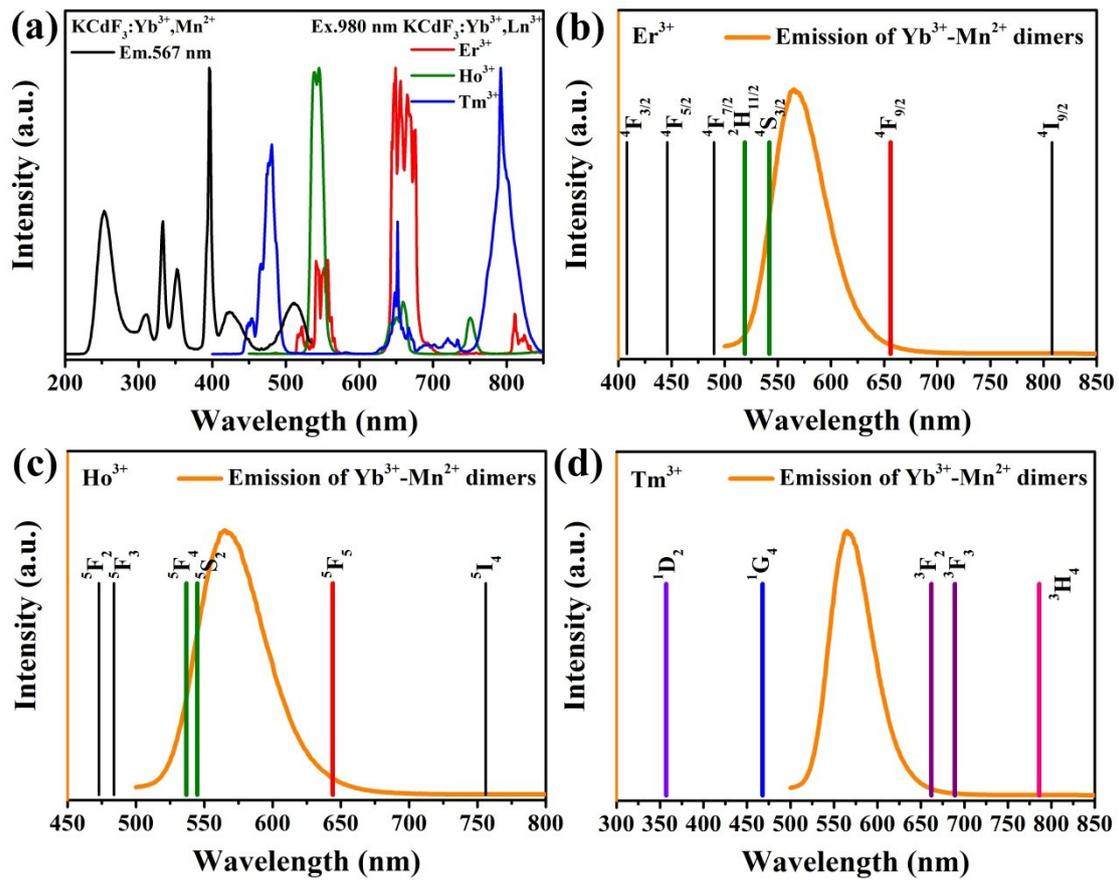


Fig. S6 (a) The normalized excitation spectrum of Mn²⁺ and the normalized UC spectra of Ln³⁺ (Er³⁺, Tm³⁺, Ho³⁺) upon the excitation of the 980 nm LD. (b-d) The UC spectra of Mn²⁺ as well as the energy level of Ln³⁺ (Er³⁺, Ho³⁺, Tm³⁺ for Fig. S6b-d, respectively).

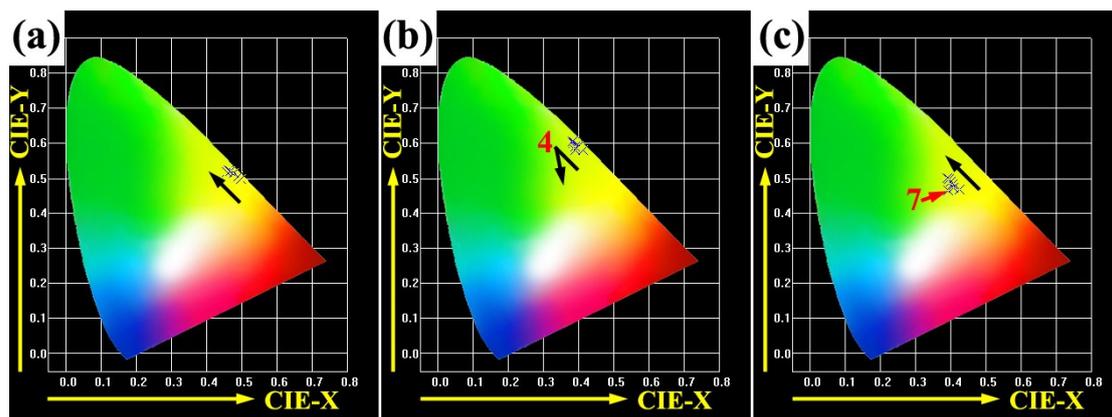


Fig. S7 Temperature dependent CIE chromaticity diagram for UCNPs (a) $\text{KCdF}_3:2\% \text{Yb}^{3+}$, $5\% \text{Mn}^{2+}$, $0.01\% \text{Er}^{3+}$, (b) $\text{KCdF}_3:2\% \text{Yb}^{3+}$, $5\% \text{Mn}^{2+}$, $0.01\% \text{Ho}^{3+}$, (c) $\text{KCdF}_3:2\% \text{Yb}^{3+}$, $5\% \text{Mn}^{2+}$, $0.05\% \text{Tm}^{3+}$. The compositions of the samples named certain serial numbers can be seen in Table S4.

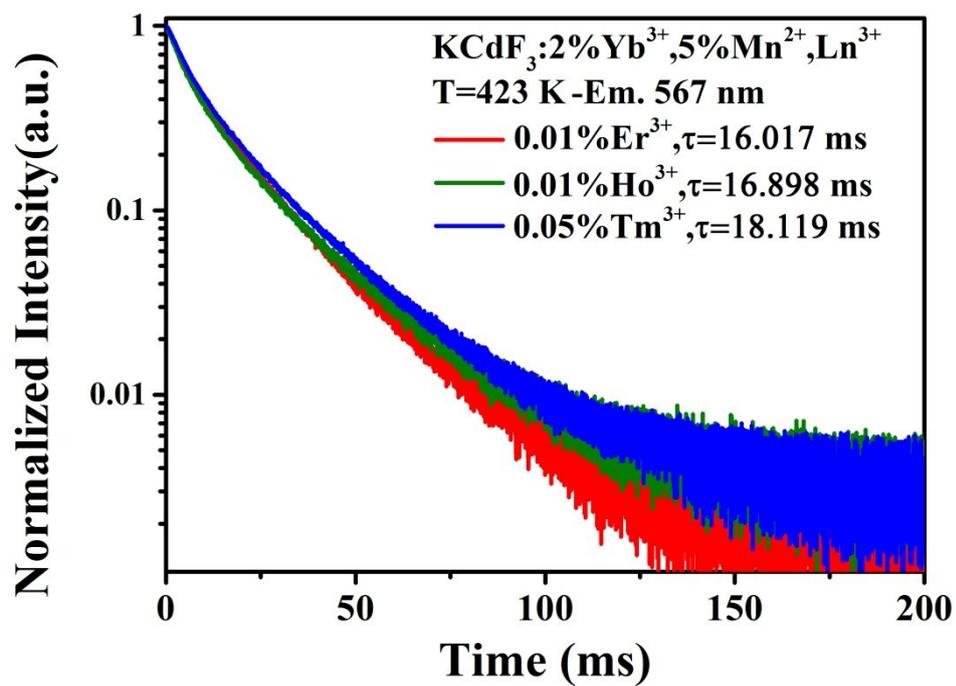


Fig. S8 UC decay curves for emission 567 nm (Mn²⁺) in KCdF₃:2%Yb³⁺,5%Mn²⁺,Ln³⁺ (Ln³⁺=0.01%Er³⁺/0.01%Ho³⁺/0.05%Tm³⁺) at the temperature of 423 K.

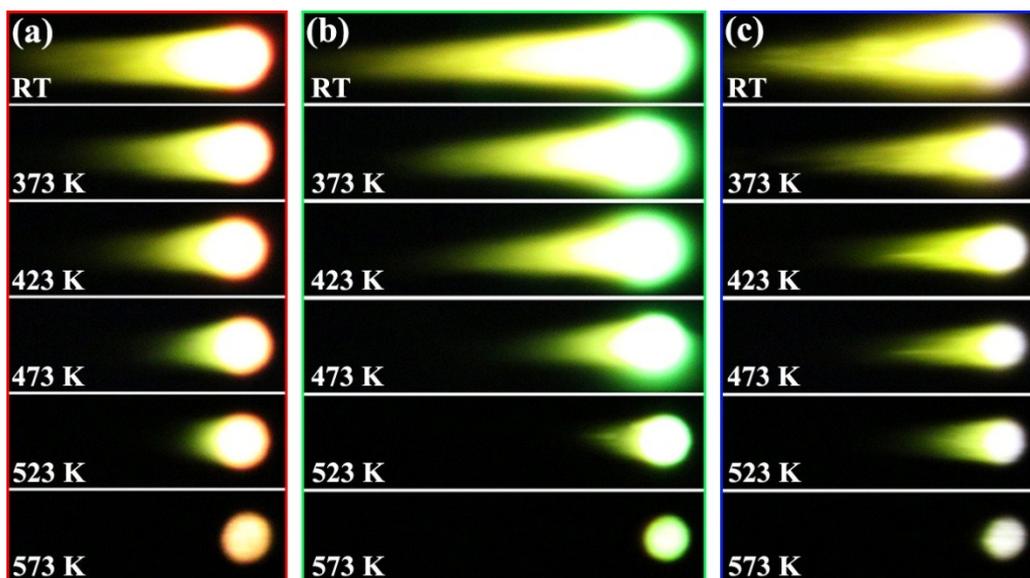


Fig. S9 Temperature dependent luminescent photographs of UCNPs (a) $\text{KCdF}_3:2\% \text{Yb}^{3+}$, $5\% \text{Mn}^{2+}$, $0.01\% \text{Er}^{3+}$, (b) $\text{KCdF}_3:2\% \text{Yb}^{3+}$, $5\% \text{Mn}^{2+}$, $0.01\% \text{Ho}^{3+}$, (c) $\text{KCdF}_3:2\% \text{Yb}^{3+}$, $5\% \text{Mn}^{2+}$, $0.05\% \text{Tm}^{3+}$. The pump power density, the spot size and the average speed of the 980 nm LD are about 13.41 W/cm^2 , 3.5 mm and 2.57 cm/s, respectively.