Supporting information

Structure, Enhancement and white luminescence of multifunctional $Lu_6O_5F_8$:20%Yb^{3+},1%Er^{3+} (Tm^{3+}) nanoparticles via further doping Li^+ under different excitation sources

Linna Guo, Yuhua Wang*, Yanzhao Wang, Jia Zhang, Pengyu Dong and Wei Zeng

Department of Materials Science, School of Physical Science and Technology, Lanzhou University, Lanzhou, 730000, People's Republic of China

* Corresponding author. Tel.:+86 931 8912772.
Fax: +86 931 8913554.
E -mail address: wyh@lzu.edu.cn. (Y.H. Wang).

TG and DTA curves of precursor are shown in Fig. S1. Four major peaks were identified on the DTA curve. The first endothermic peak centered at 184 ˚C was mainly due to the evaporation of adsorbed water and the release of molecular water. The exothermic peak at 590 ˚C was attributed to the crystallization of ultimate phase. Inset of the figure shows the XRD patterns of precursor and after calcinated at 590 ˚C, revealing that the precursor is amorphous, but continued refinement of peak shapes and crystallite growth were observed after the precursor calcinated at 590˚C.

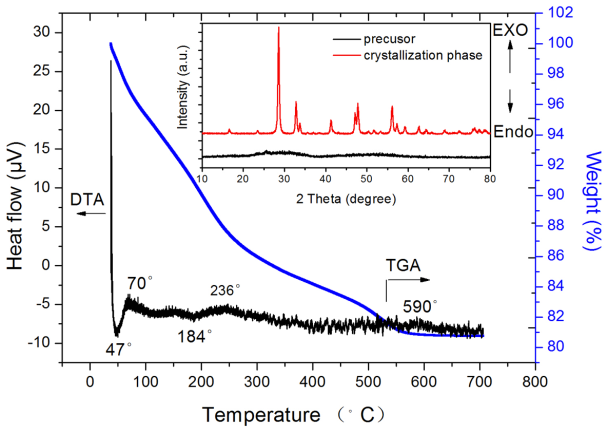

Fig. S1 TG-DTA curves of the precursor prepared by a coprecipitation method. Inset shows the XRD patterns of the precursor and after calcinated at 590˚ C

Table 1. Parameters of the rietveld refinement of $Lu_6O_5F_8$

Formula	$Lu_6O_5F_8$
Crystal system	orthorhombic
Lattice parameters/pm, °	a=5.415
	b=32.67
	c=5.458
	α=β=γ=90˚
Formula units/cell	4
Molar mass /g ·mol^{-1}	1281.78
Measured reflections	3500
Observed reflections	382
Radiation/pm	Cu-kα1（λ=154.06 pm）
2θ Range/°	10≤2θ≤80
Refinement	Retrieved refinement with Maud software
Reliability factors	sig= 1.2281519
	Rw (%)=9.577053
	Rwnb (%, no bkg)=7.7210436
	Rb (%)=6.7005153
	Rexp (%)=7.797938

The indexing of XRD patterns and the detailed PDF card information of $Lu_6O_5F_8$ are obtained through materials JADE software, as shown in the Table 2.

Lutecium Oxide Fluoride
Lu6O5F8
Radiation=CuKa1 Lambda=1.54060 Filter=
Calibration= d-Cutoff= 17.7 $I/I_C(R/R)$=

Orthorhombic-(Unknow), Pcmb (57) Z=4 mp=
Cell=5.415*32.67*5.458
Density (c)=5.159 Density (m)= 5.61 Mwt=1281.79 Vol=965.56

Table 2 PDF card information of the $Lu_6O_5F_8$ host

No.	2Theta	d(Å)	I(f)	h	k	l	1/(2d)	2pi/d
1	5.411	16.3316	217113.4	0	2	0	0.030615	0.384726
2	16.707	5.3064	11454970	1	0	0	0.094226	1.184077
3	17.574	5.0467	18034.93	1	2	0	0.099075	1.245009
4	19.955	4.4495	19917.2	1	4	0	0.112372	1.412110
5	23.54	3.7795	5622493	1	1	1	0.132293	1.662438
6	24.787	3.592	109324.8	1	3	1	0.139198	1.749216
7	25.832	3.449	59941.71	1	4	1	0.14497	1.821741
8	27.121	3.2879	55884.08	1	5	1	0.152073	1.911003
9	27.304	3.2663	69109.86	0	10	0	0.153078	1.923640
10	28.623	3.1187	2.33E+08	1	6	1	0.160323	2.014681
11	30.31	2.9489	36398.45	1	7	1	0.169555	2.130688
12	32.157	2.7836	26945.22	1	8	1	0.179624	2.257216
13	32.812	2.7295	33644508	0	0	2	0.183184	2.301955
14	32.906	2.7219	37003710	0	12	0	0.183695	2.308382
15	32.929	2.7201	53044.95	0	1	2	0.183817	2.309910
16	33.28	2.6922	48957.6	0	2	2	0.185722	2.333848
17	33.784	2.6532	22107753	2	0	0	0.188452	2.368154
18	33.857	2.6476	53487.31	0	3	2	0.18885	2.373163
19	34.142	2.6262	67024.39	1	9	1	0.190389	2.392501
20	34.24	2.6189	67136.1	2	2	0	0.19092	2.399170
21	35.649	2.5185	2835437	0	5	2	0.198531	2.494813
22	37.038	2.4273	1835887	1	0	2	0.20599	2.588549
23	37.123	2.4219	2074414	1	12	0	0.206449	2.594321
24	37.46	2.4009	104197.2	1	2	2	0.208255	2.617012
25	37.801	2.38	68204.32	2	1	1	0.210084	2.639994
26	37.981	2.3691	19504.72	1	3	2	0.211051	2.652140
27	38.113	2.3612	28004.79	2	2	1	0.211757	2.661014
28	38.2	2.3561	651561	0	7	2	0.212215	2.666774
29	38.456	2.3409	1316604	1	11	1	0.213593	2.684090

30	38.59	2.3331	866818.3	0	14	0	0.214307	2.693063
31	39.611	2.2753	132101.9	1	5	2	0.219751	2.761476
32	41.31	2.1855	27018081	2	6	1	0.228781	2.874942
33	41.392	2.1814	116317.5	0	9	2	0.229211	2.880345
34	41.957	2.1533	2692609	1	7	2	0.232202	2.917933
35	42.319	2.1358	462531.3	1	14	0	0.234104	2.941842
36	43.147	2.0967	1765906	1	13	1	0.23847	2.996702
37	43.194	2.0945	82866.69	0	10	2	0.23872	2.999850
38	43.95	2.0602	341134.3	2	8	1	0.242695	3.049794
39	43.968	2.0594	33896.48	2	10	0	0.242789	3.050979
40	45.119	2.0095	31242.46	0	11	2	0.248818	3.126741
41	45.492	1.9939	20351.37	2	9	1	0.250765	3.151204
42	47.155	1.9274	40061860	0	12	2	0.259417	3.259928
43	47.81	1.9025	29650306	2	0	2	0.262812	3.302594
44	47.879	1.8999	32617040	2	12	0	0.263172	3.307114
45	47.896	1.8993	51661.59	2	1	2	0.263255	3.308158
46	48.153	1.8897	50420.71	2	2	2	0.264592	3.324964
47	48.58	1.8741	86962.7	2	3	2	0.266795	3.352641
48	48.971	1.8601	483852.5	2	11	1	0.268803	3.377875
49	49.295	1.8486	29308.82	0	13	2	0.270475	3.398889
50	49.929	1.8266	1723753	2	5	2	0.273733	3.439826
51	50.372	1.8116	4752777	1	12	2	0.275999	3.468307
52	50.752	1.7989	110173.1	1	16	1	0.277948	3.492793
53	51.679	1.7688	5593177	3	0	0	0.282678	3.552230
54	51.903	1.7617	3140201	2	7	2	0.283817	3.566547
55	52.21	1.752	31173.13	2	14	0	0.285388	3.586293
56	52.918	1.7303	92063.98	2	13	1	0.288967	3.631269
57	53.215	1.7213	24265.62	1	0	3	0.290478	3.650256
58	53.295	1.7189	5361706	1	1	3	0.290884	3.655352
59	53.859	1.7022	56187.53	0	15	2	0.293738	3.691214
60	53.929	1.7002	74906.31	1	3	3	0.294083	3.695557
61	54.455	1.685	34749.95	2	9	2	0.296736	3.728893
62	54.48	1.6843	100189.5	1	4	3	0.296859	3.730443
63	54.559	1.682	35158.26	1	14	2	0.297265	3.735544
64	54.615	1.6804	182521.9	3	1	1	0.297548	3.739101
65	55.183	1.6645	55029.41	1	5	3	0.300391	3.774818
66	55.932	1.644	23259.75	2	10	2	0.304136	3.821889
67	56.034	1.6412	33483231	1	6	3	0.304655	3.828409
68	56.158	1.6379	38754818	1	18	1	0.305269	3.836123
69	56.273	1.6348	15009.32	0	16	2	0.305848	3.843397
70	57.029	1.6149	60943.95	1	7	3	0.309617	3.890758
71	57.278	1.6085	109143.6	2	15	1	0.310849	3.906239
72	57.312	1.6076	23570414	3	6	1	0.311023	3.908426

73	57.535	1.6019	15092.98	2	11	2	0.312129	3.922333
74	58.771	1.5711	821421.9	0	17	2	0.318248	3.999227
75	59.135	1.5623	28352.57	1	16	2	0.320041	4.021753
76	59.259	1.5594	20252207	2	12	2	0.320636	4.029233
77	59.411	1.5557	158253.1	3	8	1	0.321399	4.038816
78	59.432	1.5552	120723.3	1	9	3	0.321502	4.040114
79	61.559	1.5065	74890.7	1	17	2	0.331895	4.170717
80	61.821	1.5008	55809.22	1	20	1	0.333156	4.186557
81	61.898	1.4991	491583	2	1	3	0.333533	4.191305
82	62.355	1.4892	2286221	1	11	3	0.335751	4.219168
83	62.475	1.4866	48678.29	2	3	3	0.336338	4.226547
84	62.565	1.4847	23504.26	0	22	0	0.336768	4.231956
85	62.579	1.4844	7034410	3	0	2	0.336836	4.232811
86	62.637	1.4832	7357798	3	12	0	0.337109	4.236236
87	63.05	1.4744	57564.5	2	14	2	0.339121	4.261520
88	63.225	1.4708	27003.22	3	3	2	0.339951	4.271951
89	63.553	1.464	123987.4	3	11	1	0.34153	4.291793
90	63.724	1.4604	23263.99	3	4	2	0.342372	4.302373
91	64	1.4548	18541.3	1	12	3	0.34369	4.318934
92	64.008	1.4546	724573	0	19	2	0.343737	4.319528
93	64.363	1.4475	821391.8	3	5	2	0.345423	4.340715
94	64.402	1.4467	4370815	2	6	3	0.345614	4.343116
95	64.516	1.4444	5805280	2	18	1	0.346164	4.350031
96	65.108	1.4327	24575.69	2	15	2	0.348991	4.385555
97	65.763	1.42	2549964	1	13	3	0.352113	4.424778
98	66.051	1.4145	322400.3	3	7	2	0.353482	4.441983
99	66.316	1.4095	50002.66	3	14	0	0.354736	4.457741
100	66.368	1.4085	20374.93	2	8	3	0.354988	4.460905
101	66.67	1.4029	19866.77	1	19	2	0.356405	4.478712
102	68.788	1.3648	3769610	0	0	4	0.366354	4.603741
103	68.856	1.3636	22185.18	0	1	4	0.366676	4.607792
104	69.008	1.361	6315572	0	24	0	0.367377	4.616595
105	69.062	1.36	33308.16	0	2	4	0.367647	4.619989
106	69.403	1.3542	65179.05	0	3	4	0.369222	4.639776
107	69.537	1.3519	565257.9	2	17	2	0.36985	4.647670
108	69.567	1.3514	123937.6	0	21	2	0.369987	4.649390
109	69.782	1.3477	85366.13	2	20	1	0.371002	4.662154
110	70.284	1.3393	286693.2	2	11	3	0.373329	4.691395
111	70.437	1.3368	20545.77	3	16	0	0.374028	4.700169
112	70.49	1.3359	1351564	0	5	4	0.37428	4.703335
113	70.762	1.3315	53880.93	3	15	1	0.375516	4.718877
114	70.822	1.3305	149333.6	1	23	1	0.375799	4.722424
115	71.061	1.3266	1773158	4	0	0	0.376903	4.736307

116	71.234	1.3238	21719.01	0	6	4	0.377701	4.746325
117	71.331	1.3222	21968.33	4	2	0	0.378158	4.752069
118	71.361	1.3218	1100582	1	0	4	0.378272	4.753507
119	71.577	1.3183	990266.1	1	24	0	0.379276	4.766127
120	71.725	1.3159	76391.81	1	16	3	0.379968	4.774820
121	71.966	1.3121	15894.14	1	3	4	0.381069	4.788648
122	72.108	1.3099	1618130	0	7	4	0.381709	4.796691
123	72.128	1.3096	108510.5	1	21	2	0.381796	4.797790
124	72.47	1.3042	38716.81	0	22	2	0.383377	4.817655
125	72.537	1.3032	7087468	3	12	2	0.383671	4.821352
126	72.845	1.2984	18249.03	3	16	1	0.385089	4.839175
127	73.029	1.2956	22911.18	2	22	0	0.385922	4.849634
128	73.037	1.2955	401186.5	1	5	4	0.385951	4.850008
129	73.509	1.2884	184357.4	2	13	3	0.388078	4.876735
130	73.527	1.2881	470686.5	4	1	1	0.388169	4.877871
131	73.93	1.2821	36090.58	1	17	3	0.389985	4.900698
132	74.059	1.2801	29119.46	4	3	1	0.390594	4.908355
133	74.242	1.2774	77626.09	0	9	4	0.39142	4.918730
134	74.372	1.2755	569123.6	2	19	2	0.392003	4.926057
135	74.632	1.2717	69111.83	1	7	4	0.393174	4.940776
136	74.931	1.2674	421989.3	3	1	3	0.394508	4.957539
137	75.46	1.2598	25768.96	3	3	3	0.396888	4.987447
138	75.499	1.2593	24386.01	0	10	4	0.397046	4.989427
139	75.71	1.2563	16788.16	0	26	0	0.397994	5.001341
140	75.844	1.2544	10812979	4	6	1	0.398597	5.008917
141	76.242	1.2488	12480500	1	18	3	0.400384	5.031378
142	76.512	1.2451	16249.88	3	5	3	0.401574	5.046330
143	77.2	1.2357	131888.8	1	25	1	0.404629	5.084717
144	77.204	1.2357	57673.85	2	15	3	0.404629	5.084717
145	77.233	1.2353	6536255	3	6	3	0.40476	5.086364
146	77.338	1.2338	8317675	3	18	1	0.405252	5.092548
147	77.887	1.2265	17193.82	3	15	2	0.407664	5.122858
148	77.984	1.2252	15864.97	1	10	4	0.408097	5.128294
149	78.193	1.2225	21609.6	1	26	0	0.408998	5.139620
150	78.382	1.22	4535256	0	12	4	0.409836	5.150152
151	78.539	1.218	6085829	0	24	2	0.410509	5.158609
152	78.662	1.2164	22181.85	1	19	3	0.411049	5.165394
153	78.874	1.2136	3910315	2	0	4	0.411997	5.177312
154	78.939	1.2128	22520.13	2	1	4	0.412269	5.180727
155	79.06	1.2112	30110.32	3	8	3	0.412814	5.187570
156	79.083	1.2109	5130472	2	24	0	0.412916	5.188856
157	79.135	1.2103	18866.69	2	2	4	0.413121	5.191428
158	79.459	1.2062	64982.56	2	3	4	0.414525	5.209074

159	79.616	1.2042	15459.16	2	21	2	0.415213	5.217726
160	80.163	1.1973	20987.03	3	9	3	0.417606	5.247795
161	80.497	1.1932	1808660	2	5	4	0.419041	5.265827
162	80.502	1.1931	1605170	4	0	2	0.419076	5.266269
163	80.554	1.1925	1641486	4	12	0	0.419287	5.268918
164	80.842	1.189	295896.9	1	12	4	0.420521	5.284428
165	80.997	1.1871	450936.1	1	24	2	0.421195	5.292886
166	81.191	1.1848	24046.69	1	20	3	0.422012	5.303161
167	81.208	1.1845	24822.22	2	6	4	0.422119	5.304504
168	81.753	1.178	44673.36	0	14	4	0.424448	5.333774
169	82.037	1.1747	212621.6	3	17	2	0.425641	5.348757
170	82.047	1.1745	1610888	2	7	4	0.425713	5.349668
171	82.116	1.1737	262306.9	4	5	2	0.426003	5.353315
172	82.269	1.1719	73235.03	3	20	1	0.426658	5.361537
173	82.395	1.1705	54463.98	2	22	2	0.427168	5.367950
174	82.733	1.1665	24857.73	0	28	0	0.428633	5.386357
175	82.746	1.1664	781954.7	3	11	3	0.428669	5.386819
176	83.617	1.1564	2669590	2	18	3	0.432376	5.433401
177	83.619	1.1564	49394.39	0	15	4	0.432376	5.433401
178	83.66	1.156	228806.1	4	7	2	0.432526	5.435281
179	83.831	1.154	59256.72	1	21	3	0.433276	5.444701
180	84.19	1.15	39756.95	1	14	4	0.434783	5.463639
181	84.469	1.1469	95889.18	4	13	1	0.435958	5.478407
182	84.554	1.146	35692.35	2	25	1	0.4363	5.482710
183	84.993	1.1412	51976.57	0	26	2	0.438135	5.505771
184	85.165	1.1393	40856.63	1	28	0	0.438866	5.514952
185	85.323	1.1376	64580.7	2	10	4	0.439522	5.523194
186	85.528	1.1354	70065.3	2	26	0	0.440373	5.533896
187	85.825	1.1323	643197.7	3	13	3	0.441579	5.549046
188	86.198	1.1283	17816.97	4	14	1	0.443145	5.568719
189	86.657	1.1235	403004	3	19	2	0.445038	5.592510
190	86.667	1.1234	15610.15	2	11	4	0.445077	5.593008
191	86.927	1.1207	18305.12	4	10	2	0.44615	5.606483
192	87.455	1.1153	62718.18	1	28	1	0.44831	5.633628
193	87.654	1.1133	34793.62	3	22	1	0.449115	5.643749
194	87.717	1.1126	776895.8	0	17	4	0.449398	5.647299
195	88.136	1.1084	7134964	2	12	4	0.451101	5.668698
196	88.29	1.1069	9642959	2	24	2	0.451712	5.676380
197	89.404	1.096	54805.15	3	15	3	0.456204	5.732833
198	89.46	1.0954	892822.7	1	23	3	0.456454	5.735973
199	89.733	1.0928	25159.21	2	13	4	0.45754	5.749621
200	89.738	1.0928	3758405	4	12	2	0.45754	5.749621

The HRTEM image and the SAED pattern with lattice index of the host are investigated, as shown in the Fig. S2. HRTEM image (Fig. S2a) shows the clear and continuous lattice fringes which is arranged in one direction, indicating high crystallinity. The measured lattice spacing is 0.314 nm which is close to the (161) lattice plane (0.312 nm) of orthorhombic $Lu_6O_5F_8$ structure. SAED pattern (Fig. S2b) taken from the edge of the nanoparticles exhibits clear diffraction rings corresponding to the specific (1 6 1), (0 0 2), (2 0 2), (1 6 3), (3 12 2) and (2 12 4) planes of the orthorhombic structure $Lu_6O_5F_8$. It is worthwhile noting that the lattice index calculated from the HRTEM image and SAED pattern agrees well with the XRD and Rietveld refinement data.

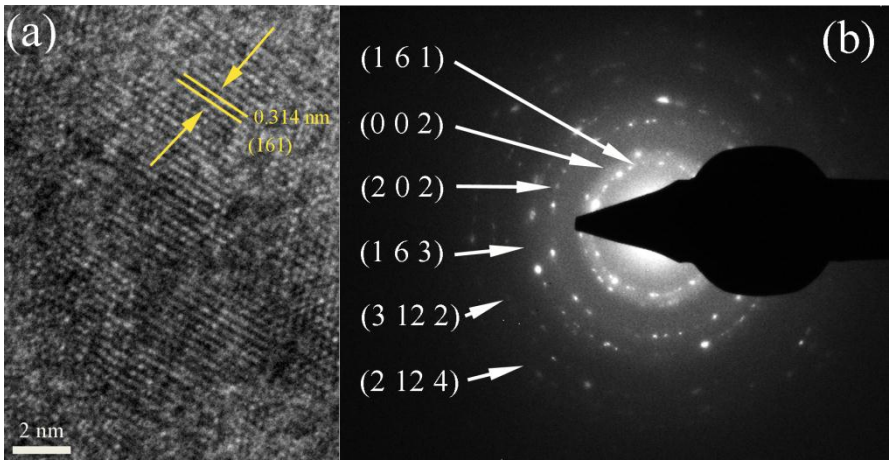

Fig. S2 HRTEM image (a) and SAED pattern (b) of $Lu_6O_5F_8$ nanoparticles

Fig. S3 shows the upconversion emission spectra of the $Lu_6O_5F_8$:20%Yb^{3+},1%Er^{3+},3%Li^+ nanoparticles and $NaYF_4$:20%Yb^{3+},2%Er^{3+} nanocrystals as the commercial UC phosphor under the same measurement condition. It is found that the red emission intensity of $Lu_6O_5F_8$:20%Yb^{3+},1%Er^{3+},3%Li^+ is much stronger than that of the commercial phosphor, but the green emission intensity of $Lu_6O_5F_8$:20%Yb^{3+},1%Er^{3+},3%Li^+ is weaker than that of the commercial phosphor. On the whole, the intergrated emission intensity in $Lu_6O_5F_8$:20%Yb^{3+},1%Er^{3+},3%Li^+ is 5.5 times as strong as that of the commercial phosphor.

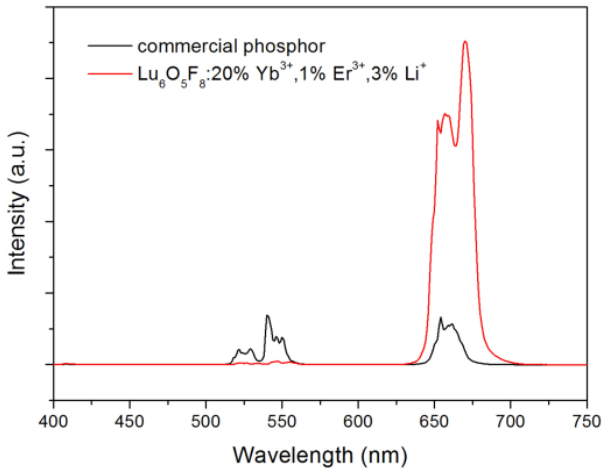

Fig. S3 The upconversion emission spectra of $Lu_6O_5F_8$:20%Yb^{3+},1%Er^{3+},3%Li^+ nanoparticles and the commercial phosphor

Diffuse reflectance spectra in the UV, visible and NIR regions were measured on a series of samples with different Li^+ concentrations, as shown in Fig. S4. The sharp bands are assigned to the intraconfigurational f-f transtions from the $^4I_{15/2}$ ground state to the $^4G_{11/2}$, $^2H_{11/2}$ and $^4F_{9/2}$ excited states of Er^{3+} and $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{3+}, and all the peaks are labelled in the figure. The position and intensitis of reflection peaks of Er^{3+} and Yb^{3+} are basically not affected by the Li^+ doping, and no other peaks are observed. It is indicated that the Li^+ ions cannot absorb 980 nm photons and cannot transfer its energy to Er^{3+}.

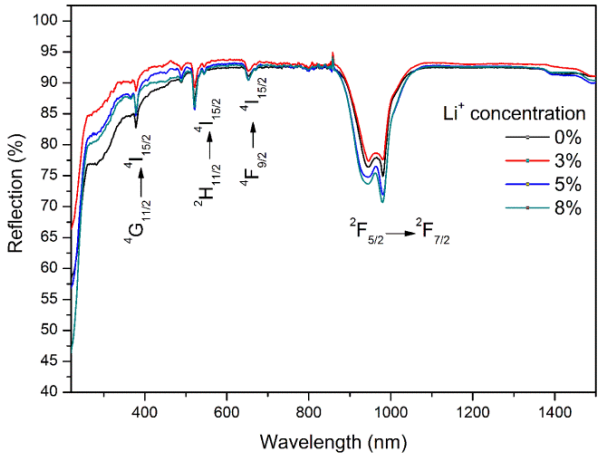

Fig. S4 Reflection spectra of $Lu_6O_5F_8$:20%Yb^{3+},1%Er^{3+} nanoparticles with different concentrations of Li^+.

To further understand the reasons for the red emission intensity of UC is more predominately than that of DC, the pump power dependence of UC emission intensity was performed, as exemplified in Fig. S5. It is well known that $I_{em} \propto I_p^n$ exists in UC processes, where n denotes the number of NIR photons absorbed to generate one frequency upconverted photon. Fitting data points yielded approximately slopes were 1.67, 1.69 and 1.64 for 525, 553 and 658 nm emissions in $Lu_6O_5F_8$:20%Yb^{3+},1%Er^{3+} sample, when introducing 3%Li^+, which are changed slightly. These results indicate that the green and red emissions are two-photon processes in samples both with and without Li^+ ions.

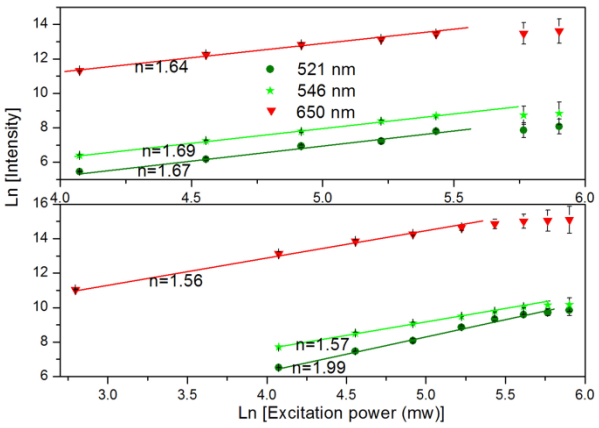

Fig. S5 Pump power dependence of the green and red UC emissions in $Lu_6O_5F_8$:20%Yb^{3+}, 1%Er^{3+} and $Lu_6O_5F_8$:20%Yb^{3+}, 1%Er^{3+},3%Li^+ nanoparticles, respectively