Electronic Supplementary Material (ESI) for CrystEngComm.

Lanthanide coordination polymers constructed from 5-(1H-tetrazol-5-yl)isophthalic acid ligand: white light emission and color tuning

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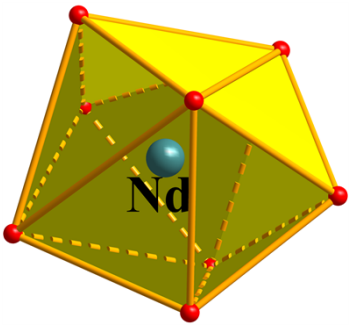
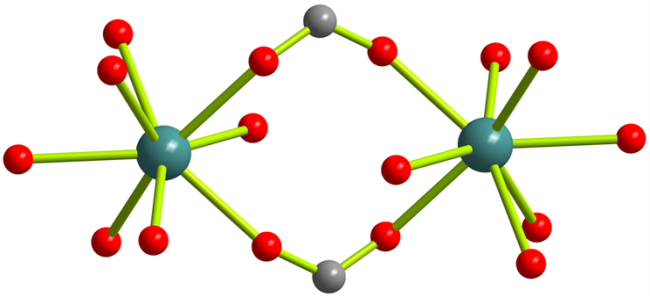
Supporting Information

Table of Contents



(a)



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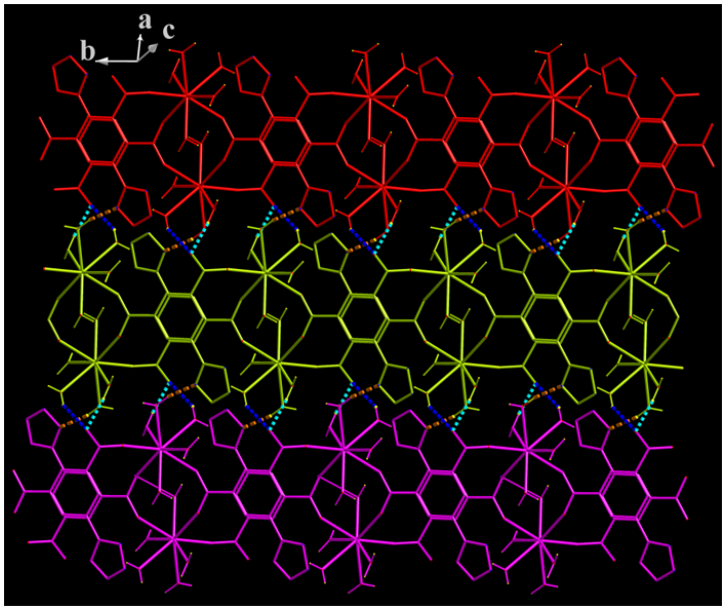

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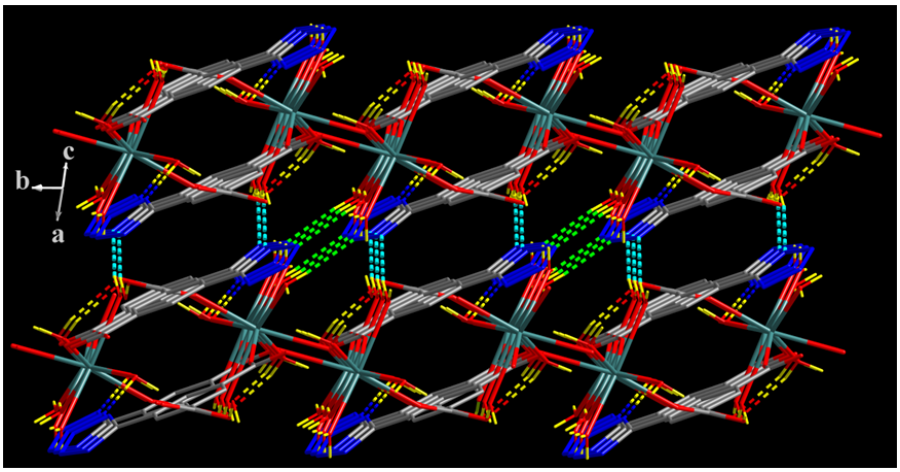


(d)

Fig. S1 (a) The coordination geometry of Nd(III) in **1**; (b) binuclear SBU of **1**; (c) The 2D structure formed by hydrogen bonds(only hydrogen atoms of coordinated water molecules and hydrogen bonds are retained); (d)3D supramolecular structure constructed by the hydrogen bonds.

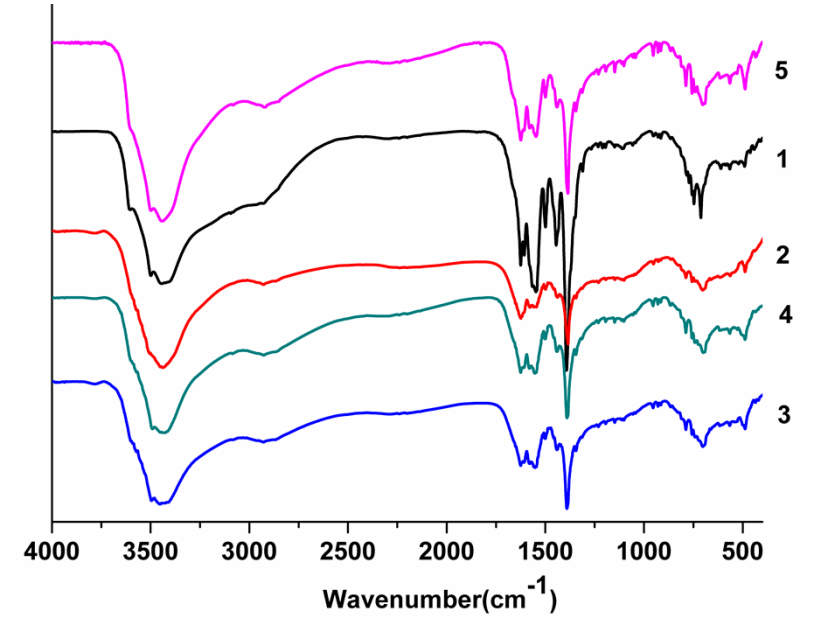


Fig. S2 IR spectra of compounds **1-5**

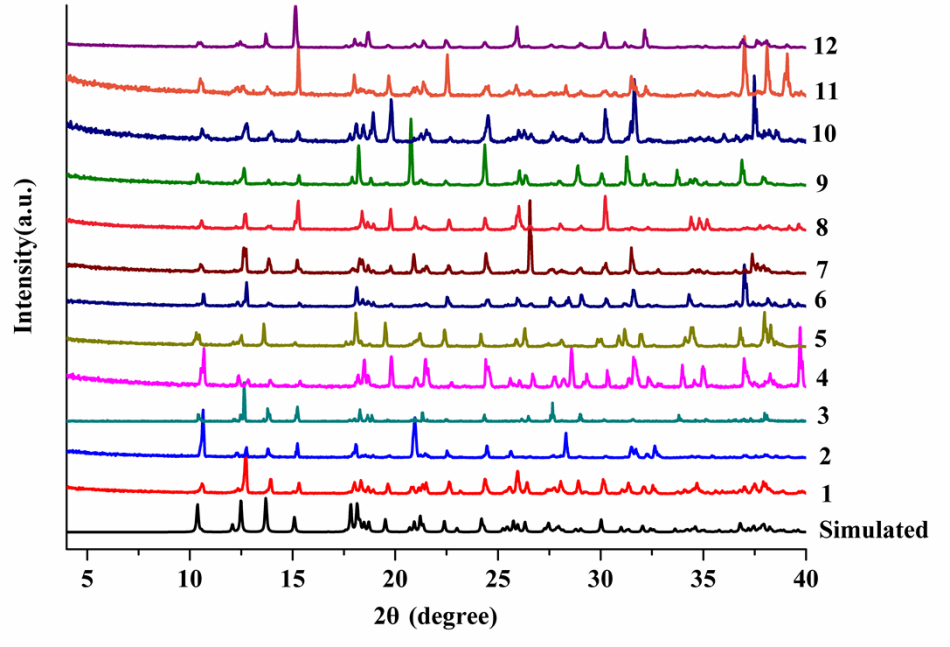


Fig. S3 PXRD patterns for compounds **1-12**

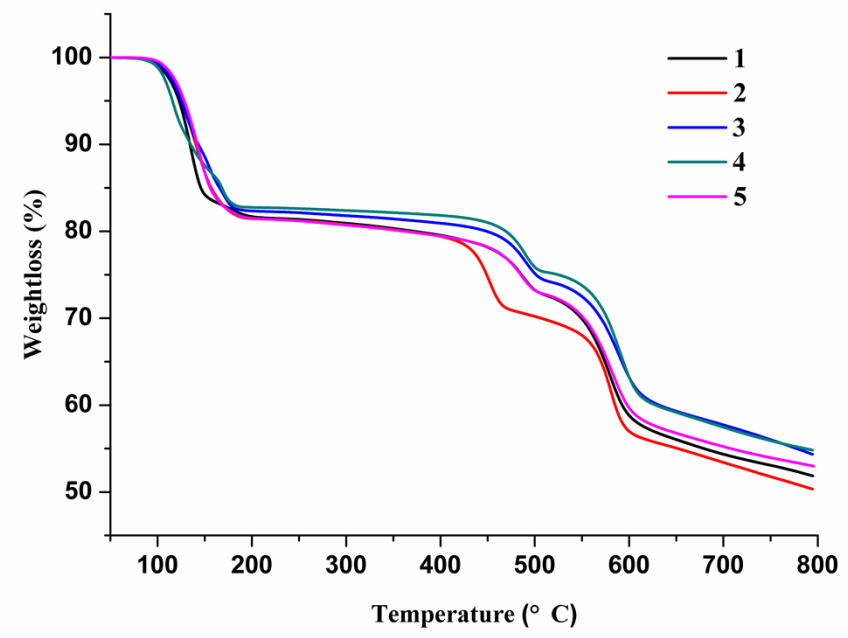


Fig. S4 TGA curves of the compounds **1-5** measured in nitrogen atmosphere.

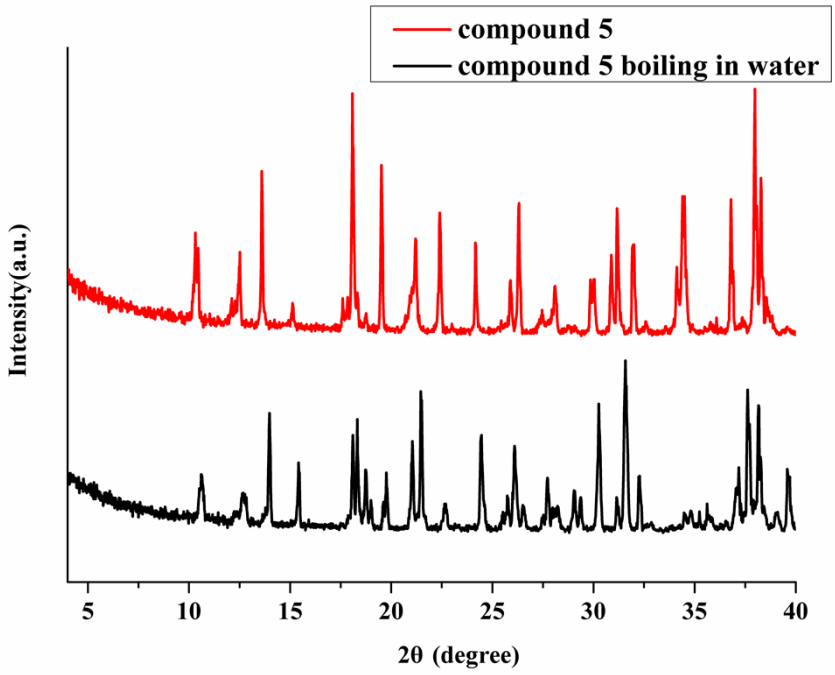


Fig. S5 PXRD patterns for compound **5** and compound **5** boiling in water for 24 h.

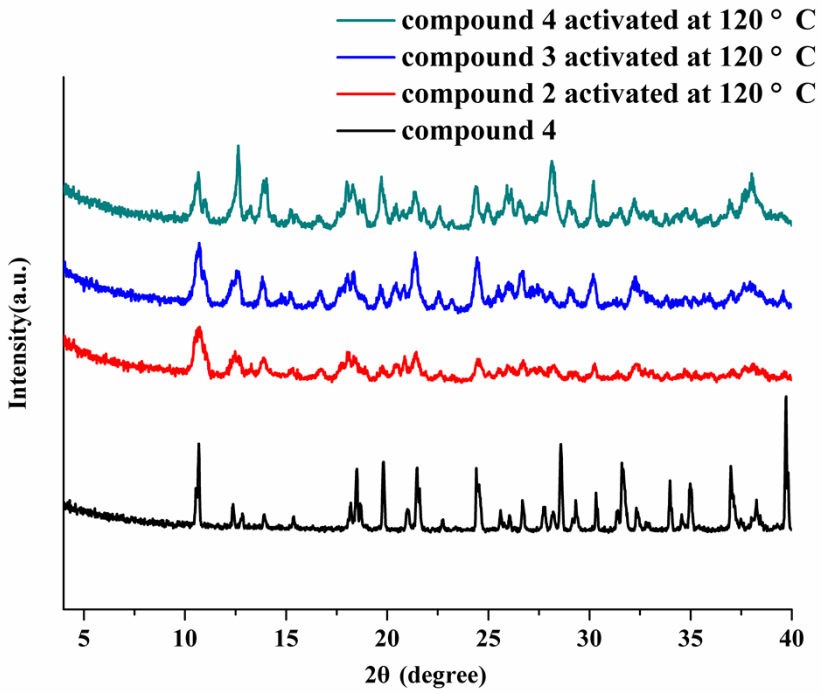


Fig. S6 PXRD patterns for compound **4** and compounds **2**-**4** activated at 120 °C.

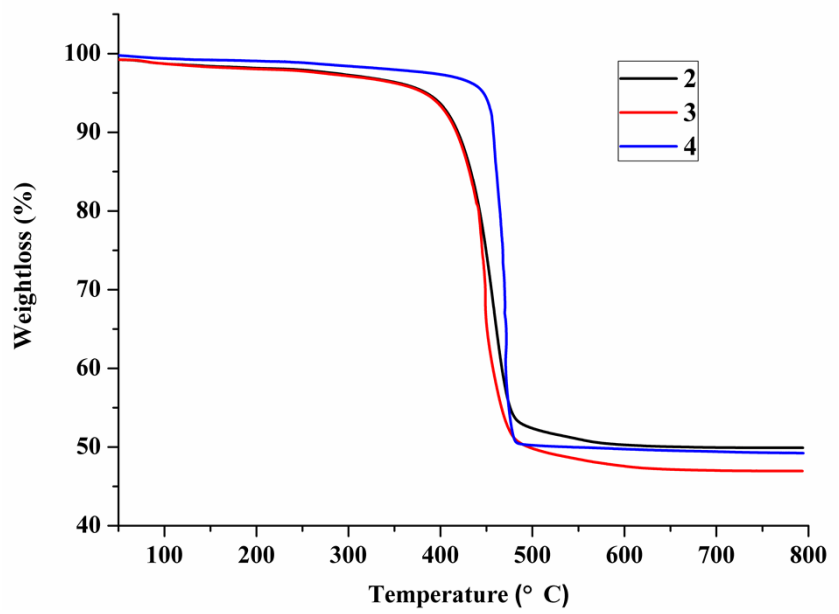


Fig. S7 TGA curves of the compounds **2**-**4** upon dehydration measured in air atmosphere.

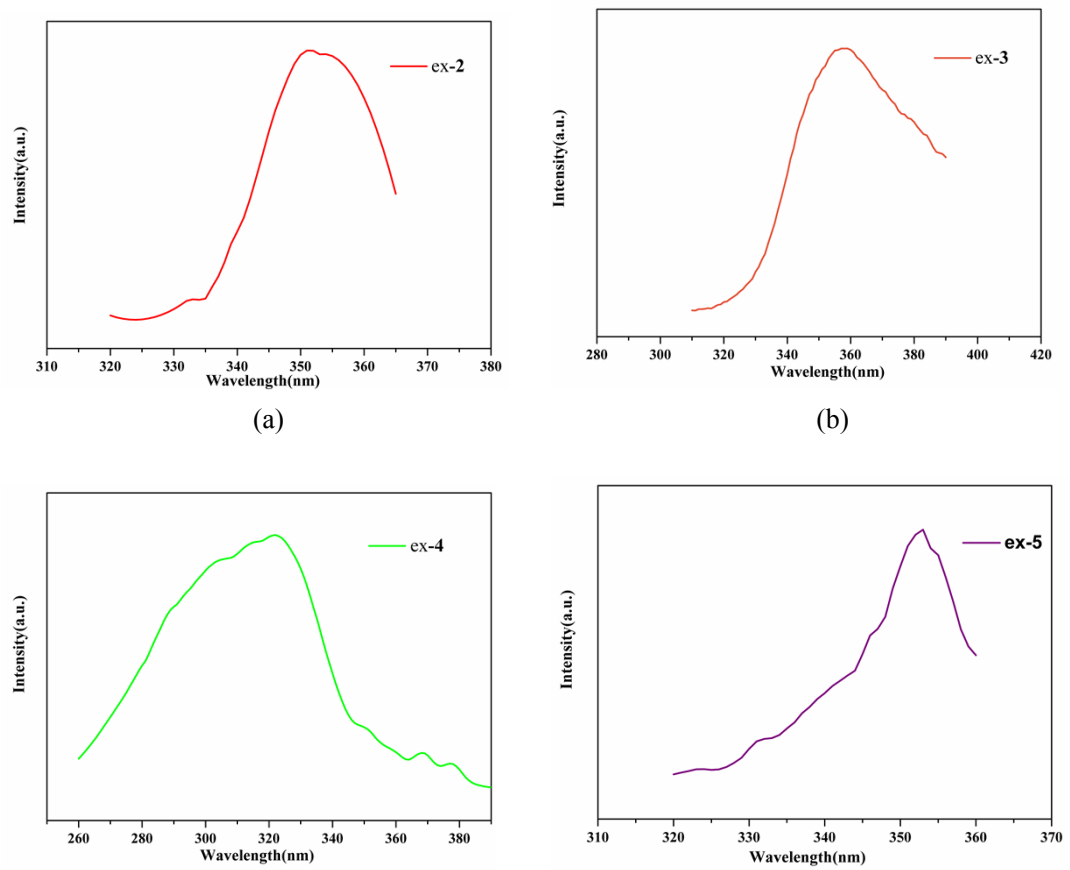


Fig. S8 Solid-state excitation spectra of (a) Eu-**2**, (b) Gd-**3**, (c) Tb-**4** and (d) Sm-**5** at room temperature.

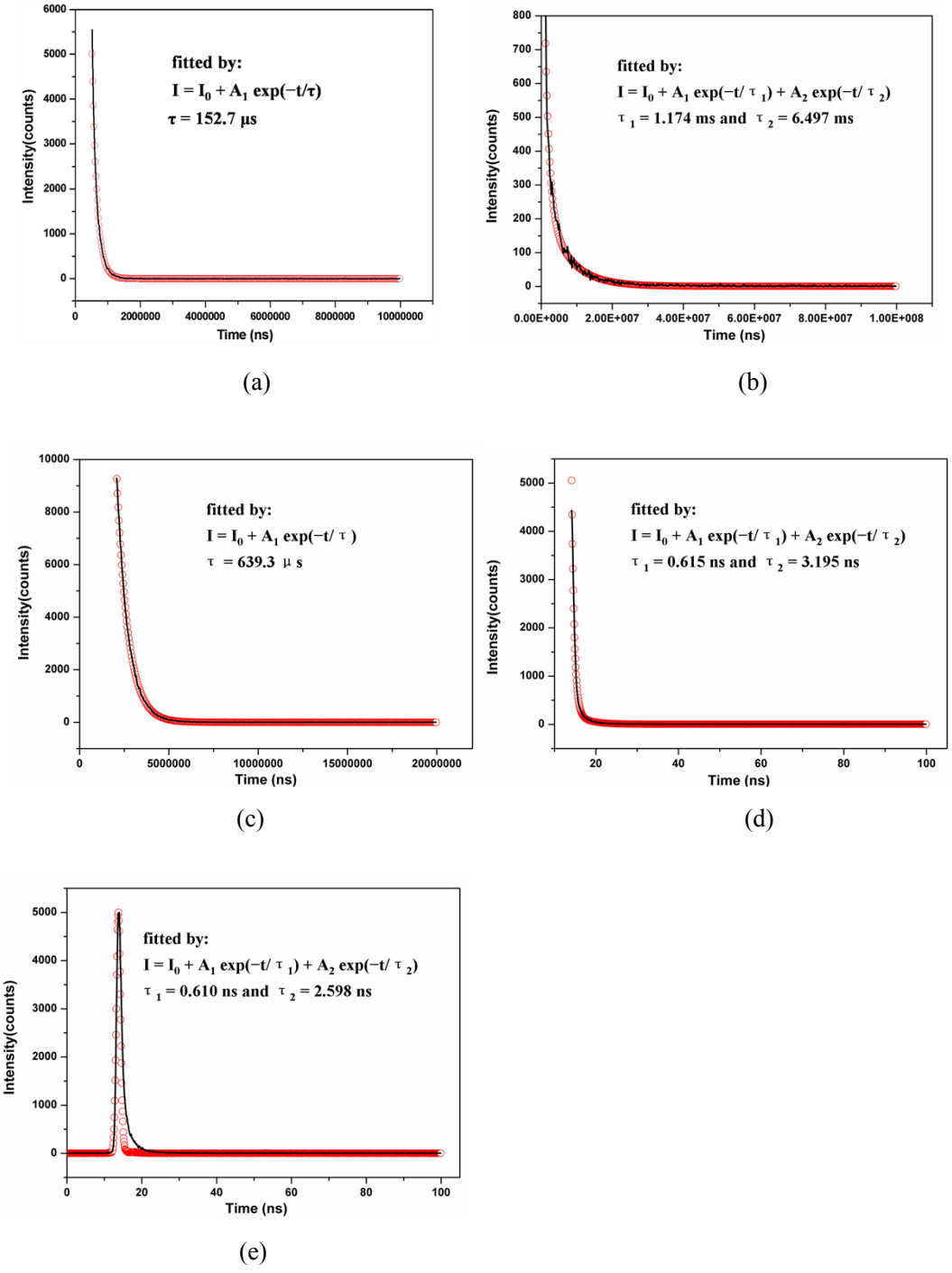


Fig. S9 Luminescence decay profiles for compounds **2**-(a), **3**-(b), **4**-(c), **5**-(d) and H_3TZI ligand-(e) recorded at room temperature. The $^5D_0$ decay curve of compound **2** with emission was monitored at 614 nm (λ_{ex} = 352 nm). The red line is the best fitting to the data using a mono-exponential function, giving the value of τ = 152.7μs. The decay curve of compound **3** with emission was monitored at 495 nm (λ_{ex} = 358 nm). The $^5D_4$ decay curve of compound **4** with emission was monitored at 543 nm (λ_{ex} = 322 nm). The red line is the best fitting to the data using a mono-exponential function, giving the value of τ = 639.3μs. The decay curve of compound **5** with emission was monitored at 512 nm (λ_{ex} = 353 nm).

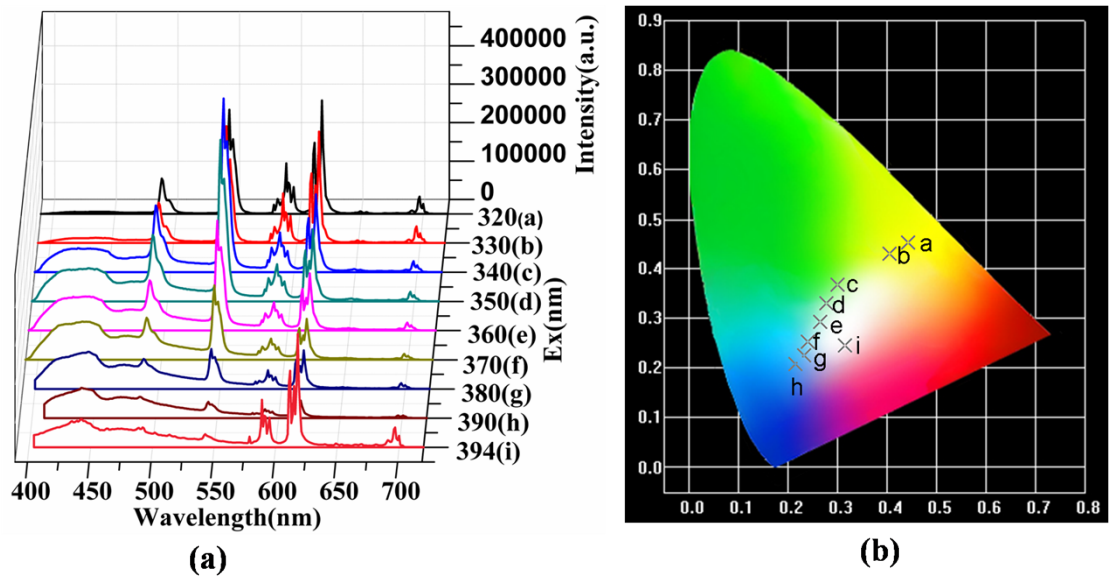
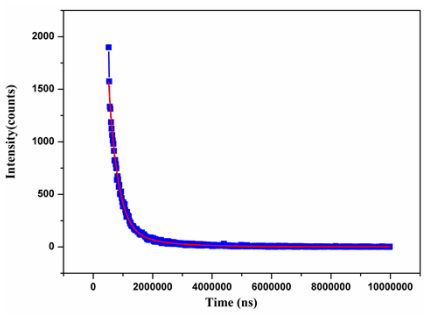
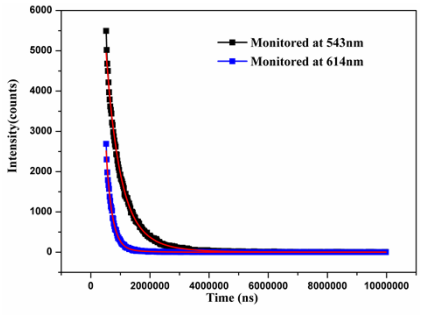


Fig.S10 (a) Solid-state emission spectra of compound $Eu_{0.15}$ $Gd_{0.70}$ $Tb_{0.15}$ with excitation wavelengths varying from 320 to 394 nm. (b) The CIE chromaticity diagram for the compound $Eu_{0.15}$ $Gd_{0.70}$ $Tb_{0.15}$ under excitation wavelengths from 320 to 394 nm (a→i).



(a)



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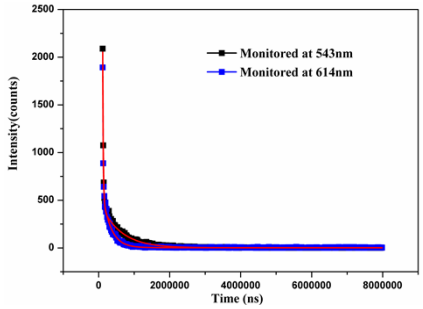

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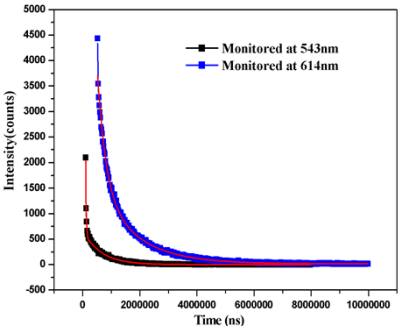

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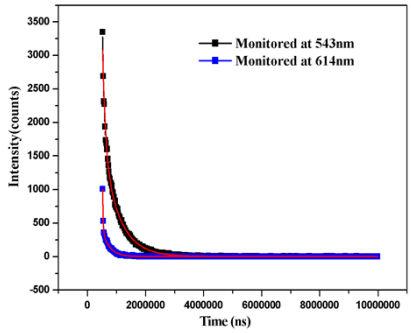

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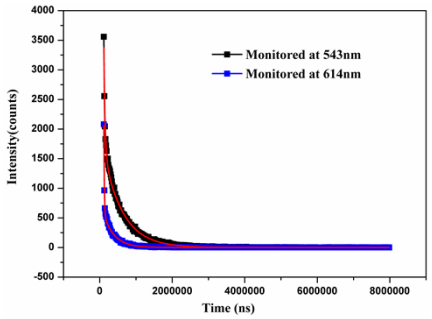

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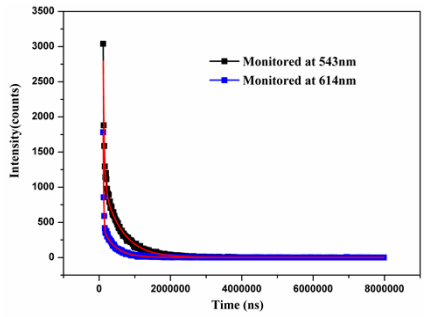

(g)

Fig. S11 Luminescence decay profiles for compounds **6-12** recorded at room temperature. **6-**(a), **7-**(b), **8-**(c), **9-**(d), **10-**(e), **11-**(f) and **12-**(g). The $^5D_0$ decay curve of compound **6** with emission was monitored at 614 nm (λ_{ex} = 352 nm). The decay curves of compounds **7-12** were recorded with emission monitored by the $^5D_4 \rightarrow {}^7F_5$ transition at 543 nm and the $^5D_0 \rightarrow {}^7F_2$ transition at 614 nm (λ_{ex} = 365 nm).

Table S1. Crystal data and structure refinement for compounds **1- 5**

Compounds	**1**	**2**	**3**	**4**	**5**
Formula	$C_9H_{13}NdN_4O_9$	$C_{18}H_{26}Eu_2N_8O_{18}$	$C_9H_{13}GdN_4O_9$	$C_{18}H_{26}N_8O_{18}Tb_2$	$C_9H_{13}N_4O_9Sm$
Fw (g mol^{-1})	465.47	946.39	478.48	960.33	471.59
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a(Å)	7.9987(6)	7.9812(3)	7.9767(5)	7.9698(4)	7.9849(16)
b(Å)	9.8130(6)	9.7491(4)	9.7325(5)	9.7137(5)	9.783(2)
c(Å)	10.4856(6)	10.4153(4)	10.3966(6)	10.3770(5)	10.443(2)
α(°)	116.667(4)	116.8030(10)	116.8210(10)	116.8630(10)	116.75(3)
β(°)	107.471(4)	107.3700(10)	107.3330(10)	107.2860(10)	107.36(3)
γ(°)	95.656(4)	95.6700(10)	95.6690(10)	95.6960(10)	95.71(3)
V(Å^3)	674.77(8)	663.93(4)	661.32(7)	658.07(6)	668.6(2)
Z	2	1	2	1	2
D_{calc} (g· cm^{-3})	2.291	2.367	2.403	2.423	2.342
μ(mm^{-1})	3.907	4.784	5.075	5.435	4.452
F(000)	454	460	462	464	458
θ range (°)	2.36 - 25.14	2.38 - 28.36	2.39 - 28.28	2.38 - 28.31	2.37 - 25.02
Limiting indices	$-9 \le h \le 9$	$-10 \le h \le 10$	$-9 \le h \le 10$	$-7 \le h \le 10$	$-8 \le h \le 9$
	$-10 \le k \le 11$	$-13 \le k \le 13$	$-12 \le k \le 10$	$-12 \le k \le 9$	$-11 \le k \le 11$
	$-12 \le l \le 12$	$-13 \le l \le 13$	$-13 \le l \le 13$	$-13 \le l \le 13$	$-12 \le l \le 12$
Refl. Collected / unique	3855 / 2403	4947 / 3288	4839 / 3229	4848 / 3238	3788 / 2361
R_{int}	0.0480	0.0316	0.0329	0.0330	0.0212
Data / restraints / parameters	2403 / 7 / 247	3288 / 0 / 260	3229 / 0 / 248	3238 / 0 / 260	2361 / 0 / 248
GOF	1.093	1.013	0.922	1.039	1.572
R_1 [$I>2\sigma(I)$]	0.0273	0.0210	0.0284	0.0259	0.0341
wR_2 [$I>2\sigma(I)$]	0.0701	0.0514	0.0764	0.0664	0.0768
R_1 (all data)	0.0282	0.0225	0.0293	0.0275	0.0365
wR_2 (all data)	0.0707	0.0519	0.0773	0.0674	0.0774
Largest diff. peak and hole (e·Å^{-3})	1.671 and -1.481	1.385 and -1.310	1.428 and -1.408	0.744 and -0.613	0.780 and -1.354
CCDC No.	1028649	1029007	1033880	1028648	1029044

Table S2. Selected bond lengths [Å] and angles [°] for compounds **1- 5**

1			
Nd(1)-O(1)	2.360(3)	Nd(1)-O(9)	2.482(3)
Nd(1)-O(3)#1	2.391(3)	Nd(1)-O(6)	2.494(3)
Nd(1)-O(2)#2	2.456(3)	Nd(1)-O(5)	2.527(3)
Nd(1)-O(8)	2.463(3)	Nd(1)-O(7)	2.529(3)
O(1)-Nd(1)-O(3)#1	83.59(10)	O(9)-Nd(1)-O(6)	136.28(10)
O(1)-Nd(1)-O(2)#2	84.75(10)	O(1)-Nd(1)-O(5)	68.84(10)
O(3)#1-Nd(1)-O(2)#2	155.89(10)	O(3)#1-Nd(1)-O(5)	97.60(10)
O(1)-Nd(1)-O(8)	142.41(10)	O(2)#2-Nd(1)-O(5)	97.75(10)
O(3)#1-Nd(1)-O(8)	94.24(10)	O(8)-Nd(1)-O(5)	147.92(10)
O(2)#2-Nd(1)-O(8)	82.36(10)	O(9)-Nd(1)-O(5)	139.99(10)
O(1)-Nd(1)-O(9)	71.30(10)	O(6)-Nd(1)-O(5)	77.87(10)
O(3)#1-Nd(1)-O(9)	81.13(10)	O(1)-Nd(1)-O(7)	127.75(11)
O(2)#2-Nd(1)-O(9)	75.15(10)	O(3)#1-Nd(1)-O(7)	135.23(10)
O(8)-Nd(1)-O(9)	71.29(10)	O(2)#2-Nd(1)-O(7)	67.69(10)
O(1)-Nd(1)-O(6)	134.35(10)	O(8)-Nd(1)-O(7)	78.62(11)
O(3)#1-Nd(1)-O(6)	70.52(10)	O(9)-Nd(1)-O(7)	134.60(10)
O(2)#2-Nd(1)-O(6)	131.14(10)	O(6)-Nd(1)-O(7)	64.74(10)
O(8)-Nd(1)-O(6)	78.20(10)	O(5)-Nd(1)-O(7)	71.98(11)
2			
Eu(1)-O(3)#1	2.3230(19)	Eu(1)-O(2)	2.434(2)
Eu(1)-O(5)#2	2.346(2)	Eu(1)-O(6)	2.439(2)
Eu(1)-O(7)	2.409(2)	Eu(1)-O(4)	2.477(2)
Eu(1)-O(1)	2.416(2)	Eu(1)-O(8)	2.484(2)
O(3)#1-Eu(1)-O(5)#2	83.18(7)	O(2)-Eu(1)-O(6)	136.36(8)
O(3)#1-Eu(1)-O(7)	142.65(8)	O(3)#1-Eu(1)-O(4)	68.79(8)
O(5)#2-Eu(1)-O(7)	94.78(8)	O(5)#2-Eu(1)-O(4)	96.62(8)
O(3)#1-Eu(1)-O(1)	84.53(7)	O(7)-Eu(1)-O(4)	147.83(8)
O(5)#2-Eu(1)-O(1)	156.06(7)	O(1)-Eu(1)-O(4)	97.95(8)
O(7)-Eu(1)-O(1)	82.76(8)	O(2)-Eu(1)-O(4)	140.33(8)
O(3)#1-Eu(1)-O(2)	71.63(8)	O(6)-Eu(1)-O(4)	77.12(8)
O(5)#2-Eu(1)-O(2)	81.10(8)	O(3)#1-Eu(1)-O(8)	127.60(8)
O(7)-Eu(1)-O(2)	71.23(9)	O(5)#2-Eu(1)-O(8)	135.82(8)
O(1)-Eu(1)-O(2)	75.56(7)	O(7)-Eu(1)-O(8)	78.33(9)
O(3)#1-Eu(1)-O(6)	133.98(8)	O(1)-Eu(1)-O(8)	67.17(8)
O(5)#2-Eu(1)-O(6)	70.78(8)	O(2)-Eu(1)-O(8)	134.16(8)
O(7)-Eu(1)-O(6)	78.46(8)	O(6)-Eu(1)-O(8)	65.06(9)
O(1)-Eu(1)-O(6)	131.17(7)	O(4)-Eu(1)-O(8)	72.54(8)
3			
Gd(1)-O(2)	2.319(2)	Gd(1)-O(1)	2.419(3)
Gd(1)-O(4)	2.339(2)	Gd(1)-O(5)	2.435(3)
Gd(1)-O(7)	2.396(3)	Gd(1)-O(3)	2.457(3)
Gd(1)-O(8)	2.406(2)	Gd(1)-O(6)	2.469(3)

O(2)-Gd(1)-O(4)	83.10(9)	O(2)-Gd(1)-O(1)	71.82(9)
O(2)-Gd(1)-O(7)	142.86(10)	O(4)-Gd(1)-O(1)	80.95(9)
O(4)-Gd(1)-O(7)	94.50(10)	O(7)-Gd(1)-O(1)	71.21(10)
O(2)-Gd(1)-O(8)	84.60(9)	O(8)-Gd(1)-O(1)	75.45(9)
O(4)-Gd(1)-O(8)	155.82(10)	O(2)-Gd(1)-O(5)	133.71(9)
O(7)-Gd(1)-O(8)	82.95(9)	O(4)-Gd(1)-O(5)	70.88(9)
O(7)-Gd(1)-O(5)	78.45(10)	O(8)-Gd(1)-O(5)	131.30(9)
O(1)-Gd(1)-O(5)	136.42(10)	O(2)-Gd(1)-O(3)	68.75(10)
O(4)-Gd(1)-O(3)	96.59(9)	O(7)-Gd(1)-O(3)	147.77(11)
O(8)-Gd(1)-O(3)	98.22(9)	O(1)-Gd(1)-O(3)	140.48(10)
O(5)-Gd(1)-O(3)	76.82(10)	O(2)-Gd(1)-O(6)	127.71(10)
O(4)-Gd(1)-O(6)	135.94(11)	O(7)-Gd(1)-O(6)	78.24(11)
O(8)-Gd(1)-O(6)	67.24(10)	O(1)-Gd(1)-O(6)	134.00(10)
O(5)-Gd(1)-O(6)	65.07(10)	O(3)-Gd(1)-O(6)	72.76(10)
		4	
Tb(1)-O(1)	2.303(2)	Tb(1)-O(6)	2.402(3)
Tb(1)-O(4)#1	2.314(3)	Tb(1)-O(8)	2.416(3)
Tb(1)-O(5)	2.381(3)	Tb(1)-O(7)	2.443(3)
Tb(1)-O(2)#2	2.396(2)	Tb(1)-O(9)	2.462(3)
O(1)-Tb(1)-O(4)#1	83.11(9)	O(1)-Tb(1)-O(5)	142.88(10)
O(4)#1-Tb(1)-O(5)	94.76(11)	O(5)-Tb(1)-O(6)	71.05(11)
O(1)-Tb(1)-O(2)#2	84.20(9)	O(2)#2-Tb(1)-O(6)	75.58(9)
O(4)#1-Tb(1)-O(2)#2	156.00(9)	O(1)-Tb(1)-O(8)	133.82(9)
O(5)-Tb(1)-O(2)#2	83.30(10)	O(4)#1-Tb(1)-O(8)	70.84(10)
O(1)-Tb(1)-O(6)	72.02(10)	O(5)-Tb(1)-O(8)	78.40(11)
O(4)#1-Tb(1)-O(6)	81.15(9)	O(2)#2-Tb(1)-O(8)	131.39(10)
O(6)-Tb(1)-O(8)	136.26(10)	O(1)-Tb(1)-O(9)	127.49(10)
O(1)-Tb(1)-O(7)	68.81(10)	O(4)#1-Tb(1)-O(9)	136.15(10)
O(4)#1-Tb(1)-O(7)	96.18(10)	O(5)-Tb(1)-O(9)	78.18(11)
O(5)-Tb(1)-O(7)	147.69(12)	O(2)#2-Tb(1)-O(9)	67.00(10)
O(2)#2-Tb(1)-O(7)	98.10(10)	O(6)-Tb(1)-O(9)	133.66(11)
O(6)-Tb(1)-O(7)	140.76(10)	O(8)-Tb(1)-O(9)	65.33(11)
O(8)-Tb(1)-O(7)	76.70(10)	O(7)-Tb(1)-O(9)	72.89(10)
		5	
Sm(1)-O(4)#1	2.339(4)	Sm(1)-O(5)	2.442(5)
Sm(1)-O(2)	2.360(4)	Sm(1)-O(8)	2.457(5)
Sm(1)-O(3)#2	2.430(4)	Sm(1)-O(9)	2.487(5)
Sm(1)-O(6)	2.431(4)	Sm(1)-O(7)	2.500(5)
O(4)#1-Sm(1)-O(2)	83.10(15)	O(5)-Sm(1)-O(8)	136.03(18)
O(4)#1-Sm(1)-O(3)#2	84.52(14)	O(4)#1-Sm(1)-O(9)	68.87(16)
O(2)-Sm(1)-O(3)#2	155.93(14)	O(2)-Sm(1)-O(9)	96.66(16)
O(4)#1-Sm(1)-O(6)	142.53(16)	O(3)#2-Sm(1)-O(9)	97.99(16)
O(2)-Sm(1)-O(6)	94.68(16)	O(6)-Sm(1)-O(9)	147.90(17)
O(3)#2-Sm(1)-O(6)	82.82(15)	O(5)-Sm(1)-O(9)	140.35(19)

O(4)#1-Sm(1)-O(5)	71.56(18)	O(8)-Sm(1)-O(9)	77.49(16)
O(2)-Sm(1)-O(5)	81.03(16)	O(4)#1-Sm(1)-O(7)	127.78(16)
O(3)#2-Sm(1)-O(5)	75.50(16)	O(2)-Sm(1)-O(7)	135.68(17)
O(6)-Sm(1)-O(5)	71.15(19)	O(3)#2-Sm(1)-O(7)	67.44(16)
O(4)#1-Sm(1)-O(8)	134.31(15)	O(6)-Sm(1)-O(7)	78.42(17)
O(2)-Sm(1)-O(8)	70.81(16)	O(5)-Sm(1)-O(7)	134.31(18)
O(3)#2-Sm(1)-O(8)	131.19(15)	O(8)-Sm(1)-O(7)	64.90(18)
O(6)-Sm(1)-O(8)	78.11(16)	O(9)-Sm(1)-O(7)	72.49(17)

Symmetry transformations used to generate equivalent atoms for **1**: #1 -x,-y+1,-z+1; #2 -x,-y,-z+1, for **2**: #1 -x+1,-y,-z+1; #2 x,y-1,z; for **4**: #1 -x,-y+1,-z; #2 -x,-y,-z, for **5**: #1 -x,-y+1,-z； #2 x,y-1,z.

Table S3. Hydrogen bond lengths and bond angles for compound **1**.

D-H···A	*d*(D-H) / Å	*d*(H···A) / Å	*d*(D···A) / Å	∠DHA / °
O6-H7···N4#2	0.92	1.87	2.775(5)	167
O7-H1···O4#1	0.84	2.07	2.845(4)	152
O5-H5···O4#1	0.86	1.85	2.676(4)	160
O9-H3···N2#4	0.79	1.93	2.719(5)	174
O5-H6···N1#5	0.90	2.01	2.898(5)	170

Symmetry transformations used to generate equivalent atoms: #1: x+1, y, z+1; #2: -x+1, -y+1, -z+2; #4: x-1, y-1, z; #5: -x+1, -y+1, -z+1.

Table S4. CIE chromaticity coordinates (x, y) for compound $Eu_{0.10}Gd_{0.90}$ (**6**).

λ_{ex} / nm	$Eu_{0.10}Gd_{0.90}$
330	(0.493, 0.297)
340	(0.420, 0.293)
350	(0.332, 0.294)
360	(0.286, 0.284)
370	(0.270, 0.266)
380	(0.273, 0.263)

Table S5. CIE chromaticity coordinates (x, y) for compounds $Eu_xGd_yTb_{1-x-y}$ (**8-12**).

Compounds	Coordinations
$Eu_{0.25}Gd_{0.70}Tb_{0.05}$ (**8**)	(0.311, 0.269)
$Eu_{0.20}Gd_{0.70}Tb_{0.10}$ (**9**)	(0.339, 0.295)
$Eu_{0.25}Gd_{0.60}Tb_{0.15}$ (**10**)	(0.320, 0.310)
$Eu_{0.20}Gd_{0.55}Tb_{0.25}$ (**11**)	(0.297, 0.333)
$Eu_{0.25}Gd_{0.50}Tb_{0.25}$ (**12**)	(0.336, 0.325)

Table S6. CIE chromaticity coordinates (x, y) for compound $Eu_{0.15}Gd_{0.70}Tb_{0.15}$ (**7**).

λ_{ex} / nm	$Eu_{0.15}Gd_{0.70}Tb_{0.15}$
320	(0.443, 0.452)
330	(0.406, 0.430)
340	(0.299, 0.367)
350	(0.278, 0.330)
360	(0.264, 0.292)
370	(0.241, 0.252)
380	(0.232, 0.224)
390	(0.214, 0.208)
394	(0.314, 0.244)

Table S7. Luminescence lifetimes of the codoped compounds **6-12**.

Compounds	luminescence lifetimes (τ_{Tb3+})	luminescence lifetimes (τ_{Eu3+})
$[Eu_{0.10}Gd_{0.90}(TZI)(H_2O)_5]_n$ **6**	0	τ_1 = 0.318 ms
		τ_2 = 1.458 ms
$[Eu_{0.15}Gd_{0.70}Tb_{0.15}(TZI)(H_2O)_5]_n$ **7**	τ_1 = 0.431 ms	τ_1 = 0.198 ms
	τ_2 = 0.938 ms	τ_2 = 0.706 ms
$[Eu_{0.25}Gd_{0.70}Tb_{0.05}(TZI)(H_2O)_5]_n$ **8**	τ_1 = 19.36 us	τ_1 = 13.70 us
	τ_2 = 563.8 us	τ_2 = 236.2 us
$[Eu_{0.20}Gd_{0.70}Tb_{0.10}(TZI)(H_2O)_5]_n$ **9**	τ_1 = 19.67 us	τ_1 = 287.1 us
	τ_2 = 631.2 us	τ_2 = 1.322 ms
$[Eu_{0.25}Gd_{0.60}Tb_{0.15}(TZI)(H_2O)_5]_n$ **10**	τ_1 = 94.73 us	τ_1 = 16.82 us
	τ_2 = 565.2 us	τ_2 = 256.1 us
$[Eu_{0.20}Gd_{0.55}Tb_{0.25}(TZI)(H_2O)_5]_n$ **11**	τ_1 = 34.84 us	τ_1 = 14.56 us
	τ_2 = 533.0 us	τ_2 = 298.2 us
$[Eu_{0.25}Gd_{0.50}Tb_{0.25}(TZI)(H_2O)_5]_n$ **12**	τ_1 = 33.42 us	τ_1 = 16.38 us
	τ_2 = 523.7 us	τ_2 = 354.5 us