Supporting Information

Color-Tunable Upconversion Luminescence and Prolonged Eu^{3+} Fluorescence Lifetime in Fluoride $KCdF_3$:Yb^{3+},Mn^{2+},Eu^{3+} via Controllable and Efficient Energy Transfer

Xinxin Han,[a] Enhai Song,*[a] Weibin Chen,[ab] Yayun Zhou[a] and Qinyuan Zhang*[a]

[a]*State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, China*

[b]*Guangdong Provincial Engineering Technology Research Center for Optical Agriculture, College of Materials and Energy, South China Agricultural University, Guangzhou 510642, China.*

*Corresponding author E-mail: msehsong@scut.edu.cn(Enhai Song); qyzhang@scut.edu.cn(Qinyuan Zhang).

Table S1 Rietveld refinement data for $KCdF_3$

formula	$KCdF_3$
space group	Pbnm(62)
a (Å)	6.11845(7)
b (Å)	6.12981(7)
c (Å)	8.68419(9)
$\alpha=\beta=\gamma$ (°)	90
Z	4
V (Å^3)	325.700(6)
R_{wp} (%)	7.87
R_p (%)	5.36
χ^2	3.709

Note: The refinements are stable and give low R-factors.

Table S2 CIE chromaticity coordinates for $KCdF_3$:2%Yb^{3+}, 5%Mn^{2+}, $x$$Eu^{3+}$ (x=0-4%)

Serial number	**Eu^{3+} content (x)**	**CIE (X,Y)**
1	0%	(0.4669,0.5287)
2	0.01%	(0.4670,0.5284)
3	0.1%	(0.4881,0.5075)
4	0.5%	(0.5448,0.4513)
5	1%	(0.5790,0.4179)
6	2%	(0.6025,0.3953)
7	3%	(0.6105,0.3877)
8	4%	(0.6096,0.3875)

Table S3 UC emission lifetimes of Eu^{3+} (monitoring the$^5D_0$ energy level)

System	**UC lifetime (ms)**	**Reference**
$LiNbO_3$:Er^{3+},Eu^{3+}	0.02	A. H. Li, et.al, 2009[1]
$NaGdF_4$:Yb/Tm@$NaGdF_4$:Eu@$NaYF_4$	9.75	Q. Su, et.al, 2012[2]
$NaYF_4$: Yb^{3+},Mn^{2+},Eu^{3+}	3.83	Z. Wang, et. al, 2014[3]
$NaYF_4$: Yb^{3+},Mn^{2+},Eu^{3+}@$NaYF_4$	5.96	
$NaLuF_4$: Yb^{3+},Mn^{2+},Eu^{3+}	3.99	
$NaLuF_4$: Yb^{3+},Mn^{2+},Eu^{3+}@$NaLuF_4$	5.63	
$REPO_4$:Yb^{3+},Tb^{3+},Eu^{3+}(RE=Y,La,Gd,Lu)	1.51-2.36	A. Tymiński, et.al, 2016[4]
CaF_2:Yb^{3+},Eu^{3+}	1.71	X. Liu, et.al, 2017[5]
CaF_2:Yb^{3+},Eu^{3+}	1.85	N. Rakov, et.al, 2019[6]
$KCdF_3$: Yb^{3+},Mn^{2+},Eu^{3+}	26.06	This work

Table S4 Lifetimes of the $^5D_0$ energy level of Eu^{3+} in other reported materials

System	Excitation wavelength	Lifetime (ms)	Reference
$Y_2O_3:Eu^{3+}$	266 nm	1.08	X. Wei, et al, 2010.[7]
$ZrO_2:Eu^{3+}$	394 nm	2.44	S. D. Meetei, et al, 2014.[8]
$Gd_2O_3:Eu^{3+}$	258 nm	2.20	L. Liu, et al, 2007.[9]
$Y_2O_3:Eu^{3+}$ $Y_2O_2SO_4:Eu^{3+}$ $Y_2O_2S:Eu^{3+}$	241 nm 270 nm 261 nm	2.34 1.49 0.73	J. Liao, et al, 2015.[10]
$Y_2O_2S:Eu^{3+}$	320 nm	0.16-0.68	J. Thirumalai, et al, 2011.[11]
Gd_2O_2S:Eu,Yb	460 nm	0.17-0.55	C. D. Angel-Olarte, et al, 2019.[12]
$Gd_2O_2S:Eu^{3+}$	329 nm	0.95	B. Qian, et al, 2019.[13]
$CaSO_4:Dy^{3+},Eu^{3+}$	410 nm	1.90-2.71	S. Das, et al,2012.[14]
$Y_3Al_5O_{12}:Eu^{3+},Yb^{3+}$ $Gd_3Ga_5O_{12}:Eu^{3+},Yb^{3+}$	25450 cm^{-1} 25450 cm^{-1}	4.6 4.0	R. Martín-Rodríguez, et al, 2009.[15]
$Y_3Al_5O_{12}:Eu^{3+}$	393.5 nm	5.36-7.14	I.E. Kolesnikov, et al, 2014.[16]
$CaYAl_3O_7:Eu^{3+}$	260 nm	2.16	S. P. Tiwari, et al, 2017.[17]
$Na_2MgSiO_4:Eu^{3+}$	393.5	1.51-2.15	H. Tang, et al, 2017.[18]
$Y_2MoSiO_8:Eu^{3+}$	395 nm	1.06	G. Dong, et al,2019.[19]
$Ca_3Mg_3(PO_4)_4:Eu^{2+},Eu^{3+}$	325 nm	1.90	G. B. Nair, et al, 2020.[20]
$Pb_3Bi(PO_4)_3:Eu^{3+}$	394 nm	2.247	B. Yu, et al, 2020.[21]
$La_2Ti_2O_7$: Eu^{3+},Er^{3+}	393 nm	0.67-0.89	F. Szczepanski, et al, 2020.[22]
$YVO_4:Eu^{3+}$	300 nm	0.46	N. S. Singh, et al, 2009.[23]
$YNbO_4:Eu^{3+}$	465 nm	0.68	L. R. Đačanin, et al, 2014.[24]
$Na_2Ca_2Nb_4O_{13}:Eu^{3+}$	395 nm	0.43-0.74	R. Gao, et al, 2019.[25]
$Ba_2LaNbO_6:Eu^{3+}$ $BaCaLaNbO_6:Eu^{3+}$ $BaMgLaNbO_6:Eu^{3+}$	250-300 nm	3.04 1.74 1.04	R. Phatak, et al, 2020.[26]
$CaMoO_4:Eu^{3+}(,Na^+)$	275 nm	0.35-0.56	A. I. Becerro, et al, 2018.[27]
$La_2Mo_2O_9:Eu^{3+}$	351 nm	0.53	Y. Hua, et al, 2019.[28]
$Sr_3MoO_6:Eu^{3+}$	353 nm	0.28	Y. Hua, et al, 2019.[29]
$La_3Ga_5MO_{14}:Eu^{3+}$(M=Zr,Hf,Sn)	300/394 nm	1.10	A. Reinhardt, et al, 2019.[30]
α-$La_2W_2O_9:Eu^{3+}$	395 nm	0.64	Q. Cheng, et al, 2019.[31]
$NaGd(WO_4)_2$	395 nm	0.12-1.11	W. Zhang, et al, 2020.[32]
Eu^{3+}-doped CdO–Al_2O_3–SiO_2 glass	266 nm	1.78-2.52	Y. Cong, et al, 2008.[33]
Eu^{3+},Yb^{3+}-doped SiO_2-PbO-PbF_2-CdF_2 glass	533 nm	1.55	P. A. Loiko, et al, 2014.[34]
SiO_2-Al_2O_3-NaF-YF_3-TbF_3-EuF_3 glass Glass ceramic	393 nm	2.74 3.28	D. Chen, et al, 2015.[35]
$YNbO_4:Eu^{3+},Yb^{3+}$ doped Li_2O-Al_2O_3-SiO_2 glass Glass ceramics (after heat treatment)	532 nm	0.69 0.14-0.20	P. A. Loiko, et al, 2016.[36]
Eu^{3+} doped B_2O_3-ZnF_2-BaF_2 glass	393 nm	1.40-2.64	R. J. Amjad, et al, 2017.[37]
$LaF_3:Eu^{3+}$	396 nm	10.89	P. Huang, et al, 2020.[38]

silica glass ceramics containing $LaF_3:Eu^{3+}$		6.48	
$BaGe_4O_9:Eu^{3+}$	394 nm	2.25	C. Ji, et al,2019.[39]
$NaGdF_4$:Yb,Tm,Eu $NaGdF_4$:Yb,Tm@NaGdF4:Eu	273 nm	4.50 5.70	B. Y. Liu, et al, 2010.[40]
$GdF_3:Eu^{3+}$	396 nm	4.80-11.80	X. Zhang, et al, 2011.[41]
REOF:Eu^{3+}(RE=Y,La,Gd)	266 nm	0.88-1.23	T. Grzyb, et al, 2013.[42]
Sr_2LnF_7(Ln=La,Gd)	392/272 nm	3.90-7.60	M. Runowski, et al, 2014.[43]
$KGd_2F_7:Eu^{3+}$	466.1/526/525.2 nm	6.90/7.70/9.80	Y. Qin, et al, 2016.[44]
$NaBiF_4:Eu^{3+}$	394 nm	1.61-4.96	P. Du, et al,2018.[45]
$Na_3GaF_6:Eu^{3+}$	395 nm	0.06	D. Yang, et al, 2018.[46]
$KCdF_3$: Yb^{3+},Mn^{2+},Eu^{3+}	256 nm	34.47	This work

Table S5 Pump power dependent CIE chromaticity coordinates for $KCdF_3$:2%Yb^{3+}, 5%Mn^{2+}, 0.5%Eu^{3+}

Serial number	Power (mW)	CIE (*X,Y*)
1	94	(0.5460,0.4518)
2	153	(0.5459,0.4519)
3	212	(0.5471,0.4507)
4	270	(0.5437,0.4540)
5	329	(0.5420,0.4556)
6	387	(0.5407,0.4568)
7	446	(0.5399,0.4575)

Table S6 Temperature dependent CIE chromaticity coordinates for $KCdF_3$:2%Yb^{3+}, 5%Mn^{2+}, 0.5%Eu^{3+}

Serial number	Temperature (K)	CIE (*X,Y*)
1	RT	(0.5542,0.4436)
2	323	(0.5523,0.4453)
3	348	(0.5486,0.4487)
4	373	(0.5443,0.4527)
5	398	(0.5382,0.4583)
6	423	(0.5325,0.4633)
7	448	(0.5255,0.4696)
8	473	(0.5249,0.4695)
9	498	(0.5204,0.4727)
10	523	(0.5137,0.4770)
11	548	(0.5119,0.4769)
12	573	(0.5070,0.4779)

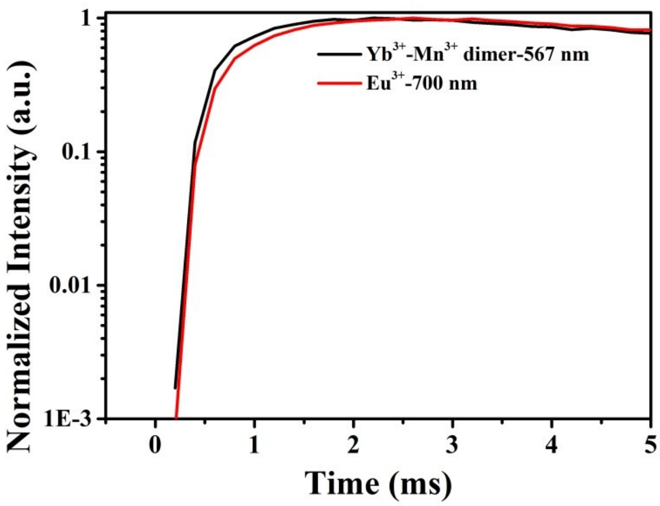

Fig. S1 The UC rising edges of sample $KCdF_3$: 2%Yb^{3+},5%Mn^{2+},0.5%Eu^{3+}.

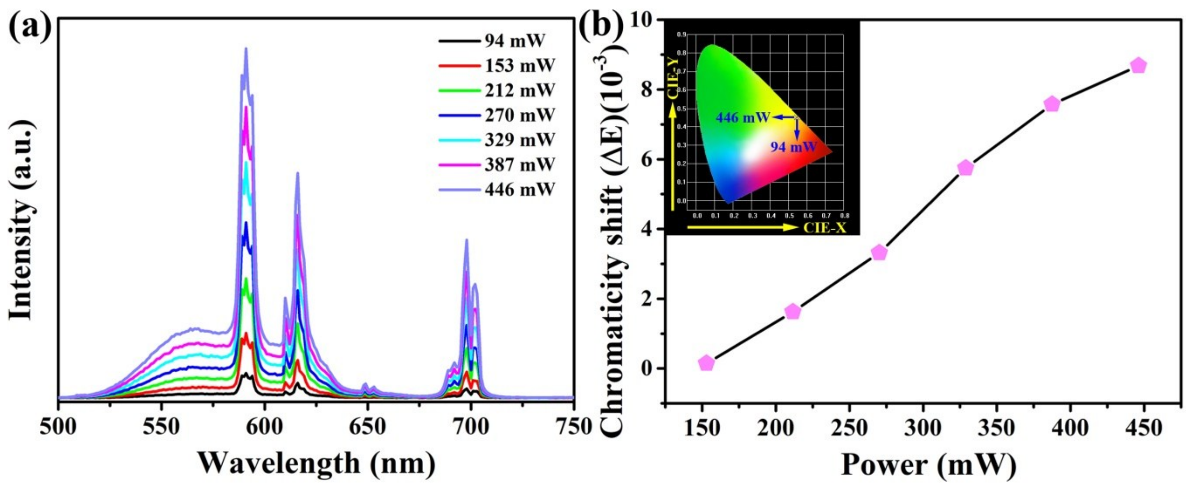

Fig. S2 (a) Pump power dependent UC emission spectra of $KCdF_3$:2%Yb^{3+}, 5%Mn^{2+}, 0.5%Eu^{3+}. (b) Chromaticity shift (ΔE) of $KCdF_3$:2%Yb^{3+}, 5%Mn^{2+}, 0.5%Eu^{3+} in the power range of 94-446 mW. The inset is the CIE chromaticity coordinates.

The chromaticity shift (ΔE) used to describe the color stability is:

$$\Delta E = \sqrt{(u'_p - u'_0)^2 + (v'_p - v'_0)^2 + (w'_p - w'_0)^2}$$

Where $u'=4x/(3-2x+12y)$, $v'=9y/(3-2x+12y)$ and $w'=1-u'-v'$. x and y are the chromaticity coordinates in CIE

1931, u' and v' are the chromaticity coordinates in the $u'v'$ uniform color space. 0 and *P* represent the initial power of 93 mW and given power, respectively.

The small chromaticity shift (ΔE) values indicate the as-prepared sample $KCdF_3$:2%Yb^{3+}, 5%Mn^{2+}, 0.5%Eu^{3+} have excellent chromaticity stability with varying pump power.

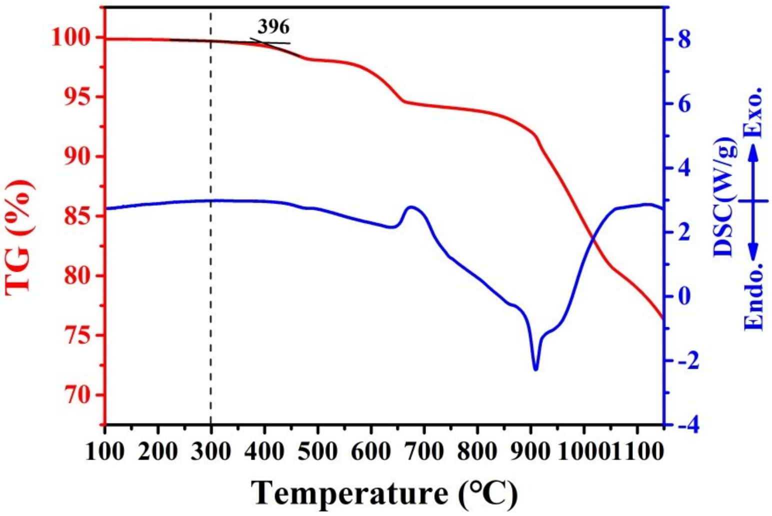

Fig. S3 TG-DSC curves of $KCdF_3$:2%Yb^{3+},5%Mn^{2+}.

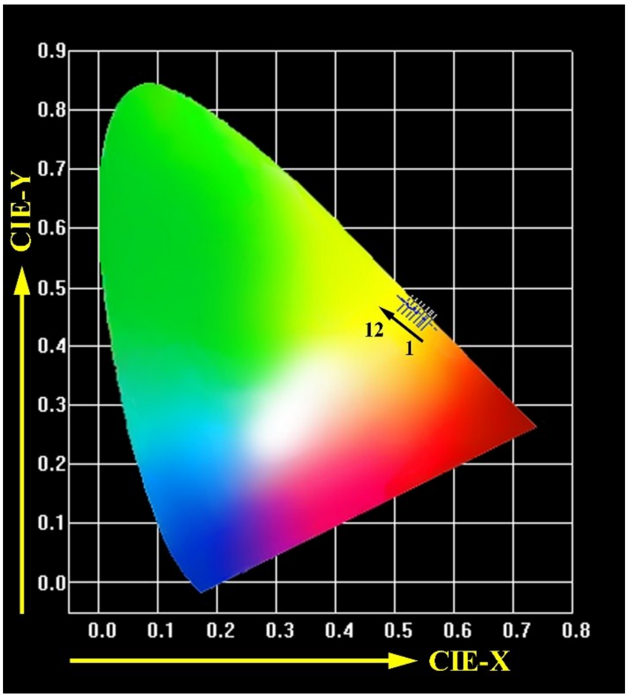

Fig. S4 Temperature dependent CIE chromaticity coordinates for $KCdF_3$:2%Yb^{3+}, 5%Mn^{2+}, 0.5%Eu^{3+}. The serial numbers "1-12" represent the increasing temperature.

References:

1 A. H. Li, Z. R. Zheng, T. Q. Lü, Q. Lü and W. L. Liu, *Opt. Express*, 2009, **17**, 3878.

2 Q. Su, S. Han, X. Xie, H. Zhu, H. Chen, C. Chen, R. Liu, X. Chen, F. Wang and X. Liu, *J. Am. Chem. Soc.*, 2012, **134**, 20849.

3 Z. Wang, J. Feng, S. Song, Z. Sun, S. Yao, X. Ge, M. Pang and H. Zhang, *J. Mater. Chem. C*, 2014, **2**, 9004.

4 A. Tymiński and T. Grzyb, *J. Lumin.*, 2016, **181**, 411.

5 X. Liu, Y. Li, T. Aidilibike, J. Guo, W. Di and W. Qin, *J. Lumin.*, 2017, **185**, 247.

6 N. Rakov, S. C. Duarte and G. S. Macie, *J. Lumin.*, 2019, **214**, 116561.

7 X. WEI, J. ZHAO, W. ZHANG, Y. LI and M. YIN, *J. Rare Earth.*, 2010, **28**, 166.

8 S. D. Meetei and S. D. Singh, *J. Lumin.*, 2014, **147**, 328.

9 L. Liu and X. Chen, *Nanotechnology*, 2007, **18**, 255704.

10 J. Lian, H. Qin, P. Liang and F. Liu, *Solid State Sci.*, 2015, **48**, 147.

11 J. Thirumalai, R. Chandramohan, S. Valanarasu, T. A. Vijayan and S. Ezhilvizhian, *Micro Nano Lett.*, 2011, **8**, 614.

12 C. D. Angel-Olarte, L. Hernández-Adame, A. Mendez-Blas and G. Palestino, *J. Alloy. Compd.*, 2019, **787**, 1032.

13 B. Qian, D. Wang, H. Wang, H. Zou, Y. Song, X. Zhou and Y. Sheng, *J. Am. Ceram. Soc.*, 2019, **103**, 356.

14 S. Das, A. Amarnath Reddy and G. Vijaya Prakash, *Ceram. Int.*, 2012, **38**, 5769.

15 R. Martín-Rodríguez, R. Valiente, S. Polizzi, M. Bettinelli, A. Speghini and F. Piccinelli, *J. Phys. Chem. C*, 2009, **113**, 12195.

16 I. E. Kolesnikov, D. V. Tolstikova, A. V. Kurochkin, A. A. Manshina and M. D. Mikhailov, *Opt. Mater.*, 2014, **37**, 306.

17 S. P. Tiwari, A. Kumar, S. Singh and K. Kumar, *Vacuum*, 2017, **146**, 537.

18 H. Tang, R. Yang and Y. Huang, *J. Alloy. Compd.*, 2017, **714**, 263.

19 G. Dong, J. Zhao, M. Li, L. Guan and X. Li, *Ceram. Int.*, 2019, **45**, 2653.

20 G. B. Nair, A. Kumar, S. J. Dhoble and H. C. Swart, *Mater. Res. Bull.*, 2020, **122**, 110644.

21 B. Yu, Y. Li, Y. Wang and L. Geng, *J. Lumin.*, 2020, **220**, 116978.

22 F. Szczepanski, A. Bayart, A. Katelnikovas, J. Blach, J. Rousseau and S. Saitzek, *J. Alloy. Compd.*, 2020, **826**, 154157.
23 N. S. Singh, R. S. Ningthoujam, M. N. Luwang, S. D. Singh and R. K. Vatsa, *Chem. Phys. Lett.*, 2009, **480**, 237.
24 L. R. Đačanin, M. D. Dramićanin, S. R. LukićPetrović, D. M. Petrović, M. G. Nikolić, T. B. Ivetić and I. O. Gúth, *Ceram. Int.*, 2014, **40**, 8281.
25 R. Cao, H. Xiao, F. Zhang, Z. Luo, T. Chen, W. Li, P. Liu and G. Zheng, *J. Lumin.*, 2019, **208**, 350.
26 R. Phatak, N. Pathak, S. Muhammed, A. Das and S. K. Sali, *J. Am. Ceram. Soc.*, 2020, **103**, 2617.
27 A. I. Becerro, M. Allix, M. Laguna, D. González-Mancebo, C. Genevois, A. Caballero, G. Lozano, N. O. Núñez and M. Ocaña, *J.Mater. Chem. C*, 2018, **10**, 12830.
28 Y. Hua and J. S. Yu, *J. Alloy. Compd.*, 2019, **783**, 969.
29 Y. Hua, S. K. Hussain and J. S. Yu, *Ceram. Int.*, 2019, **45**, 18604.
30 A. Reinhardt, A. Zych, I. Köhler and B. Albert, *J. Lumin.*, 2019, **218**, 116833.
31 Q. Cheng, F. Ren, Q. Lin, H. Tong and X. Miao, *J. Alloy. Compd.*, 2019, **722**, 905.
32 W. Zhang, R. Zhang, S. Yang, R. Wang, L. Na and R. Hua, *Mater. Res. Bull.*, 2020, **122**, 110689.
33 Y. Cong, B. Li, B. Lei, X. Wang, C. Liu, J. Liu and W. Li, *J. Lumin.*, 2008, **128**, 105.
34 P. A. Loiko, G. E. Rachkovskaya, G. B. Zakharevich, A. A. Kornienko, E. B. Dunina, A. S. Yasukevich and K. V. Yumashev, *J. Non-Cryst. Solids*, 2014, **392-393**, 39.
35 D. Chen, Z. Wang, Y. Zhou, P. Huang and Z. Ji, *J. Alloy. Compd.*, 2015, **646**, 339.
36 P. A. Loiko, O. S. Dymshits, I. P. Alekseeva, A. A. Zhilin, M. Y. Tsenter, E. V. Vilejshikova, K. V. Bogdanov, X. Mateos and K. V. Yumashev, *J. Lumin.*, 2016, **179**, 64.
37 R. J. Amjad, W. Santos, C. Jacinto and M. R. Dousti, *J. Lumin.*, 2017, **192**, 827.
38 P. Huang, P. Luo, B. Zhou, L. Wang and J. Wan, *Mater. Lett.*, 2020, **271**, 127764.
39 C. Ji, Z. Huang, X. Tian, W. Xie, J. Wen, H. He, C. Zhou and T. Zeng, *Dyes Pigments*, 2019, **160**, 772.
40 B. Y. Liu, D. Tu, H. Zhu, R. Li, W. Luo and X. Chen, *Adv. Mater.*, 2010, **22**, 3266.
41 X. Zhang, T. Hayakawa, M. Nogami and Y. Ishikawa, *J. Alloy. Compd.*, 2011, **509**, 2076.
42 T. Grzyb, W. Mariusz, T. Pędziński and S. Lis, *Opt. Mater.*, 2013, **35**, 2226.
43 M. Runowski, S. Balabhadra and S. Lis, *J. Rare Earth.*, 2014, **32**, 242.
44 Y. Qin, X. Wei, J. Wen, Y. Chen and M. Yin, *J. Nanosci. Nanotechno.*, 2016, **16**, 3873.
45 P. Du, X. Huang and S. J. Yu, *Chem. Eng. J.*, 2018, **337**, 91.
46 D. Yang, L. Liao, Q. Guo, L. Wang, L. Mei, H. Liu and T. Zhou, *J. Lumin.*, 2018, **203**, 385.