Supplementary Information

Stable and efficient narrow band red emitters with high colour purity for white LEDs and plant growth applications

Kasturi Singh and Sivakumar Vaidyanathan*

Department of Chemistry, National Institute of Technology,

Rourkela, Odisha – 769008

* To whom correspondence should be addressed. Email: vsiva@nitrkl.ac.in (V. Sivakumar) Tel: +91-661-2462654;

Experimental:

Intense red emitting phosphors $Li_3BaSrY_3(MO_4)_8$: Eu^{3+} where x = 0 – 3 (insteps of 0.3, M = W, Mo) were synthesized through a high temperature solid state reaction. Highly pure precursors were taken for the synthesis of the phosphors. The apposite amount of Li_2CO_3 (99.9%, Merck), $BaCO_3$ (99.0% MERCK), $SrCO_3$ (Extra pure 99.0%, HIMEDIA), Y_2O_3 (minimum 99.9%, Sigma Aldrich), Eu_2O_3 (99.9% REO, Alfa Aesar) and MoO_3 (ACS Reagent > 99.5%, Sigma Aldrich) and WO_3 (ACS Reagent > 99.9%, Sigma Aldrich) were taken and grinded with the help of agate mortar and pestle, followed by transferring the same into an alumina crucible. The mixtures of the samples were heated at 500º C for 6 hrs and reground, treated at temperature 850º C for 12 hrs. After the reaction hour, the reaction mixture was cooled to room temperature (RT) and ground again into fine powder and restored in vials.

Characterization:

The phase formation of the phosphors was checked using a powder X-ray diffractometer (Rigaku ULTIMA IV, Japan), which utilizes CuKα1 radiation for generation of X - rays. SEM images were taken by a JEOL T-300 scanning electron microscope using an Oxford INCAPentaFET-X3 energy dispersive X-ray spectroscopy system with a high-angle ultrathin window 30 mm Si (Li) X-ray detector that was liquid-nitrogen cooled. The Perkin Elmer, UV – 5400 UV- visible spectrofluorometer with 150 mm integrating sphere was used to record the diffuse reflectance spectra (DRS). The photoluminescence excitation and emission spectra were recorded by JOBIN YVON spectrofluorometer, where it uses a 150 W xenon lamp as excitation source. In addition, the luminescence lifetime and absolute quantum yield measurements were taken by using Edinberg Spectrofluorometer FS – 5 instruments with attaching SC – 30 integrating sphere module. A pulsed xenon lamp was used as the excitation source and the signals were detected with a photomultiplier. The CIE color coordinates were calculated from the obtained spectral emission data of the phosphors by using the MATLAB software. The Judd – Ofelt (J – O) intensity parameters were calculated to support the spectral emission profile, regarding the inverse symmetry of Eu^{3+} ion using classical Judd-Ofelt (J – O) theory. All the measurement has been carried out in room temperature (RT).

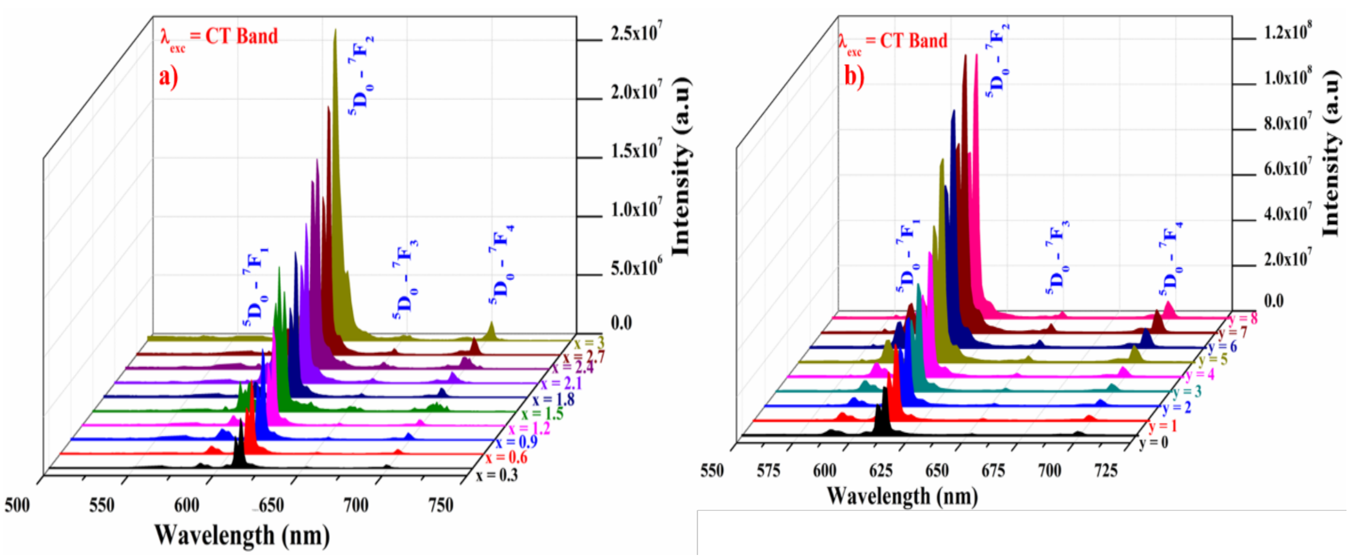

Figure S1. PL emission spectra of $Li_3BaSrY_{3-x}Eu_x(WO_4)_8$ where x = 0 – 3 at λ_{exc} = CT band, b) $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ where y = 1 – 8 at λ_{exc} = CT band.

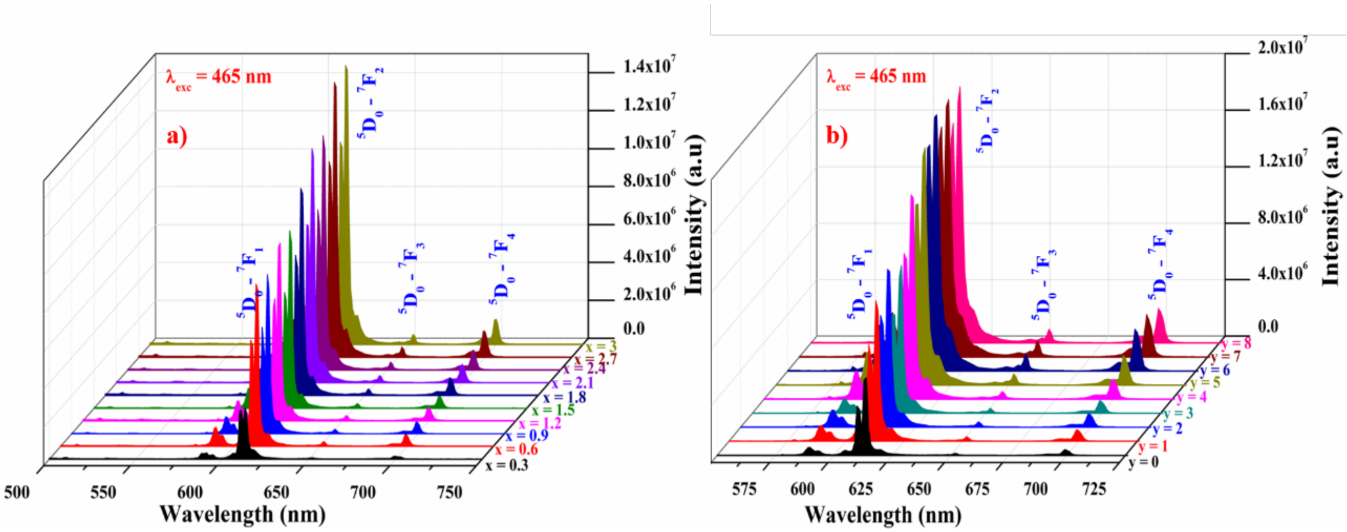

Figure S2. PL emission spectra of $Li_3BaSrY_{3-x}Eu_x(WO_4)_8$ where x = 0 – 3 at λ_{exc} = 465, b) $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ where y = 1 – 8 at λ_{exc} = 465 nm.

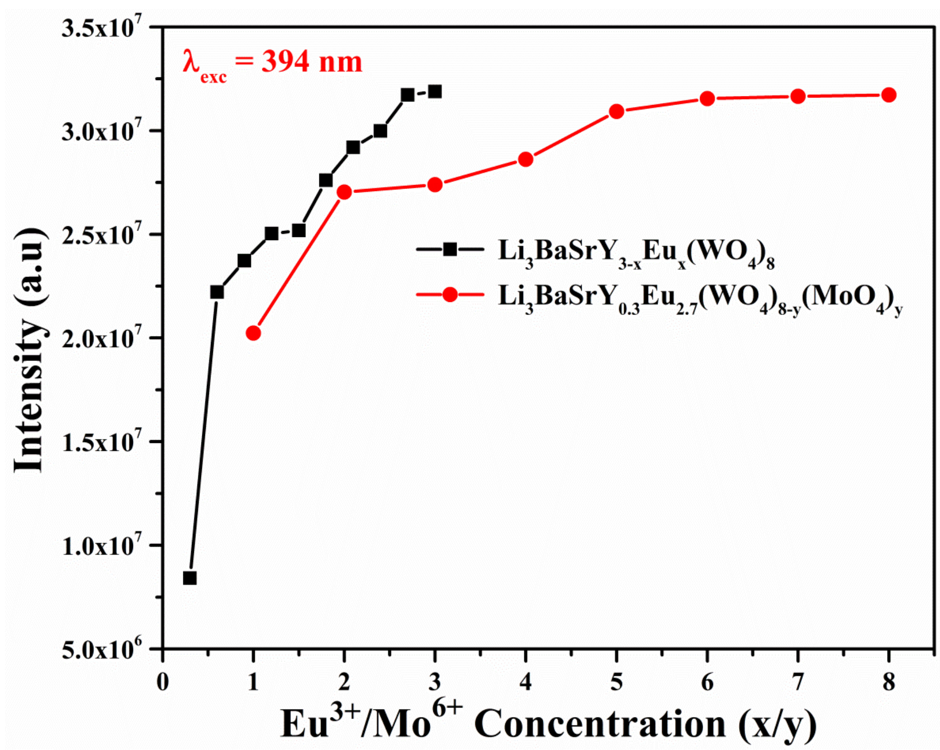

Figure S3. Eu^{3+} concentration vs Emission Intensity at λ_{exc} = 394 nm for $Li_3BaSrLa_{3-x}Eu_x(WO_4)_8$ where x = 0 – 3 and $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ where y = 1 – 8 phosphors

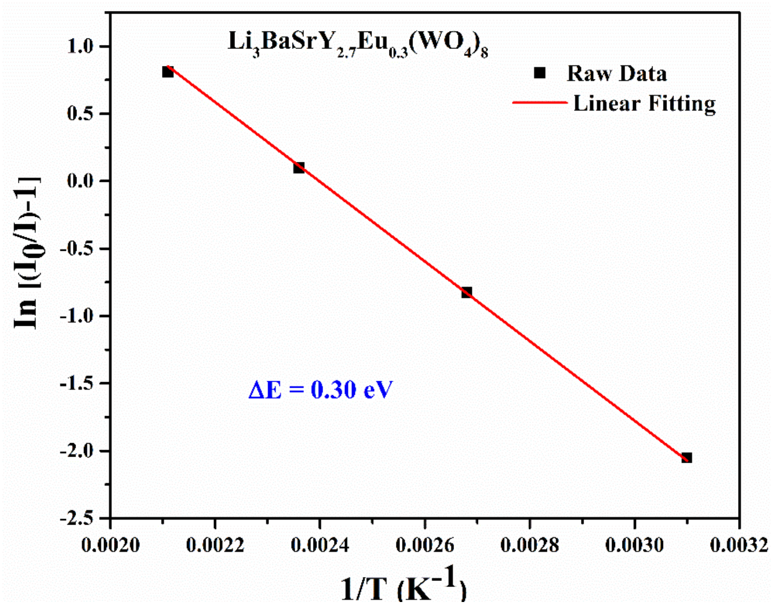

Figure S4. Plot of ln(I/I0) – 1 verses 1/KT for $Li_3BaSrLa_{2.7}Eu_{0.3}(WO_4)_8$ phosphor.

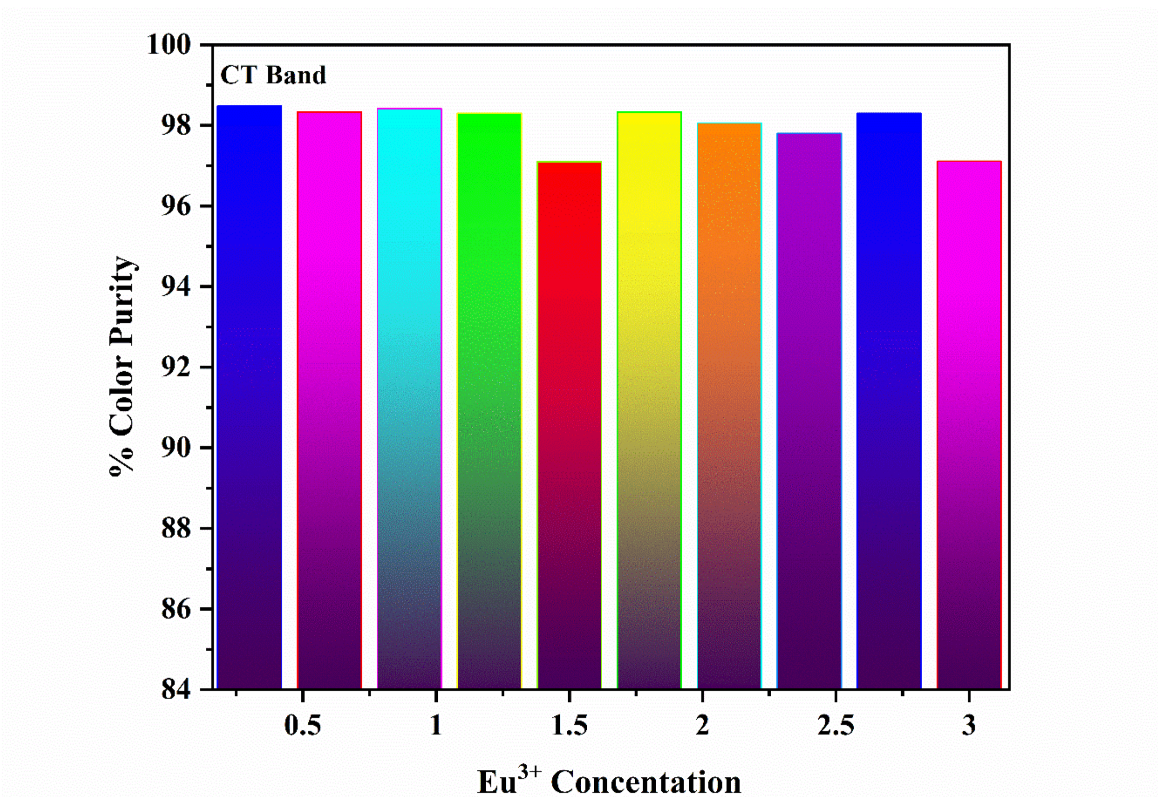

Figure S5. The color purity of $Li_3BaSrLa_{3-x}Eu_x(WO_4)_8$ phosphors where x = 0 – 3 under λ_{exc} =

CT band

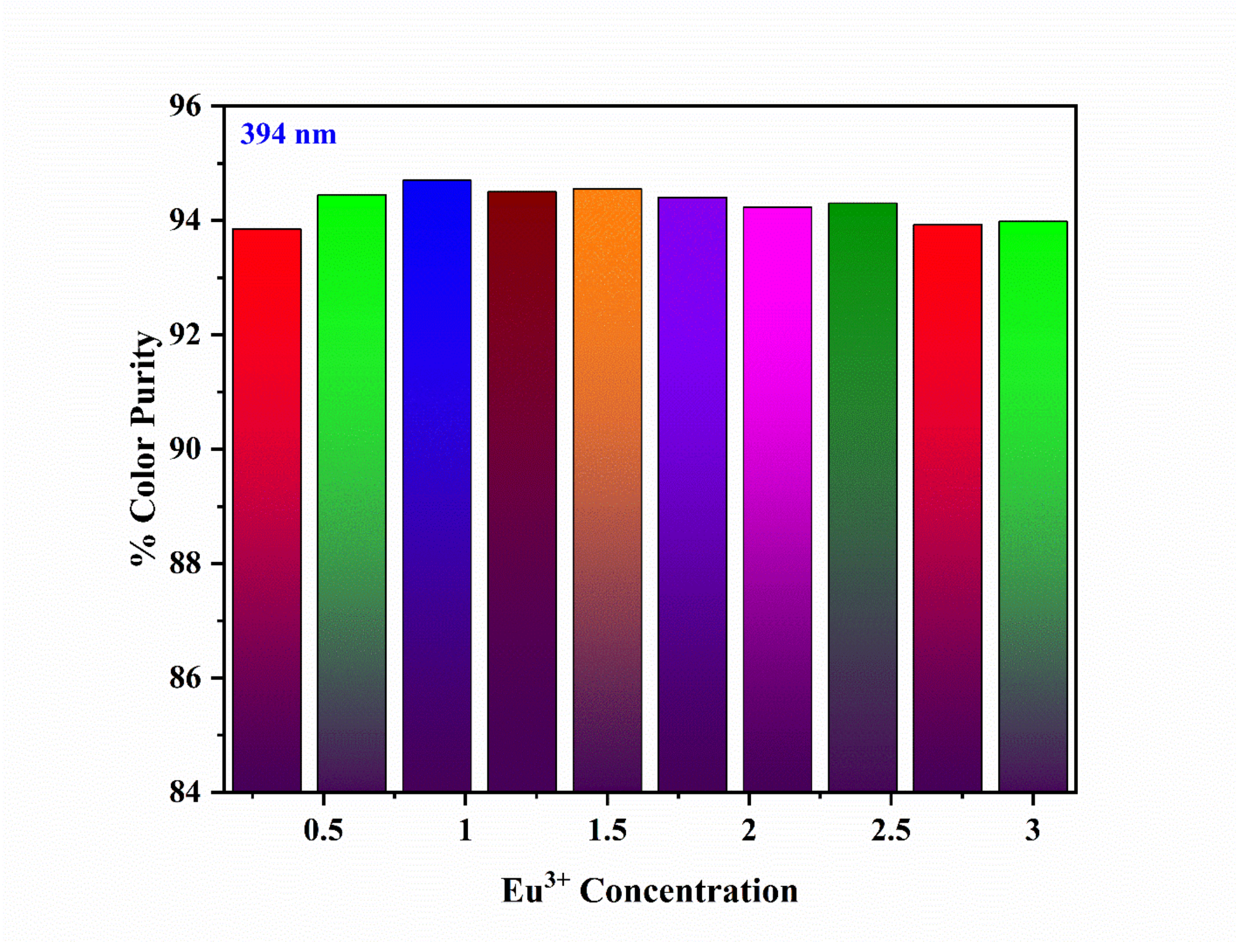

Figure S6. The color purity of $Li_3BaSrLa_{3-x}Eu_x(WO_4)_8$ phosphors where x = 0 – 3 under λ_{exc} = 394 nm

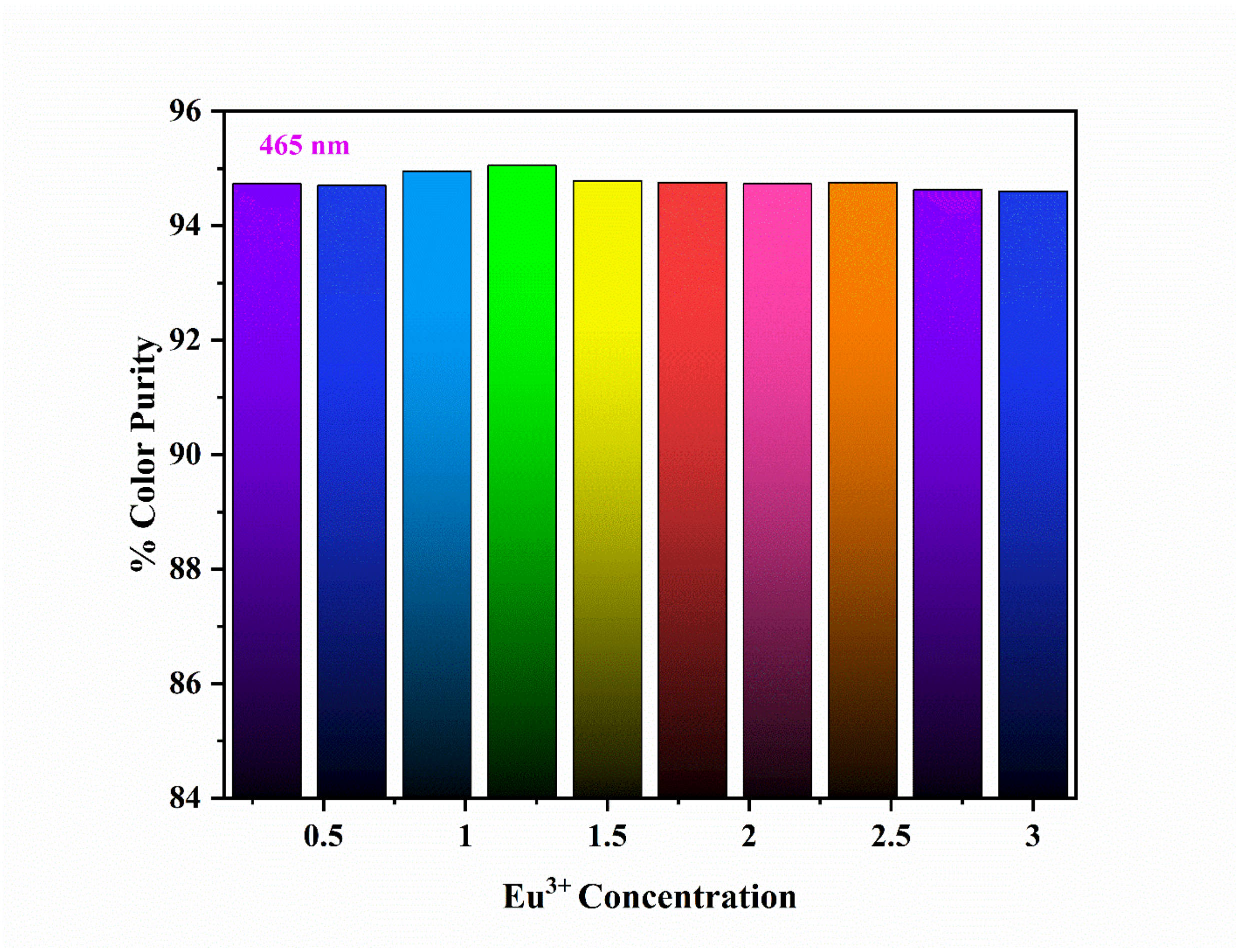

Figure S7. The color purity of $Li_3BaSrLa_{3-x}Eu_x(WO_4)_8$ phosphors where x = 0 – 3 under λ_{exc} = 465 nm

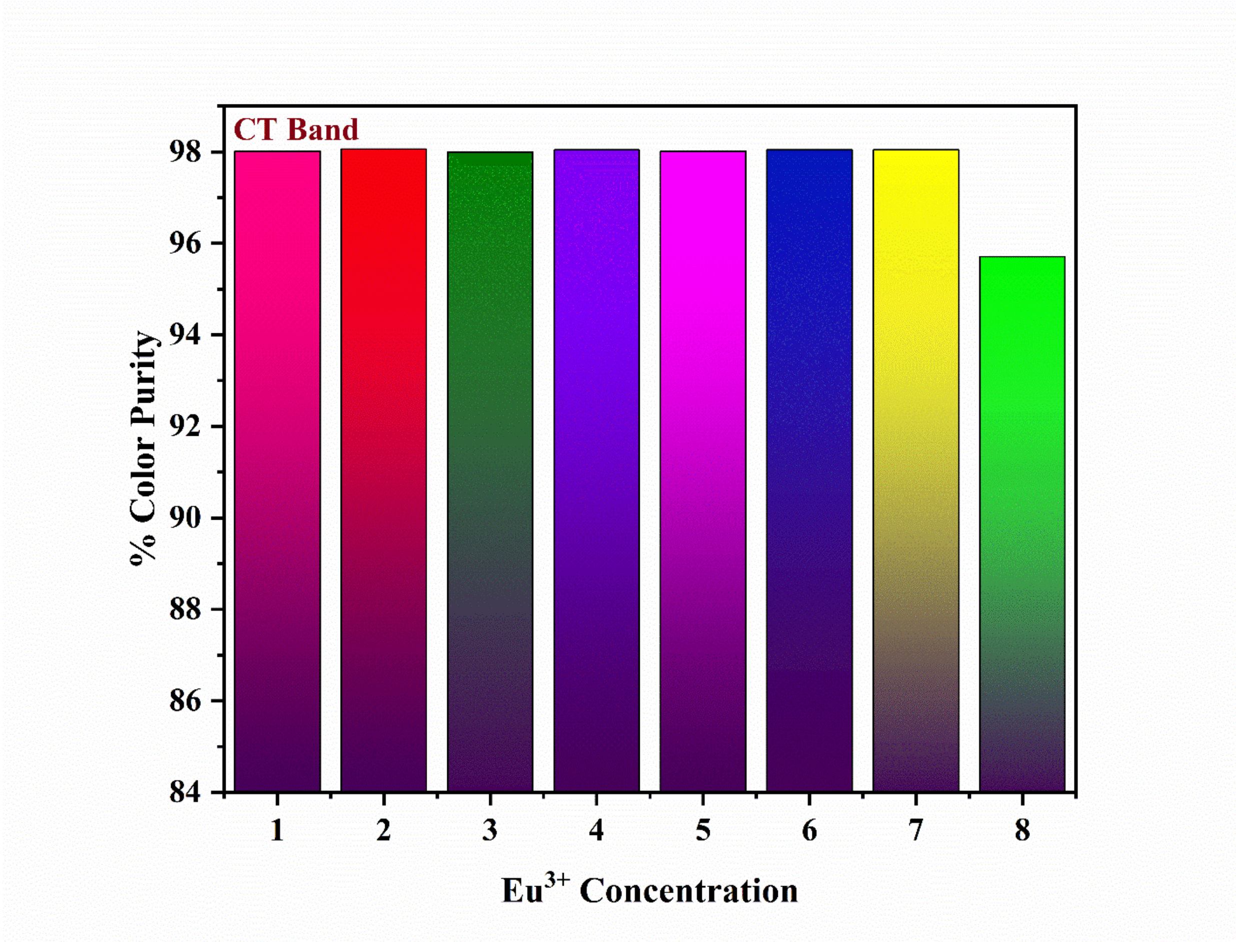

Figure S8. The color purity of under $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ where y = 1 – 8 phosphors λ_{exc} = CT band

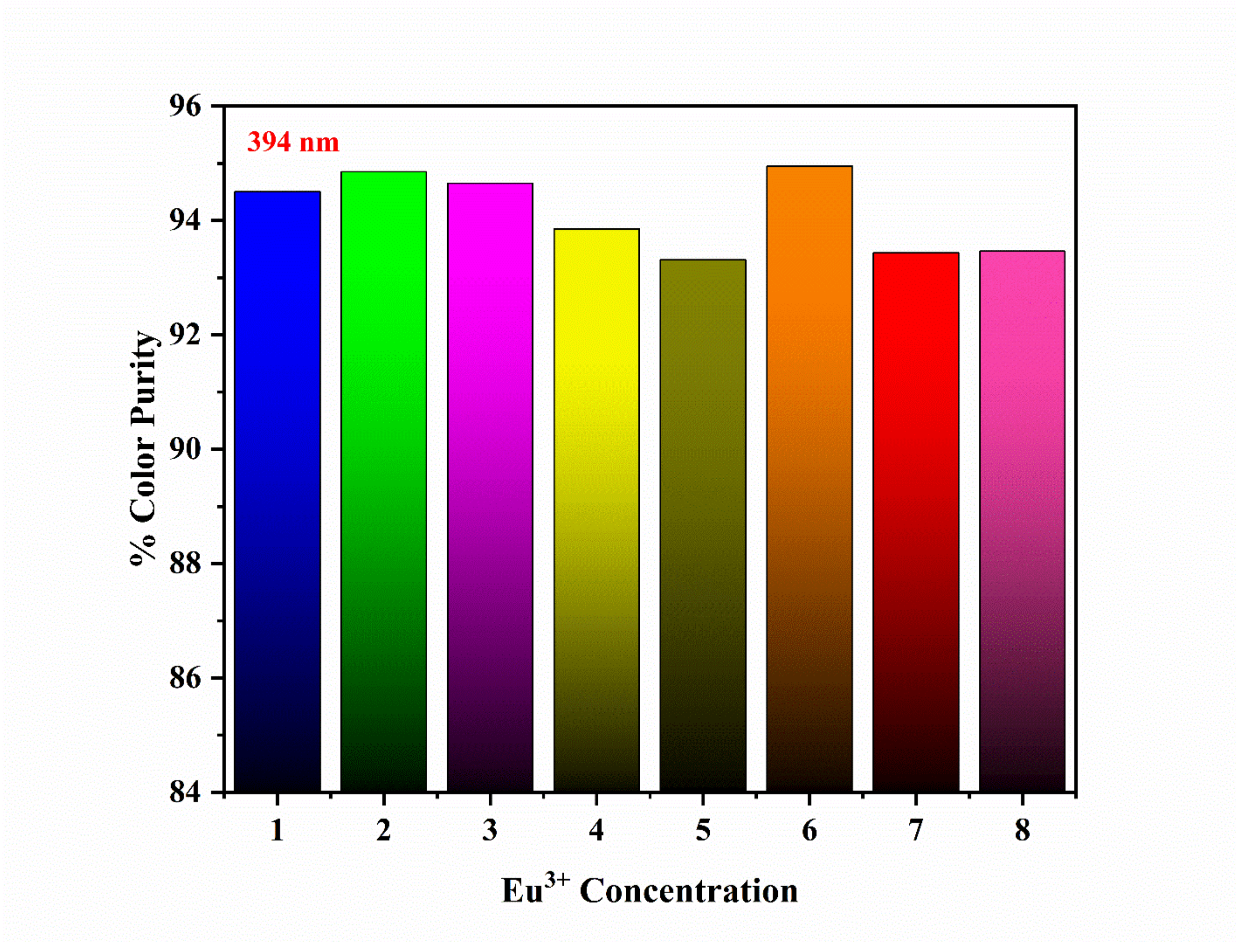

Figure S9. The color purity of under $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ where y = 1 – 8 phosphors λ_{exc} = 394 nm

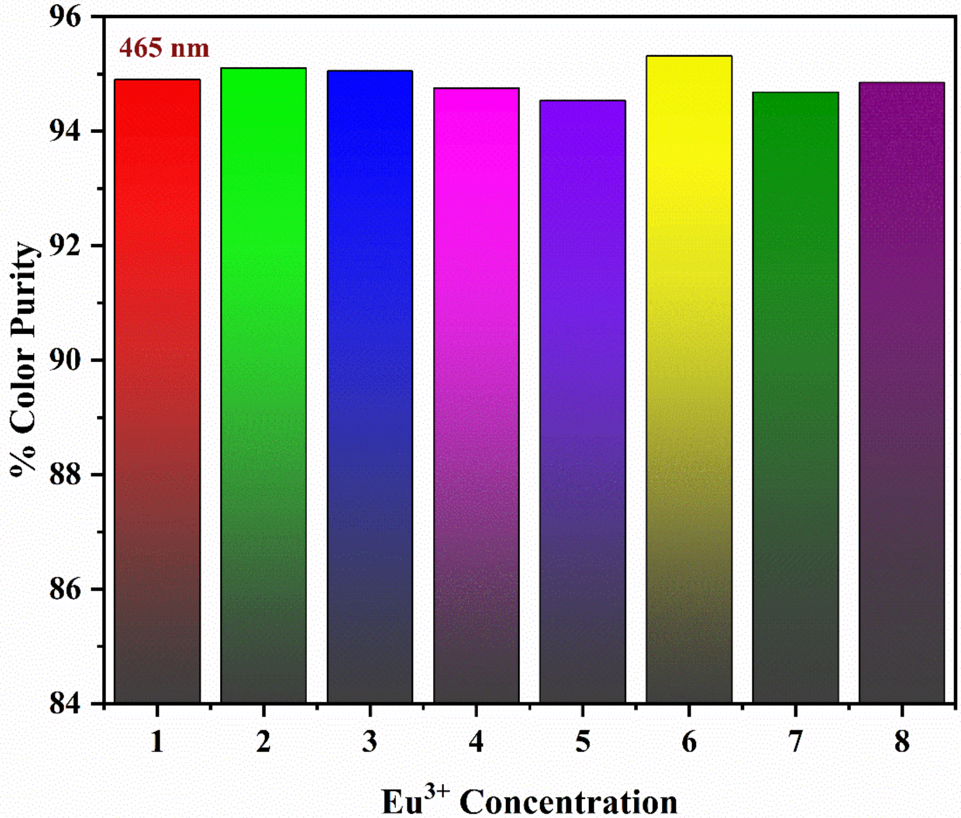

Figure S10. The color purity of under $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ where y = 1 – 8 phosphors λ_{exc} = 465 nm

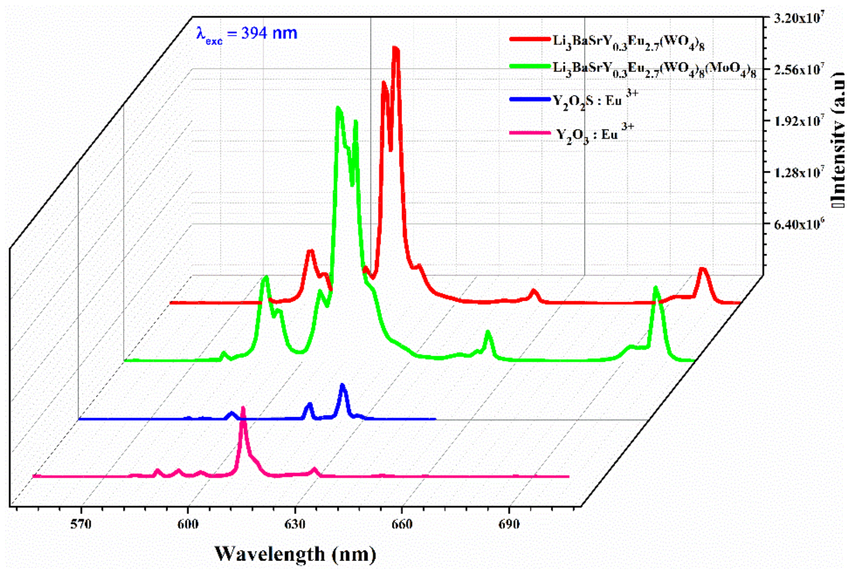

Figure S11. The comparison of emission intensity with Y_2O_2S, Y_2O_3: Eu^{3+} with $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_8$

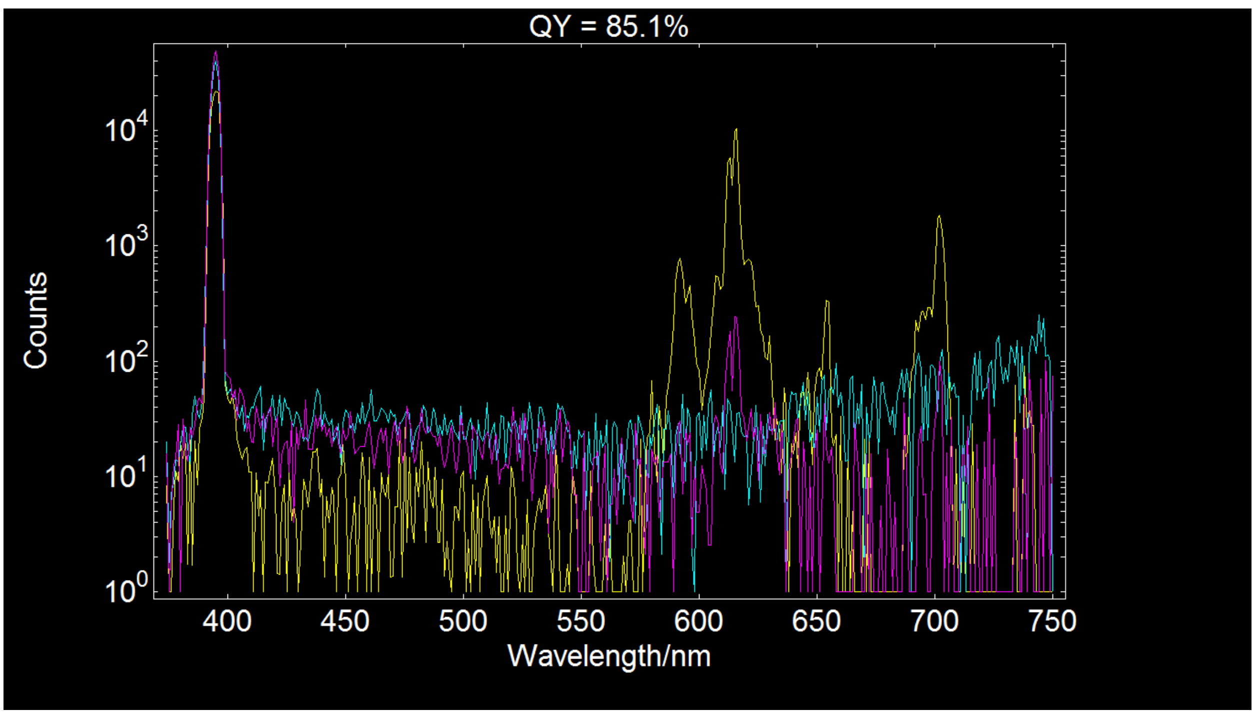

Figure S12. Quantum yield measurement of $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_1(MoO_4)_7$

Table ST1. Lattice parameters for $Li_3BaSrY_{3-x}Eu_x(WO_4)_8$, where x = 0 – 3 in steps of 0.3.

Concentration of Eu^{3+}	a (Å)	b (Å)	c (Å)	β (Å)	V (Å)
0.3	5.2655	12.7236	18.9812	92.1894	1270.752
0.6	5.2681	12.8141	19.1419	92.1589	1291.305
0.9	5.2320	12.8192	19.9946	92.8875	1272.372
1.2	5.2218	12.6723	19.1818	90.8082	1269.197
1.5	5.2816	12.7138	19.1211	91.2714	1283.666
1.8	5.1766	12.7156	19.4057	91.3821	1277.002
2.1	5.1915	12.7129	19.2176	92.7028	1266.939
2.4	5.1903	12.7096	19.2080	92.7371	1265.653
2.7	5.2468	12.6640	19.2631	91.4221	1279.561
3	5.2554	12.7407	19.2170	91.3637	1280.374

Table ST2. Lattice parameters for $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ where y = 1–8, in steps of 1.

Concentration of Eu^{3+}	a (Å)	b (Å)	C (Å)	B (Å)	V (Å)
2	5.2396	12.7726	19.144	91.5509	1280.752
3	5.2240	12.7240	19.1344	91.5379	1271.266
4	5.2252	12.7824	19.1171	91.5209	1276.421
5	5.2402	12.6736	19.1292	91.6302	1269.922
6	5.2562	12.7425	19.1495	91.5124	1274.564
7	5.2297	12.7613	19.1645	91.3970	1278.632
8	5.2298	12.8233	19.1429	91.8364	1283.673

Table ST3. Asymmetric ratio of $Li_3BaSrY_{3-x}Eu_x(WO_4)_8$ where x = 0 – 3 and $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ where y = 1 – 8

$Li_3BaSrY_{3-x}Eu_x(WO_4)_8$ where x = 0 – 3	Asymmetric ratio (β) = I_2/I_1	$Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ where y = 1 – 8	Asymmetric ratio (β) = I_2/I_1
0.3	9.62	1	6.06
0.6	7.50	2	5.38
0.9	7.83	3	8.52
1.2	7.27	4	5.93
1.5	7.33	5	6.73
1.8	6.16	6	4.89
2.1	5.83	7	5.28
2.4	5.95	8	7.72
2.7	4.50	-	-
3	4.66	-	-

Table ST4. CIE color coordinates for $Li_3BaSrY_{3-x}Eu_x(WO_4)_8$ where x = 0 – 3 phosphors

Concentration x	Co-ordinates								
	CT band			394 nm			465 nm		
	x	y	Color purity	x	y	Color purity	x	y	Color purity
0.3	0.6743	0.3254	98.48	0.6562	0.3434	93.85	0.6597	0.3400	94.73
0.6	0.6737	0.3260	98.33	0.6586	0.3410	94.45	0.6596	0.3401	94.70
0.9	0.6740	0.3257	98.41	0.6596	0.3400	94.70	0.6606	0.3390	94.95
1.2	0.6736	0.3261	98.30	0.6588	0.3409	94.50	0.6610	0.3387	95.05
1.5	0.6690	0.3307	97.10	0.6590	0.3406	94.55	0.6599	0.3398	94.78
1.8	0.6737	0.3260	98.33	0.6584	0.3412	94.40	0.6598	0.3399	94.75
2.1	0.6727	0.3270	98.06	0.6577	0.3419	94.23	0.6597	0.3400	94.73
2.4	0.6717	0.3280	97.80	0.6580	0.3416	94.30	0.6598	0.3398	94.75

2.7	0.6736	0.3261	98.30	0.6565	0.3432	93.93	0.6593	0.3403	94.63
3.0	0.6721	0.3276	97.11	0.6567	0.3429	93.98	0.6592	0.3404	94.60

Table ST5. CIE for $Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_{8-y}(MoO_4)_y$ phosphors with different excitation

Concentration y	Co-ordinates								
	CT band			394 nm			465 nm		
	x	y	Color purity	x	y	Color purity	x	y	Color purity
1	0.6725	0.3272	98.01	0.6588	0.3408	94.50	0.6604	0.3392	94.90
2	0.6727	0.3270	98.06	0.6602	0.3394	94.85	0.6612	0.3384	95.10
3	0.6724	0.3273	97.99	0.6594	0.3403	94.65	0.6610	0.3386	95.05
4	0.6726	0.3271	98.04	0.6562	0.3434	93.85	0.6598	0.3398	94.75
5	0.6725	0.3272	98.01	0.6540	0.3456	93.31	0.6589	0.3408	94.53
6	0.6726	0.3271	98.04	0.6606	0.3391	94.95	0.6620	0.3377	95.31
7	0.6726	0.3271	98.04	0.6545	0.3451	93.43	0.6595	0.3402	94.68
8	0.6636	0.3360	95.71	0.6546	0.3450	93.46	0.6602	0.3395	94.85

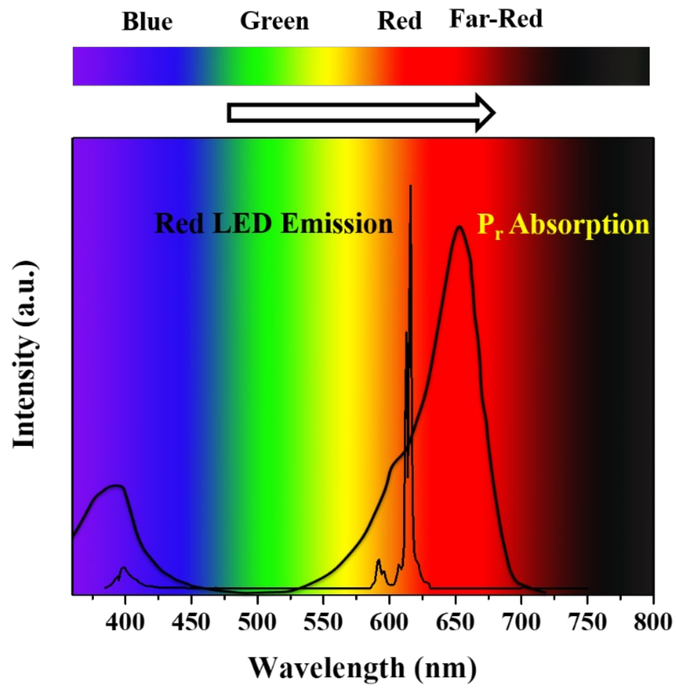

Fig. S13. The red LED emission spectrum and absorption spectrum of Pr.

Table. S6. Comparison of QY of the synthesized phosphor with other reported work.

Composition	Quantum Yield	Ref
$Li_3BaSrY_{0.3}Eu_{2.7}(WO_4)_1(MoO_4)_7$	85.1%	This work
$NaSrLa(MoO_4)_3:Eu^{3+}$	83%	1
$Ba_4La_6(SiO_4)_6O:Eu^{3+}$	65%	2
$Li_3BaSrLn_3(WO_4)_8:Eu^{3+}$	28.36%	3
$KLa_5O_5(VO_4)_2:Eu^{3+}$	29.6%	4
$BaWO_4:Eu^{3+}$	78%	5
$Li_6CaLa_2Sb_2O_{12}:Eu^{3+}$	41.29%	6
$LuVO_4:Eu^{3+}$	-	7
$Y_2O_3:Eu^{3+}$	85%	8
$Sr_2Si_5N_8: Eu^{2+}$	64%	9

References:

1. M. Rajendran, S. Vaidyanathan, *Journal of Alloys and Compounds,* **2019**, 789, 919-93175

2. B. Wei, Z. Liu, C. Xie, S. Yang, W. Tang, A. Gu, W.-T. Wong and K.-L. Wong, *J. Mater. Chem. C*, 2015, **3**, 12322–12327.
3. G. S. R. Raju, E. Pavitra, S. K. Hussain, D. Balaji and J. S. Yu, *J. Mater. Chem. C*, 2016, **4**, 1039–1050.
4. M. Colmont, S. Saitzek, A. Katelnikovas, H. Kabbour, J. Olchowka and P. Roussel, *J. Mater. Chem. C*, 2016, **4**, 7277–7285.
5. P. Jena, S. K. Gupta, N. K.
6. Verma, A. K. Singh and R. M. Kadam, *New J. Chem.*, 2017, **41**, 8947–8958.
7. J. Zhong, D. Chen, W. Zhao, Y. Zhou, H. Yu, L. Chen and Z. Ji, *J. Mater. Chem. C*, 2015, **3**, 4500–4510.
8. F. Kang, L. Li, J. Han, D. Y. Lei and M. Peng, *J. Mater. Chem. C*, 2017, **5**, 390–398.
9. A. P. Jadhav, A. U. Pawar, U. Pal and Y. S. Kang, *J. Mater. Chem. C*, 2014, **2**, 496–500.
10. R.-J. Xie, N. Hirosaki, T. Suehiro, F-F. Xu, M. Mitomo, *Chem. Mater.* **2006**, *18* (23), 5578–5583.