Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting information

Dual *vis*-NIR emissive heterometallic naphthoates of Eu-Yb-Gd: new approach toward Yb luminescence intensity increase through Eu→Yb energy transfer

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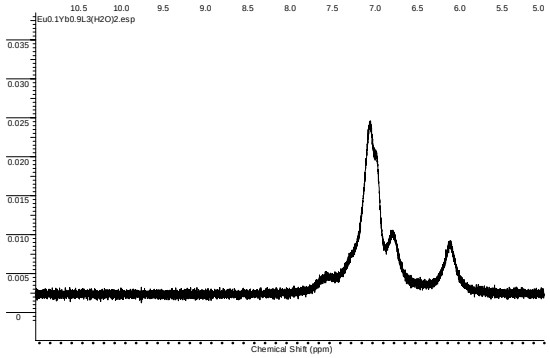


Figure S1. ^{1}H NMR data of $Eu_{0.1}Yb_{0.9}(naph)_3$

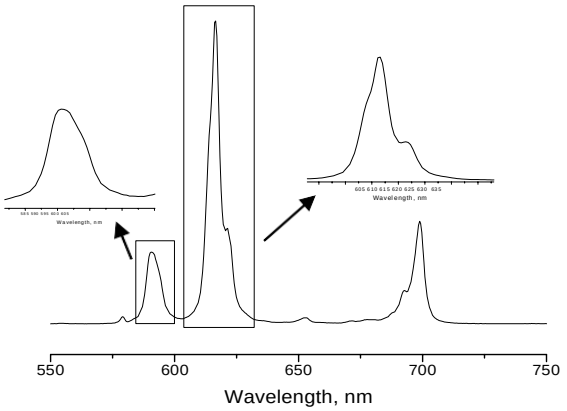
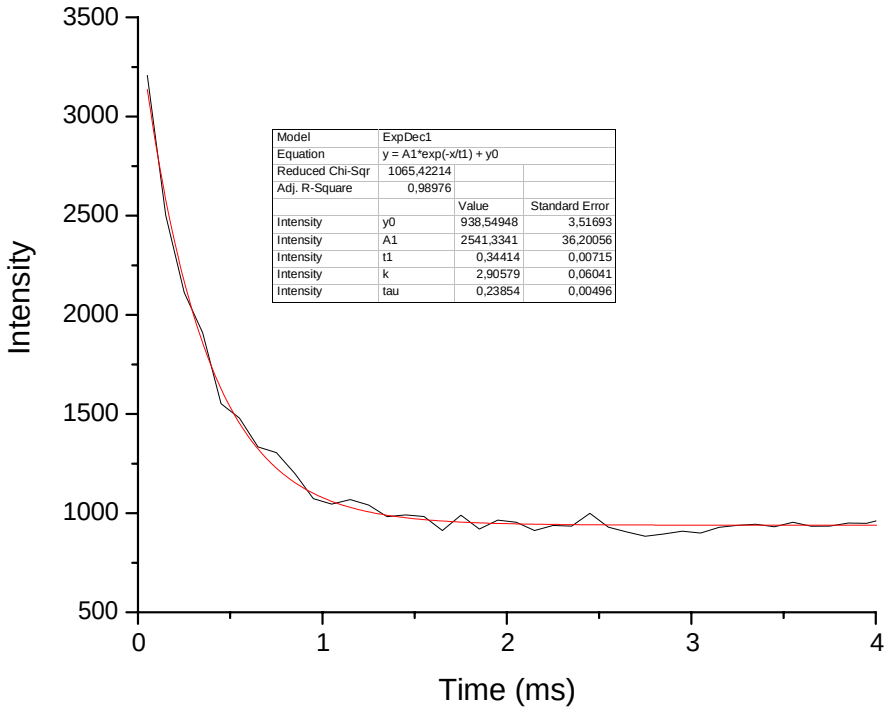
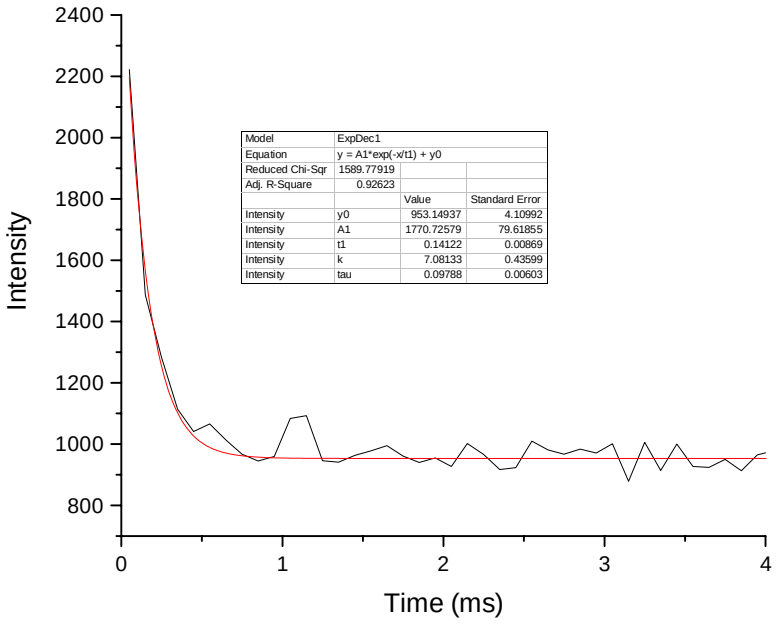


Figure S2. Study of the Stark splitting of the luminescence bands of the $Eu(naph)_3$ complex (powder, λ_{ex} = 337 nm)

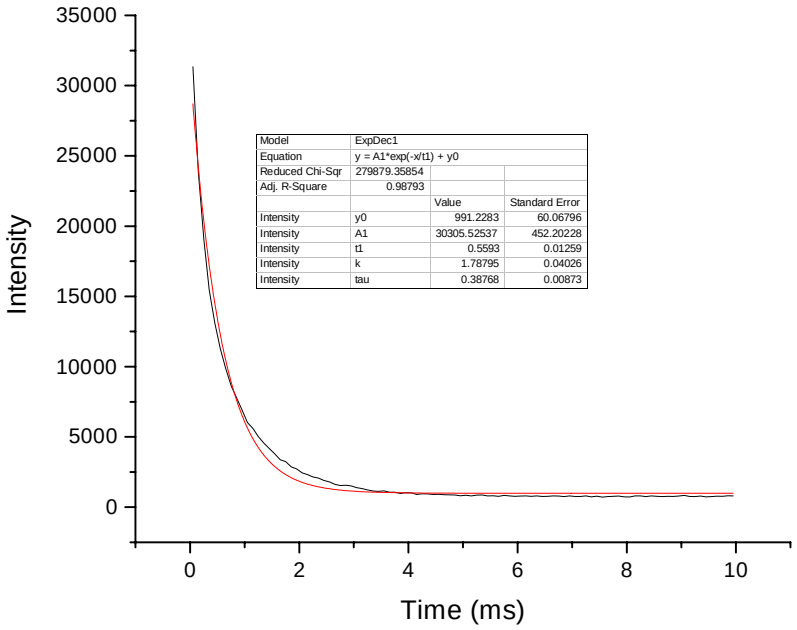


a)



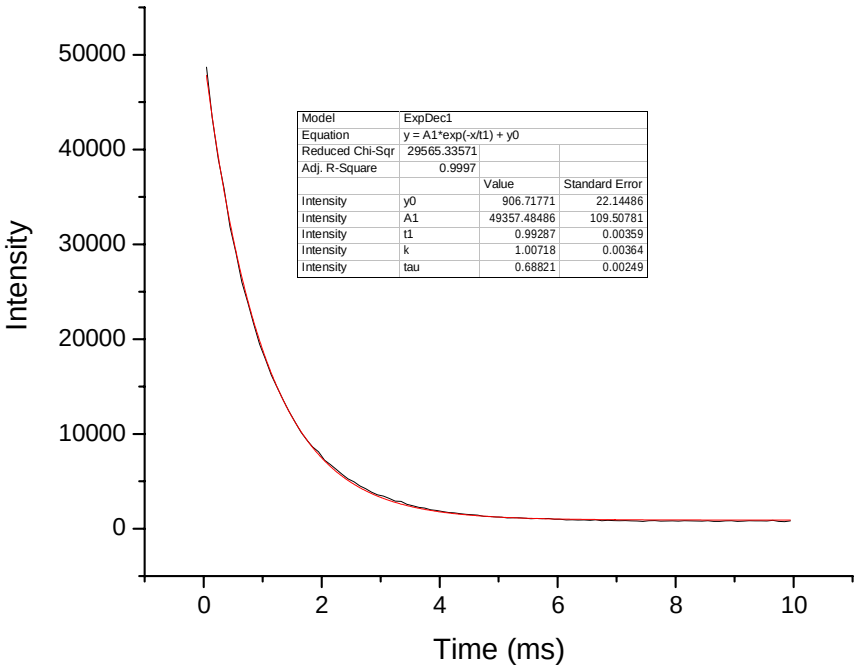
b)

Figure S3. Luminescence decay curves a) $Eu(naph)_3$, b) $Eu_{0.1}Yb_{0.9}(naph)_3$



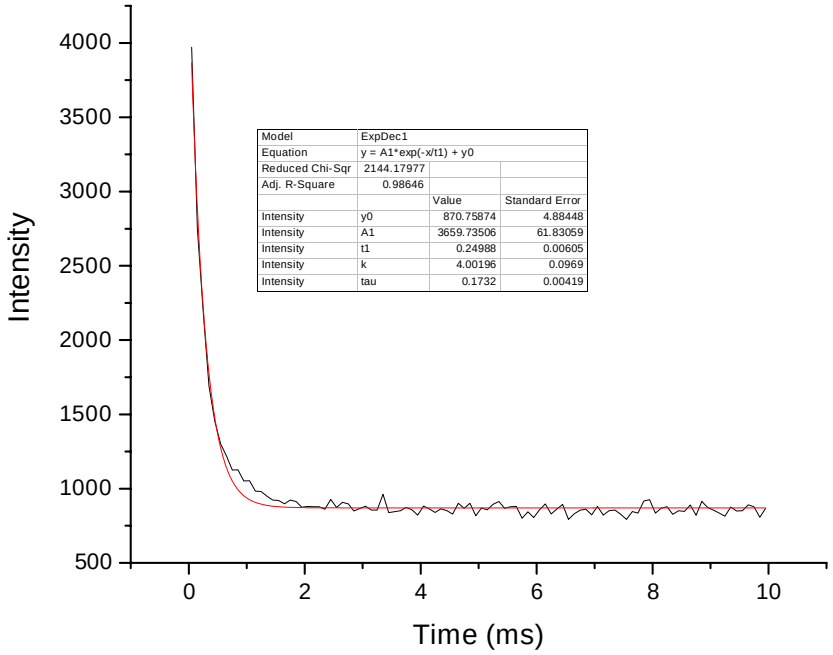
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	279879.35854		
Adj. R-Square	0.98793		
		Value	Standard Error
Intensity	y0	991.2283	60.06796
Intensity	A1	30305.52537	452.20228
Intensity	t1	0.5593	0.01259
Intensity	k	1.78795	0.04026
Intensity	tau	0.38768	0.00873

a)



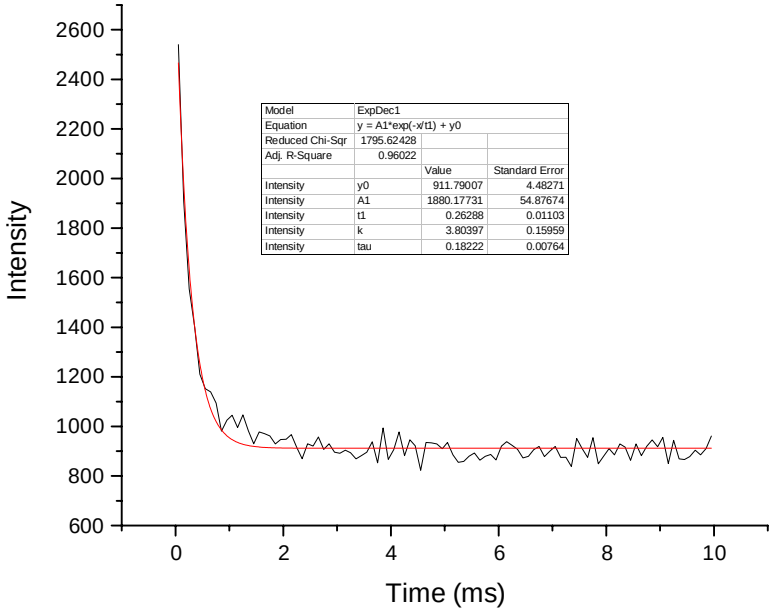
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	29565.33571		
Adj. R-Square	0.9997		
		Value	Standard Error
Intensity	y0	906.71771	22.14486
Intensity	A1	49357.48486	109.50781
Intensity	t1	0.99287	0.00359
Intensity	k	1.00718	0.00364
Intensity	tau	0.68821	0.00249

b)



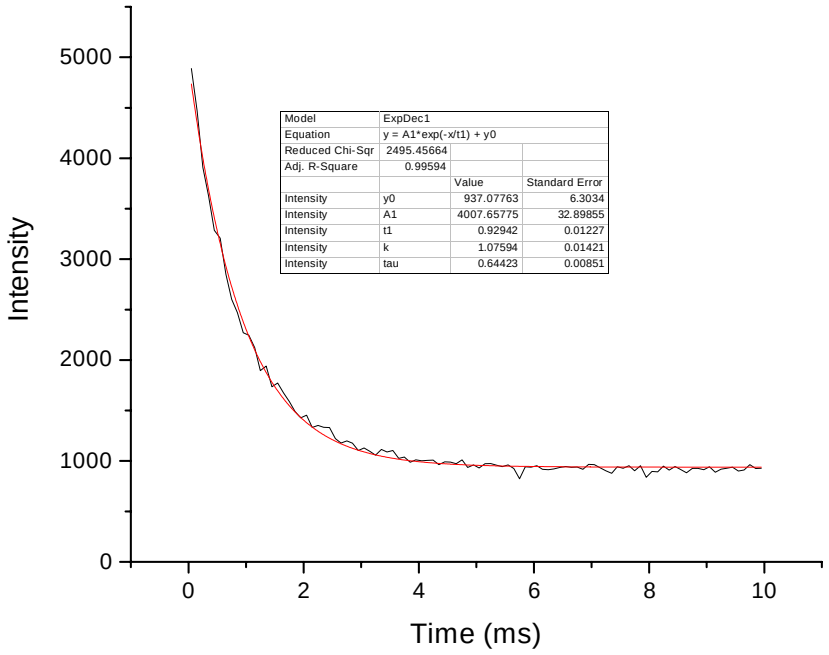
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2144.17977		
Adj. R-Square	0.98646		
		Value	Standard Error
Intensity	y0	870.75874	4.88448
Intensity	A1	3659.73506	61.83059
Intensity	t1	0.24988	0.00605
Intensity	k	4.00196	0.0969
Intensity	tau	0.1732	0.00419

c)

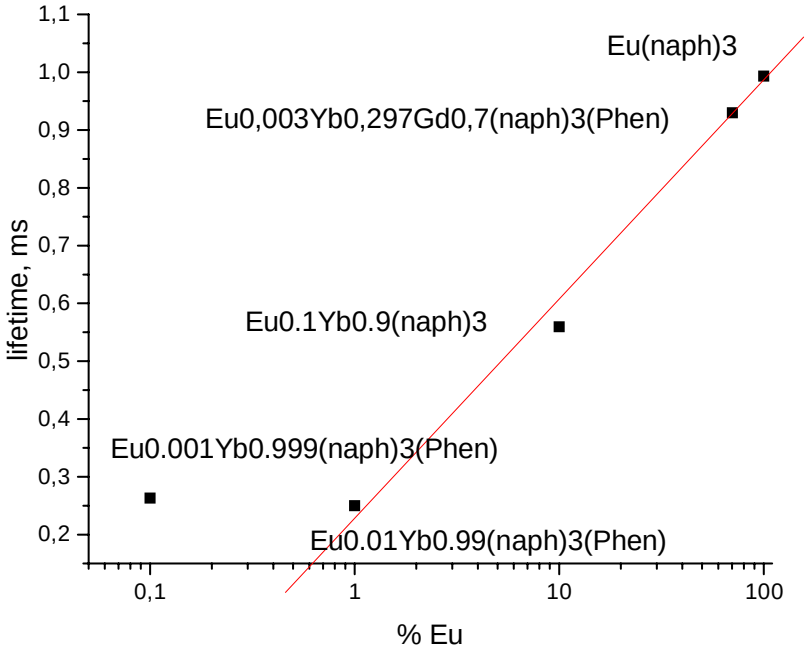


Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	1795.62428		
Adj. R-Square	0.96022		
		Value	Standard Error
Intensity	y0	911.79007	4.48271
Intensity	A1	1880.17731	54.87674
Intensity	t1	0.26288	0.01103
Intensity	k	3.80397	0.15959
Intensity	tau	0.18222	0.00764

d)



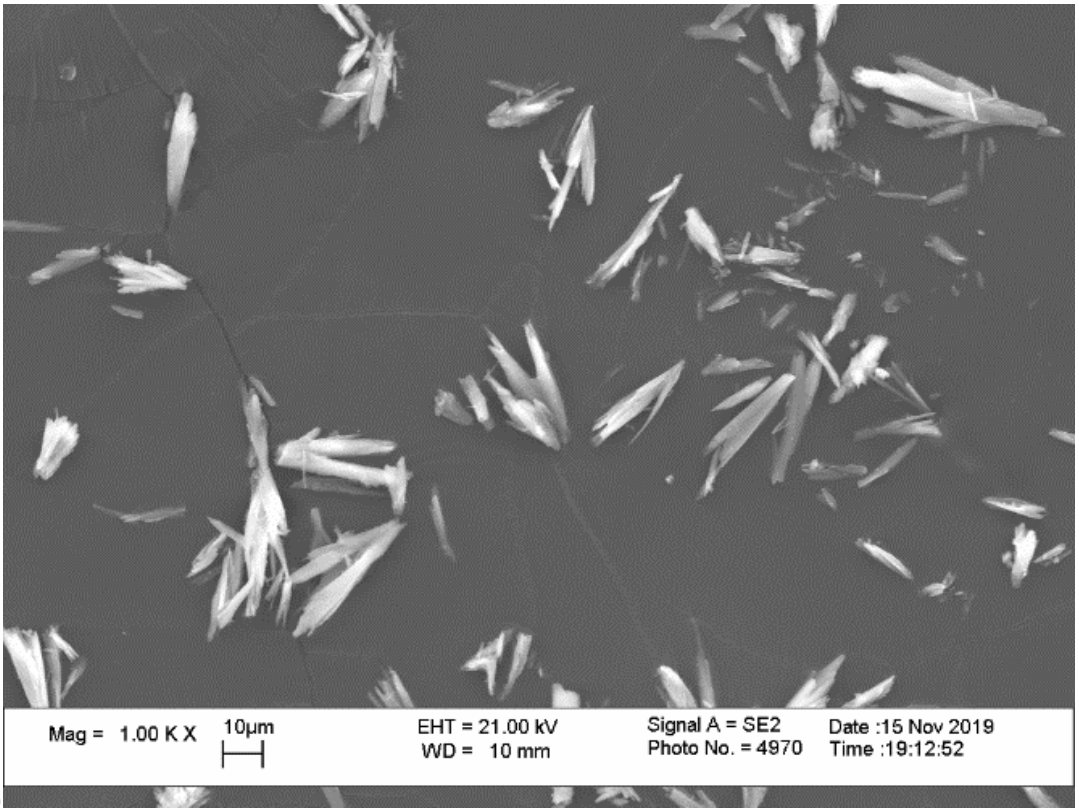
e)



f)

Figure S4. Decay curves a) $Eu_{0.1}Yb_{0.9}(naph)_3(Phen)$, b) $Eu(naph)_3(Phen)$, c) $Eu_{0.01}Yb_{0.99}(naph)_3(Phen)$, d) $Eu_{0.001}Yb_{0.999}(naph)_3(Phen)$,
e) $Eu_{0.003}Yb_{0.297}Gd_{0.7}(naph)_3(Phen)$. f) Dependence of the lifetimes of the excited state of europium on its fraction

a)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10µm
EHT = 21.00 kV
WD = 10 mm
Signal A = SE2
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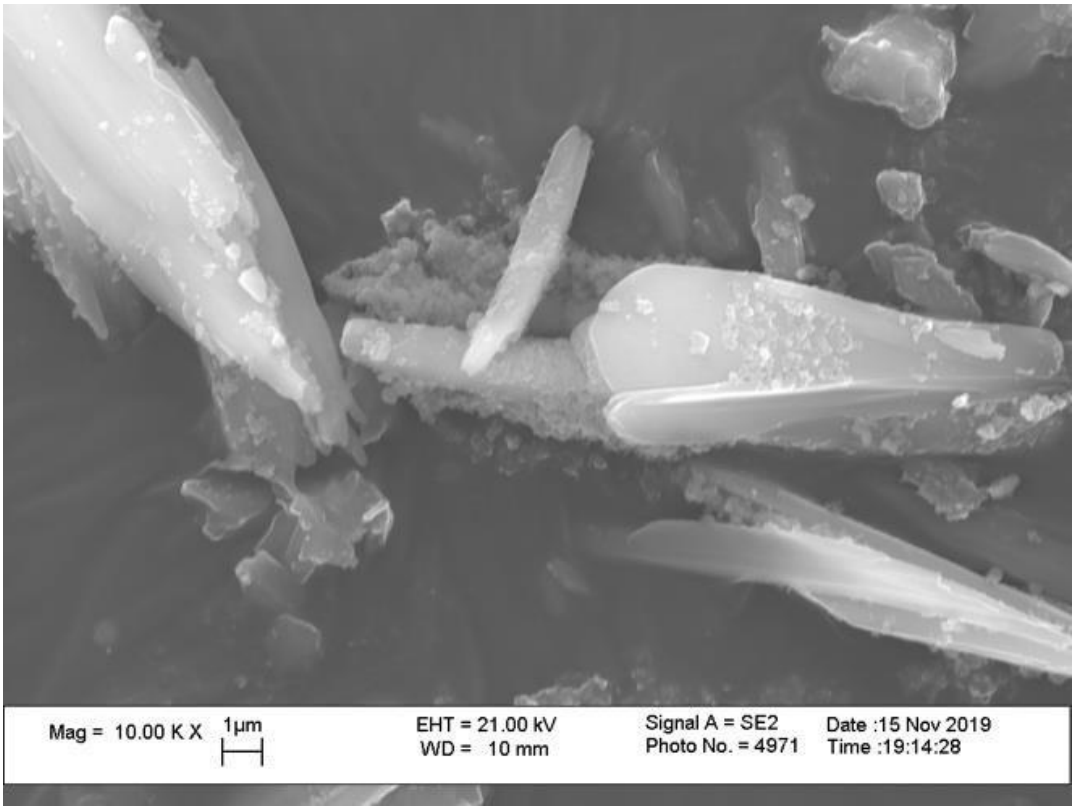
Time :19:12:52

b)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EHT = 21.00 kV
WD = 10 mm
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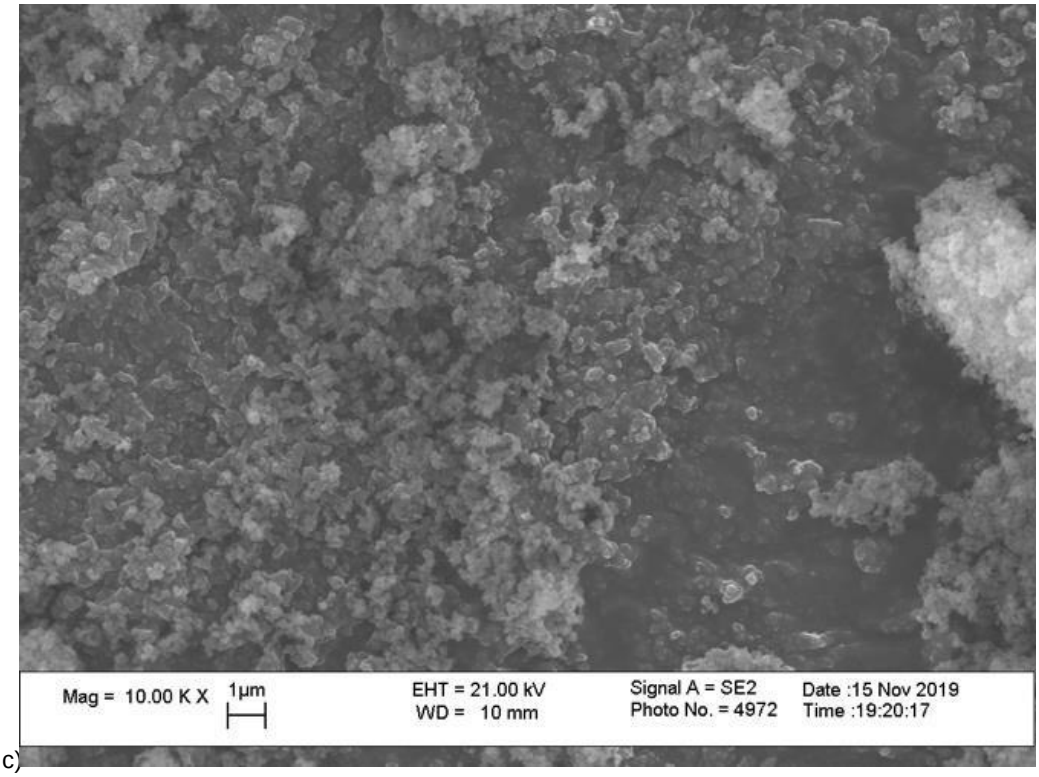
c)



d)

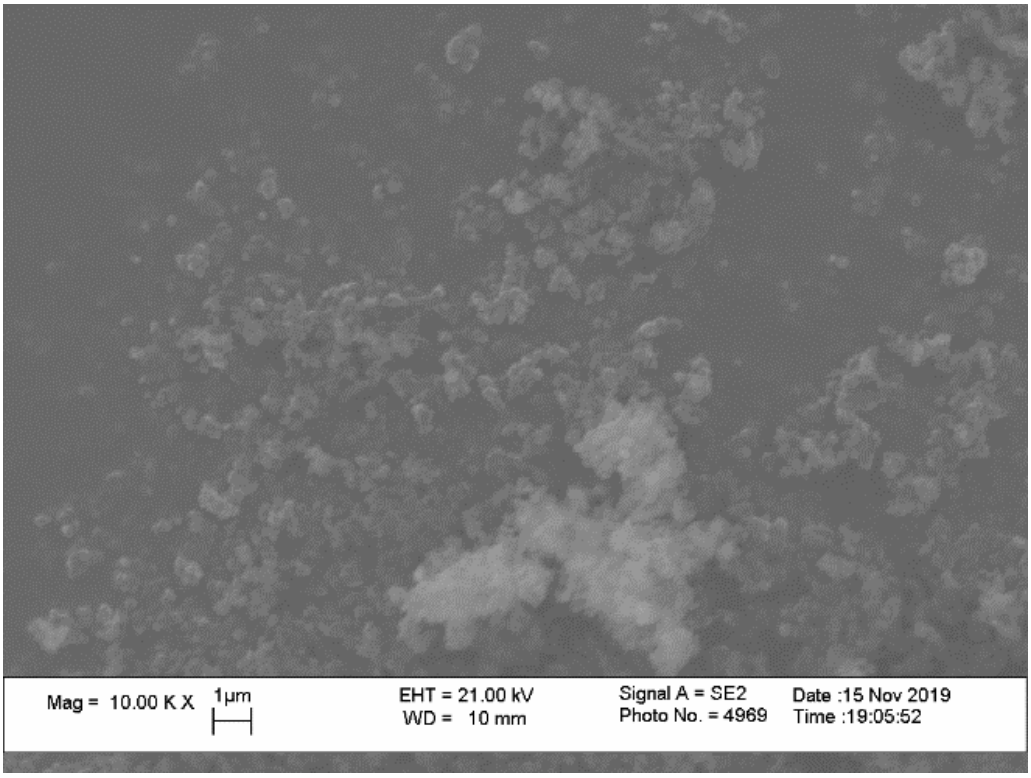


Figure S5. SEM data of a,b) $Eu_{0.1}Yb_{0.9}(naph)_3$, c) $Eu_{0.1}Yb_{0.9}(naph)_3(Phen)$, and d) $Eu_{0.01}Yb_{0.99}(naph)_3(Phen)$

Luminescent properties of trimetallic CCs

Since a further decrease in the europium fraction in mixed-ligand complexes is impractical, an attempt was made to increase the relative intensity of ytterbium luminescence by obtaining trimetallic ytterbium- europium-gadolinium CCs. As highly magnetic Gd^{3+} ion is known to increase the intersystem crossing (ISC) efficiency, it was expected that the introduction of gadolinium would make it possible to further decrease the europium fraction to reduce the relative intensity of the luminescence of europium without significantly reducing the overall luminescence efficiency.

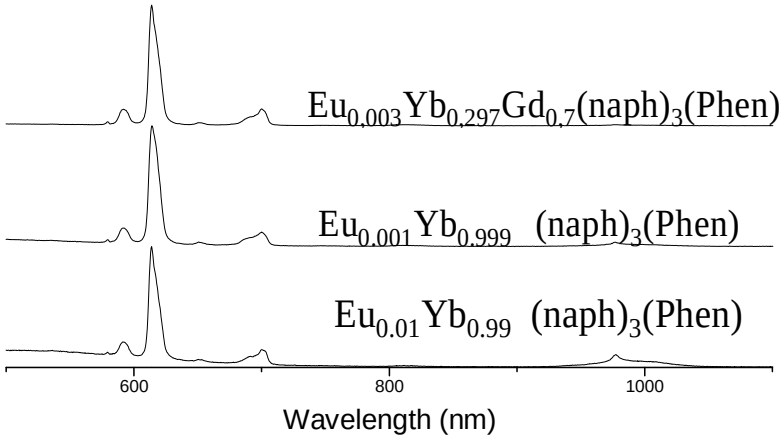


Figure S6. Luminescence spectra of $Eu_xYb_yGd_{1-x-y}(naph)_3(Phen)$

For this purpose, the $Eu_{0,003}Yb_{0,297}Gd_{0,7}(naph)_3(Phen)$ complex was obtained, in the luminescence spectrum of which, however, only the luminescence bands of euroium were observed. Moreover, the relative intensity of ytterbium luminescence in this complex, the ratio of the fractions of europium and ytterbium in which is 0.003 / 0.297 = 0.01, is lower than in the spectra of both $Eu_{0.01}Yb_{0.99}(naph)_3(Phen)$ and even $Eu_{0.001}Yb_{0.999}(naph)_3(Phen)$. Apparently, the efficiency of ligand-to-europium energy transfer was already high enough, as was shown in the previous section, and the introduction of gadolinium only led to a dilution and an increase in the euroium-ytterbium distance, which resulted in a decrease of the efficiency of ytterbium sensitization by europium, which, as was also shown in the last section, was the main fact leading to an increase in the intensity of ytterbium luminescence. Indeed, the luminescence lifetime of europium in the composition of the trimetallic CC was 0.93 ms, that is, it turned out to be practically the same as in the absence of ytterbium (0.99 ms), which indicates the absence of energy transfer.