Electronic Supplementary Material (ESI) for Dalton Transactions.

Theoretical chemistry-handled strategy for the rational design of new luminescent lanthanide complexes: An approach from multireference SOC-NEVPT2 method

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Electronic Supporting Information

1. TDDFT Calculations

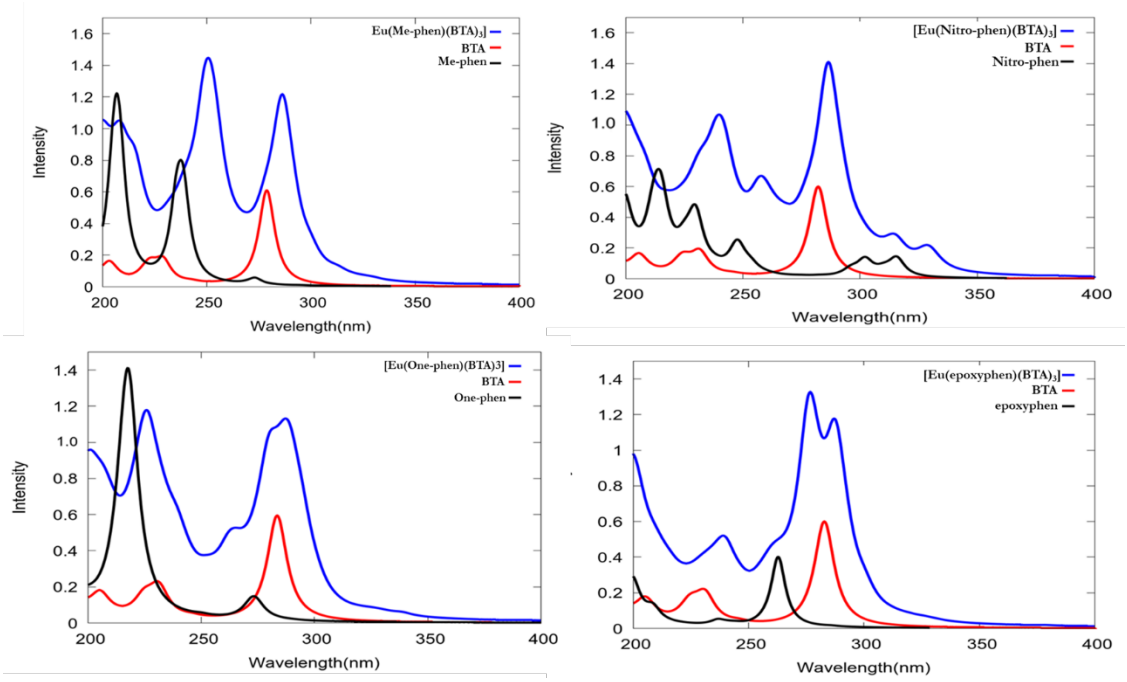


Figure S1. Electronic absorption spectra of all ligands and europium complexes proposed. All spectrum was simulated at SR-TDDFT(CAM-B3LYP/TZ2P) level of theory using methanol as solvent via COSMO model.

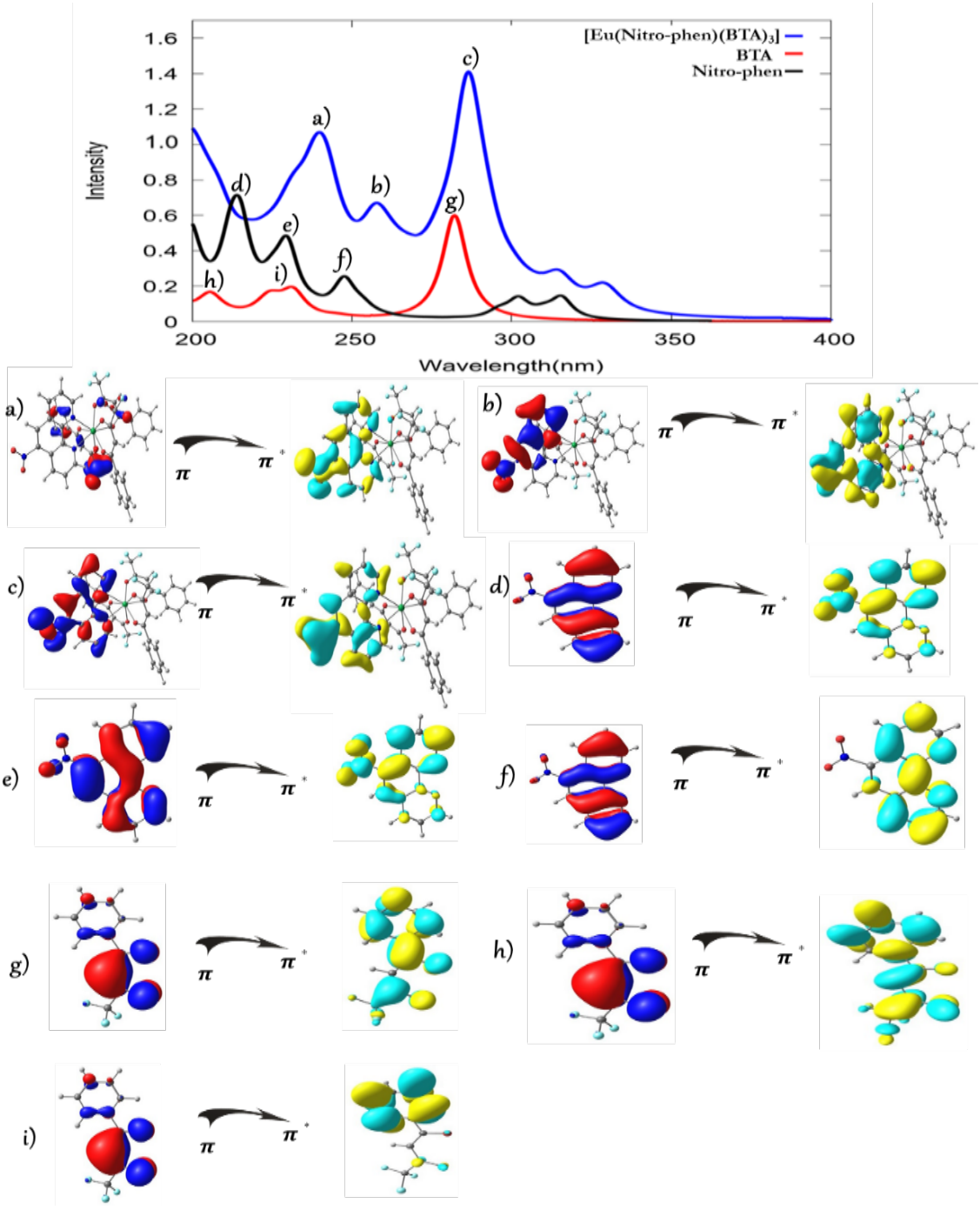


Figure S2. Electronic absorption spectra of the [Eu(**Phen-Nitro**)(**BTA**)$_3$] and the corresponding antennas (solvent included) (CAM-B3LYP/TZ2P). The plotted orbitals correspond to main electronic transitions obtained with SR-TDDFT in methanol.

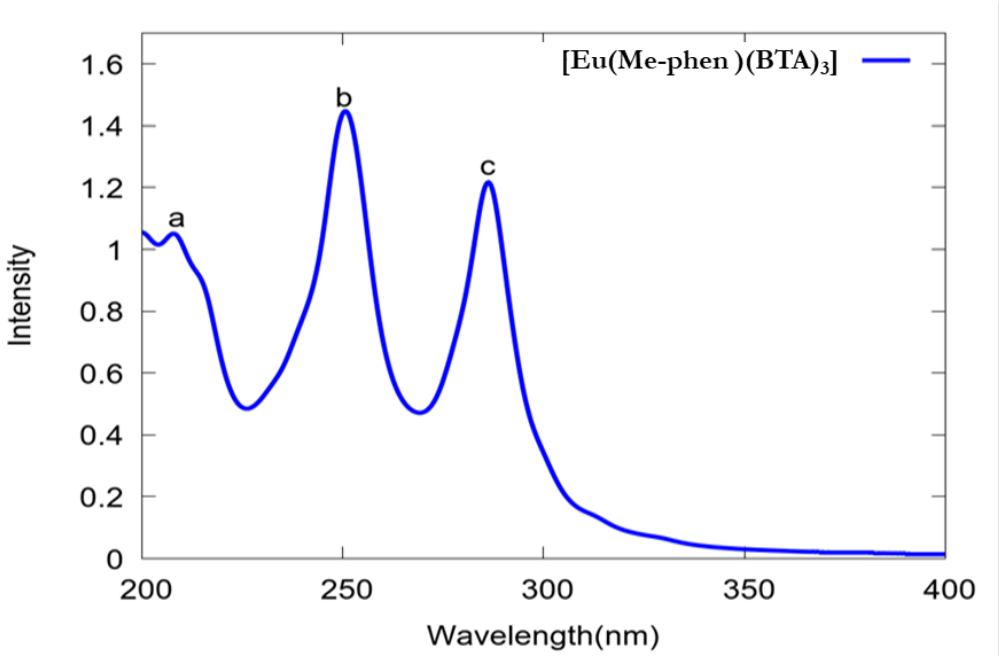
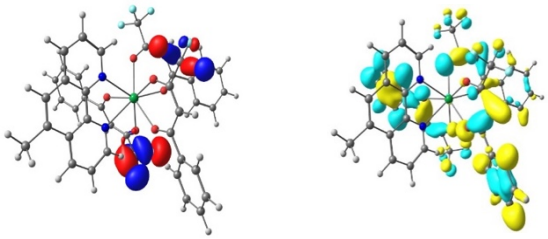
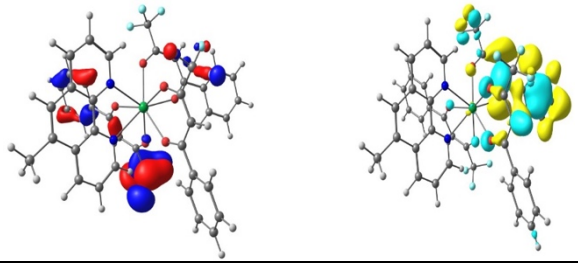
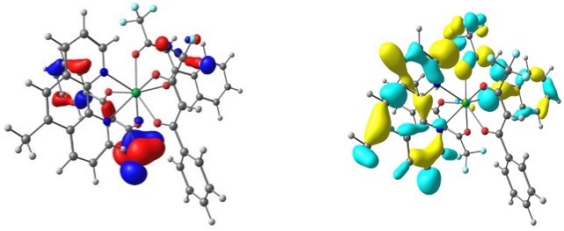


Figure S3. Absorption spectrum of [Eu(**Me-phen**)(**BTA**)$_3$] calculated with CAM-B3LYP/TZVP and methanol solvent.

Table S1. Most relevant electronic transitions for the complex [Eu(**Me-phen**)(**BTA**)$_3$]

Band	λ(nm)	E(eV)	f	Assignment
a	208	5.95	0.305	π-π
b	248	4.98	0.287	π-π
c	286	4.32	0.620	π-π

Table S2. Molecular orbitals involved in the electronic transitions for the complex [Eu(**Me-phen**)(**BTA**)$_3$]

	Transition
a	
b	
c	

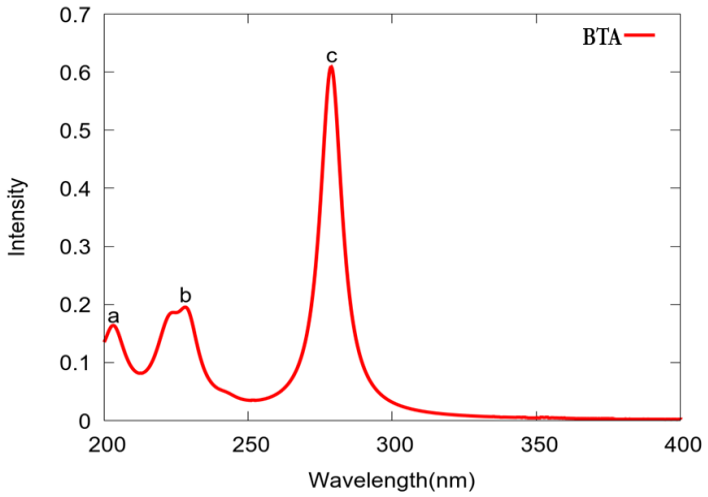
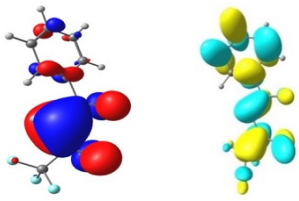


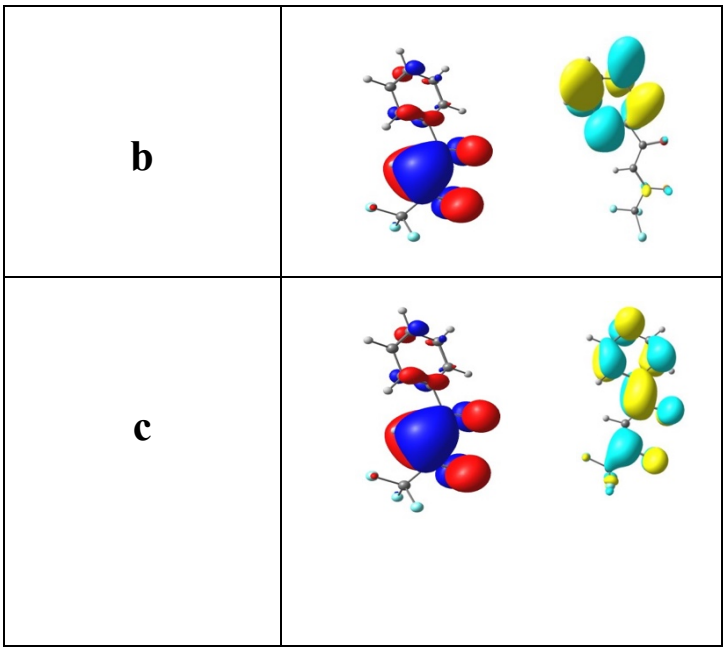
Figure S4. Absorption spectrum of **BTA** calculated with CAM-B3LYP/TZVP and methanol solvent.

Table S3. Most relevant electronic transitions for **BTA**

Band	λ(nm)	E(eV)	f	%	Transition	Assignment
a	203	6.10	0.108	79	HOMO-LUMO+2	π-π
b	229	5.41	0.132	85	HOMO-LUMO+1	π-π
c	278	4.44	0.602	98	HOMO-LUMO	π-π

Table S4. Molecular orbitals involved in the electronic transitions for **BTA**

Band	**Transition**
a	



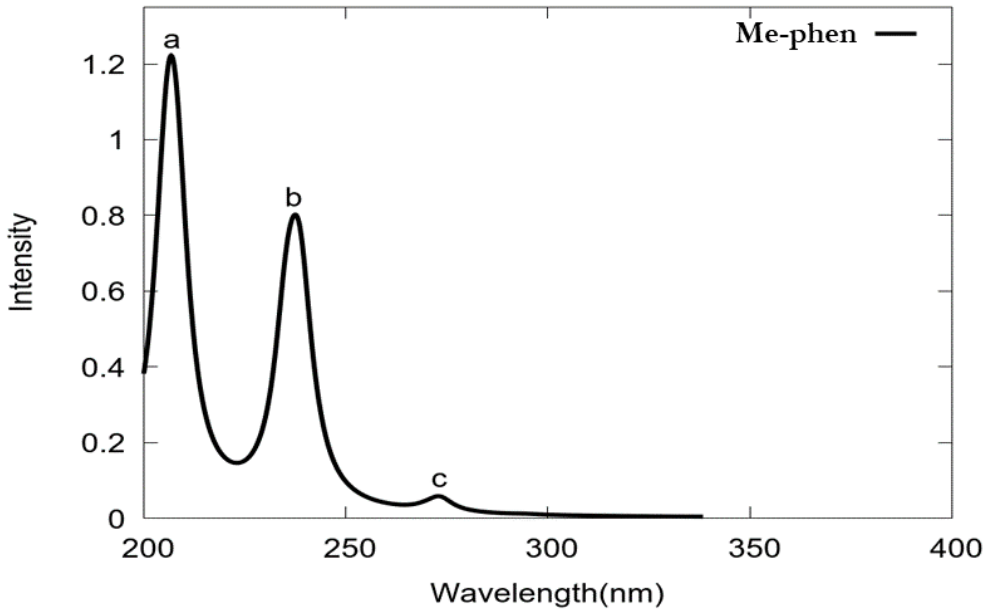


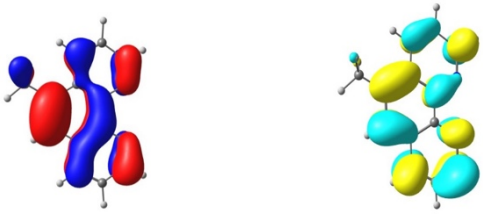
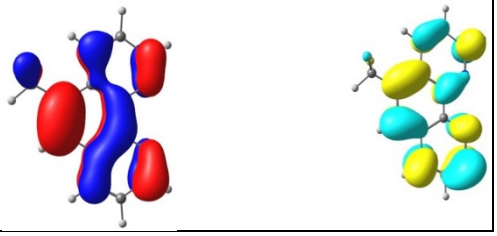
Figure S5. Absorption spectrum of **Me-phen** calculated with CAM-B3LYP/TZVP and methanol solvent.

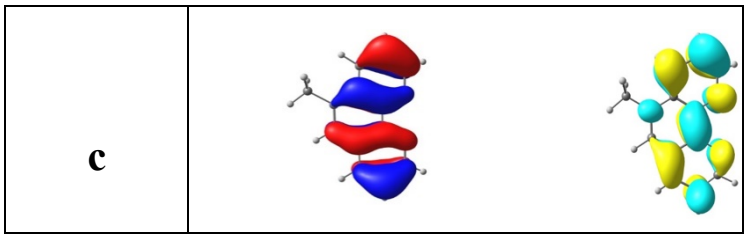
Table S5. Most relevant electronic transitions for **Me-phen**

Band	λ(nm)	E(eV)	f	%	Transition	Assignment
a	205	6.02	0.666	29	HOMO-LUMO+2	π-π

b	238	5.19	0.512	30	HOMO-1-LUMO	π-π
				24	HOMO-LUMO+1	π-π
c	273	4.53	0.037	50	HOMO-LUMO+1	π-π
				30	HOMO-LUMO	π-π

Table S6. Molecular orbitals involved in the electronic transitions for **Me-phen.**

Band	Transition
a	
b	
b	
c	



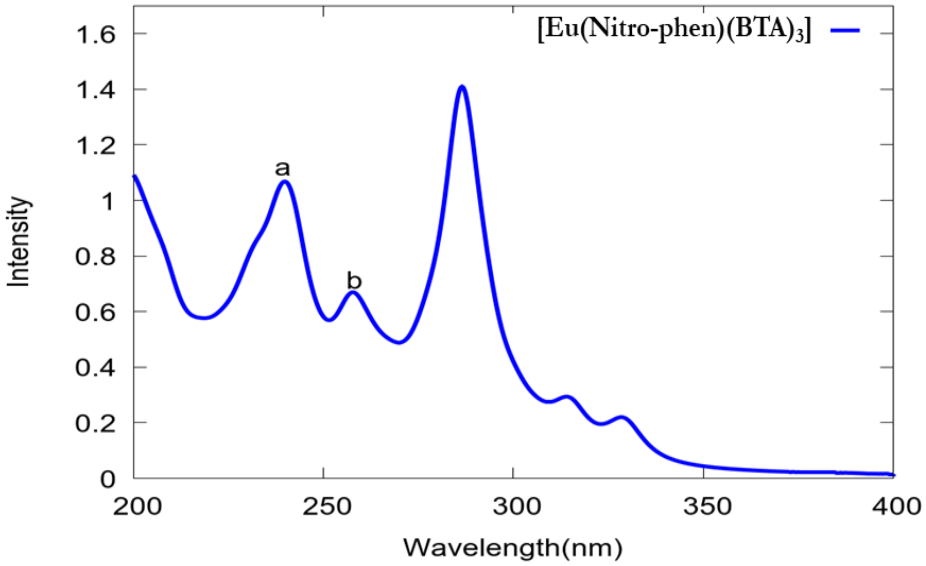
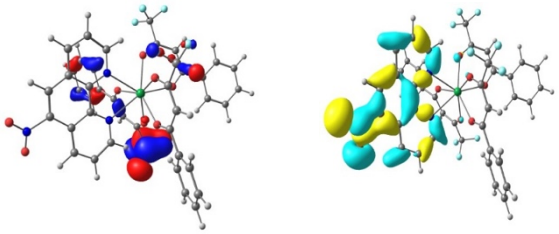
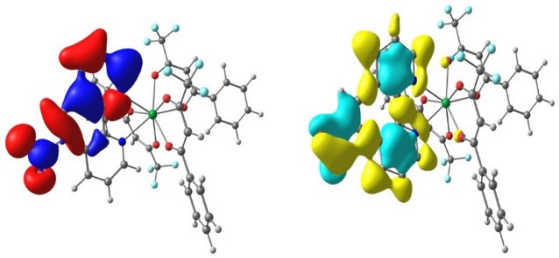
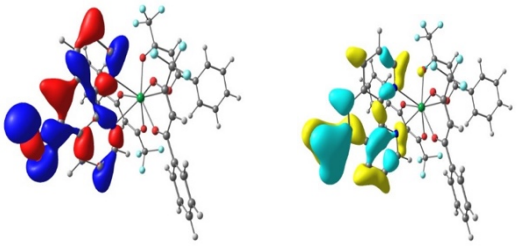


Figure S6. Absorption spectrum of [Eu(**Nitro-phen**)(**BTA**)$_3$] calculated with CAM-B3LYP/TZVP and methanol solvent.

Table S7. Most relevant electronic transitions for the complex [Eu(**Nitro-phen**)(**BTA**)$_3$]

Band	λ(nm)	E(eV)	f	Assignment
a	238	5.20	0.187	π-π
b	257	4.82	0.178	π-π
c	286	4.32	0.728	π-π

Table S8. Molecular orbitals involved in the electronic transitions for [Eu(**Nitrophen**)(**BTA**)$_3$]

Band	Transition
a	
b	
c	

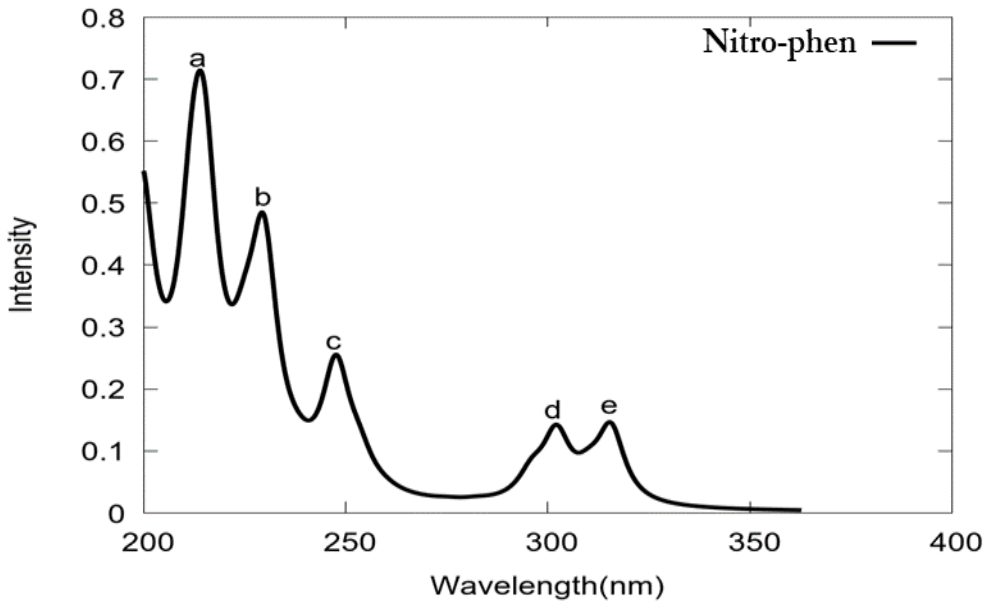
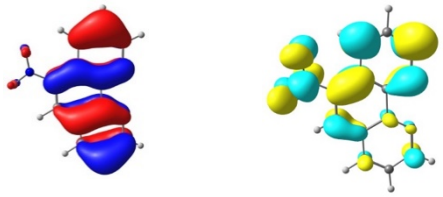
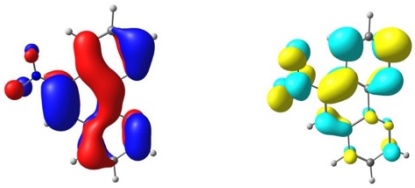
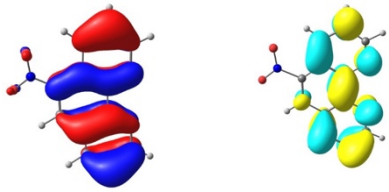
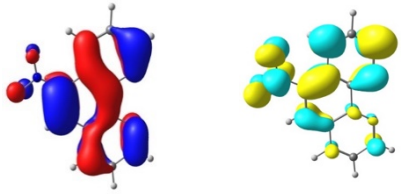
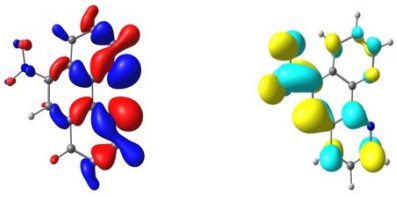


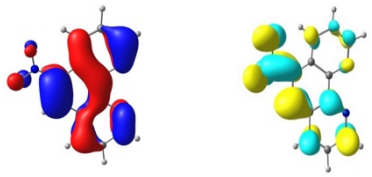
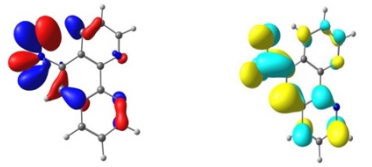
Figure S9. Absorption spectrum of **Nitro-phen** calculated with CAM-B3LYP/TZVP and methanol solvent.

Table S9. Most relevant electronic transitions for **Nitro-phen**

Band	λ(nm)	E(eV)	f	%	Transition	Assignment
a	214	5.77	0.416	35	HOMO-1-LUMO+2	π-π
b	229	5.39	0.354	41	HOMO-LUMO+2	π-π
c	247	5.00	0.191	41	HOMO-1-LUMO+1	π-π
				23	HOMO-LUMO+2	π-π
d	301	4.10	0.105	35	HOMO-1-LUMO	π-π
				14	HOMO-6- LUMO	π-π
				16	HOMO-2-LUMO	n-π
				16	HOMO-LUMO	π-π
e	315	3.92	0.118	36	HOMO-LUMO	π-π
				46	HOMO-6-LUMO	π-π

Table S10. Molecular orbitals involved in the electronic transitions for **Nitro-phen**

Band	Transition
a	
b	
c	
c	
d	

e	
e	

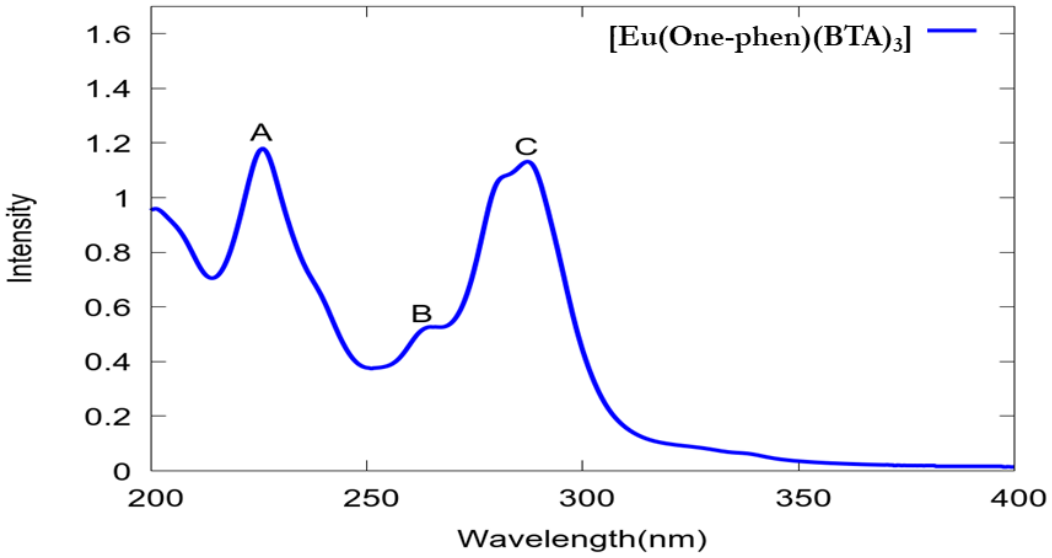
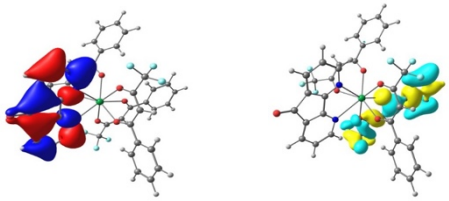
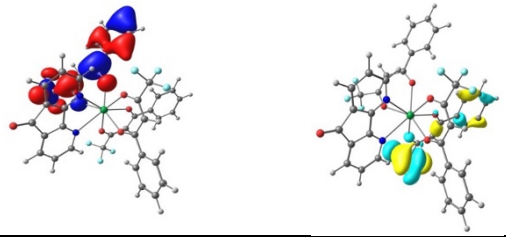
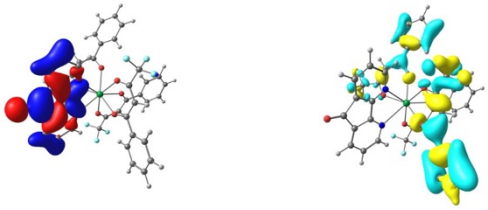


Figure S8. Absorption spectrum of [Eu(**One-phen**)(**BTA**)$_3$] calculated with CAM-B3LYP/TZVP and methanol solvent.

Table S11. Most relevant electronic transitions for the complex [Eu(**One-phen**)(**BTA**)$_3$]

Band	λ(nm)	E(eV)	f	Assignment
a	226	5.48	0.170	π-π
b	265	4.67	0.098	π-π
c	288	4.29	0.246	π-π

Table S12. Molecular orbitals involved in the electronic transitions for [Eu(**One-phen**)(**BTA**)$_3$]

Band	Transition
A	
B	
C	

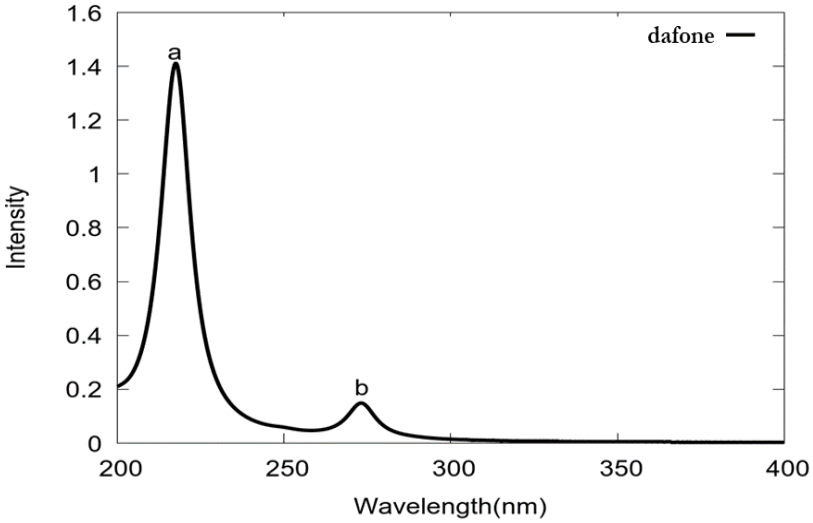
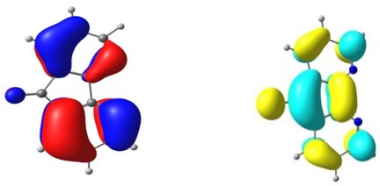
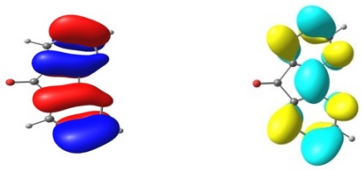
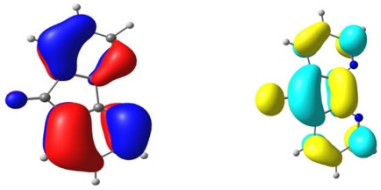


Figure S9. Absorption spectrum of **One-phen** calculated with CAM-B3LYP/TZVP and methanol solvent.

Table S13. Most relevant electronic transitions for **One-phen.**

Band	λ(nm)	E(eV)	f	%	Transition	Assignment
a	217	5.69	1.237	63	HOMO-3-LUMO	π-π
b	273	4.53	0.130	65	HOMO-LUMO+1	π-π
				26	HOMO-3-LUMO	π-π

Table S14. Molecular orbitals involved in the electronic transitions for **One-phen.**

Band	**Transition**
a	
b	
b	

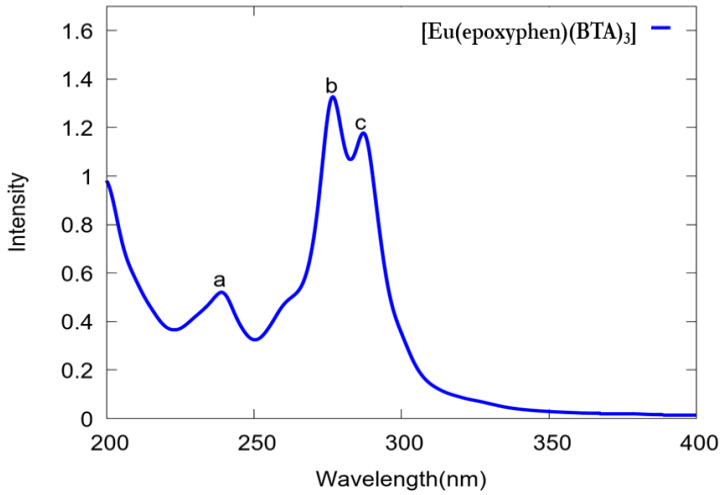
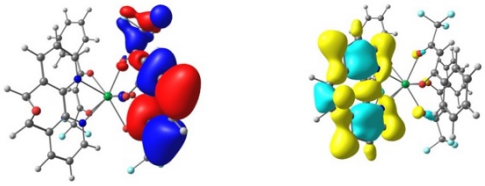
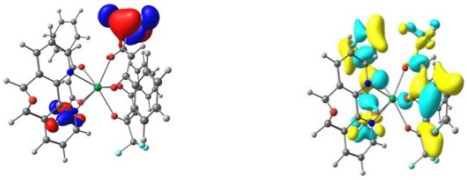
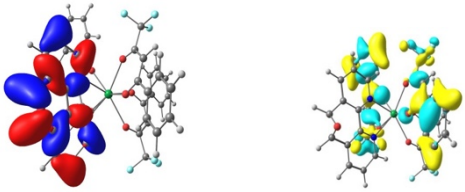


Figure S10.Absorption spectrum of [Eu(**Epoxy-phen**)(**BTA**)$_3$] calculated with CAM-B3LYP/TZVP and methanol solvent.

Table S15. Most relevant electronic transitions for the complex [Eu(**Epoxy-phen**)(**BTA**)$_3$]

Band	λ(nm)	E(eV)	f	Assignment
a	240	5.16	0.111	π-π
b	276	4.49	0.857	π-π
c	287	4.31	0.713	π-π

Table S16. Molecular orbitals involved in the electronic transitions for [Eu(**Epoxy-phen**)(**BTA**)$_3$]

Band	Transition
a	
b	
c	

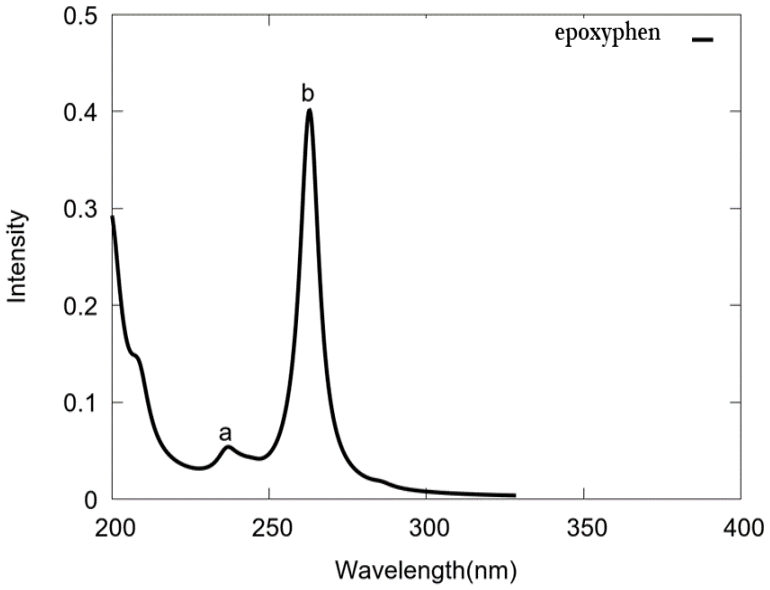
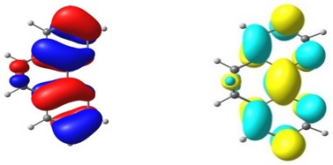
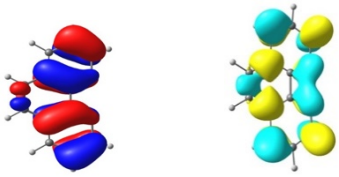


Figure S13. Absorption spectrum of **Epoxy-phen** calculated with CAM-B3LYP/TZVP and methanol solvent

Table S17. Most relevant electronic transitions for **Epoxy-phen**

Band	λ(nm)	E(eV)	f	%	Transition	Assignment
a	236	5.23	0.025	53	HOMO-LUMO+1	π-π
b	282	4.78	0.389	84	HOMO-LUMO	π-π

Table S18. Molecular orbitals involved in the electronic transitions for **Epoxy-phen**

Band	Transition
a	
b	

2. Synthesis and Characterization

2.1 FTIR spectroscopy

Ligands

In **Figures S14** and **S15** appear the most relevant IR absorption bands due to the ligands:

4,4,4-Trifluoro-1-Phenyl-1,3-butanodione (**BTA**) :1599(s), 1534(w),1253(m),689(s),773(s).

5-Methyl-1,10-Phenantroline **(Me-phen)**: 1618(w),1559(w), 1560(w), 1561(w), 1414(m), 1378(m), 737(s) ,788(s), 876(s).

5-Nitro-1,10-Phenantroline (**Nitro-phen**) : 2564(w), 2568(w), 2690(w),2956(s),1664(w), 1437(w), 1408(w), 1024(s) ,3302(m),489(w).

5H-ciclopenta [1,2-b: 5,4-b '] dipiridin-5-ona (**One-phen**): 3317(m), 2943(w), 2827(w), 1445(w), 1023(s), 604(m).

5,6-Epoxy-5,6-dihydro-[1,10]phenanthroline (**Epoxy-phen**):1564(w), 1558(w), 1555(w), 1432(m), 1215(w), 1131(w), 1012(w), 881(m) ,798(s),750(s),704(s),614(m).

Complexes

The most relevant IR absorption bands due to the complexes are shown in **Figures S16** and **S17**, respectively. We found the following characteristics peaks:

Eu(Me-phen)(BTA)$_3$: 1609(s), 1572(m),1527(m),1490(m),1429(w),1290(s), 1178(m), 1133(s),943(w),880(w),766(s),703(s), 630(s).

Eu(Nitro-phen)(BTA)$_3$: 1613(s),1571(m),1519(m), 1425(w), 1353(w), 1319(m), 1292(s), 1190(m), 1139(s),1074(w), 1070(w),942(m), 770(s).

Eu(One-phen)(BTA)$_3$:1731(s), 1609(s),1573(s),1564(m), 1516(w),1464(m),1457(m), 1414(m) 1319(w),1291(s),1243(m), 1183(s), 1132(s), 1075(m), 1025(m), 944(m), 936(w) ,764(s),699(s),629(s).

Eu(Epoxy-phen)(BTA)$_3$: 1606(s), 1575(s),1533(m), 1467(m), 1470(m),1489(m), 1321(m), 1292(s),1273(w),1184(s), 1134(s),1076(w), 1116(w), 1021(m), 944(m), 894(w), 764(s).

Based on above and according to the literature[1] were identified the following characteristic absorption bands: 1609 cm^{-1},1613 cm^{-1},1609 cm^{-1} ,1606cm^{-1} (υ_{as} C=C-C=O); 1572 cm^{-1},1571 cm^{-1} ,1573 cm^{-1},1575 cm^{-1} (υ_s C=C),);1490 cm^{-1} ,1519 cm^{-1} ,1516 cm^{-1},1489 cm^{-1} (υ_s C=C-C=O),1429 cm^{-1},1425 cm^{-1},1414 cm^{-1} ,1467 cm^{-1} (υ_{as} C=N),1326 cm^{-1},1367 cm^{-1}, 1321 cm^{-1}, 1378 cm^{-1} (υ_s C=N).It is important to note that the aromatic CH out-of-plane bending vibrations of N,N-donor were found about 700 cm^{-1} and slightly shifted to lower frequencies

with respect of free ligand, originated by the coordination to the europium ion. In the same way, the characteristic strong carbon-fluorine bands were observed around 1130-1290 cm^{-1}.

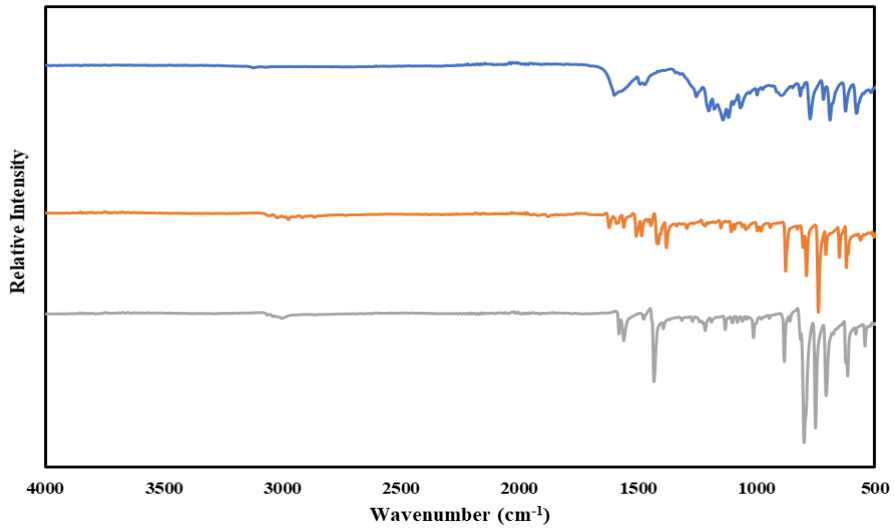


Figure S14. FT-IR spectra of a) BTA (blue line) b) Me-phen (orange line) c) Epoxy-phen (gray line)

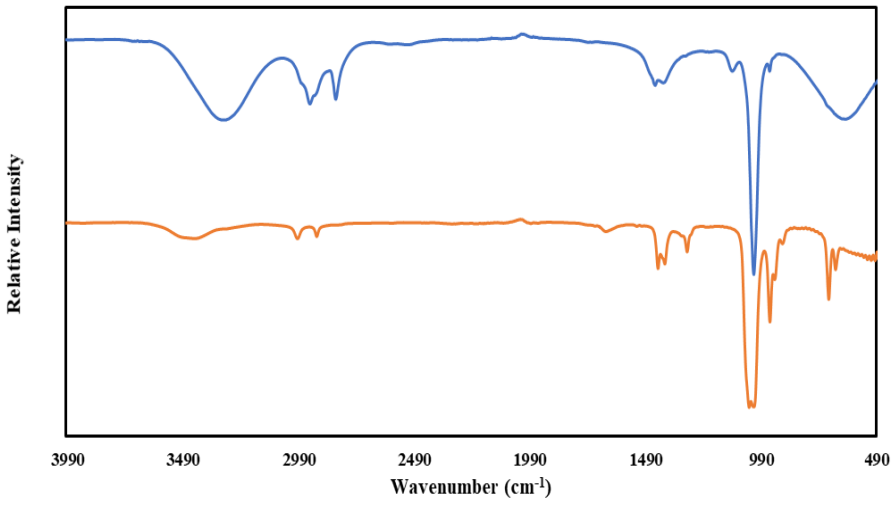


Figure S15. FT-IR spectra of a) One-phen (blue line) b) Nitro-phen (orange line).

Table S19. Cell parameters estimated for Eu^{3+}-complexes synthetized in this work *

Cell constant	Values Powder diffraction**
[Eu(**Me-phen**)(**BTA**)$_3$]	
a (Å)	11.1927
b (Å)	17.6396
c (Å)	8.5866
β	115.452
Crystal Density (g cm^{-3})	2.336
Eu(**Nitro-phen**)(**BTA**)$_3$]	
a (Å)	11.2357
b (Å)	17.8432
c (Å)	8.7322
β	112.353
Crystal Density (g cm^{-3})	2.235
[Eu(**One-phen**)(**BTA**)$_3$]	
a (Å)	13.5511
b (Å)	17.3987
c (Å)	18.5192
β	105.257
Crystal Density (g cm^{-3})	1.717
[Eu(**Epoxy-phen**)(**BTA**)$_3$]	
a (Å)	9.1075
b (Å)	11.8822
c (Å)	15.5502
β	115.452
Crystal Density (g cm^{-3})	1.992

*Crystal system: monoclinic, radiation: CuKα

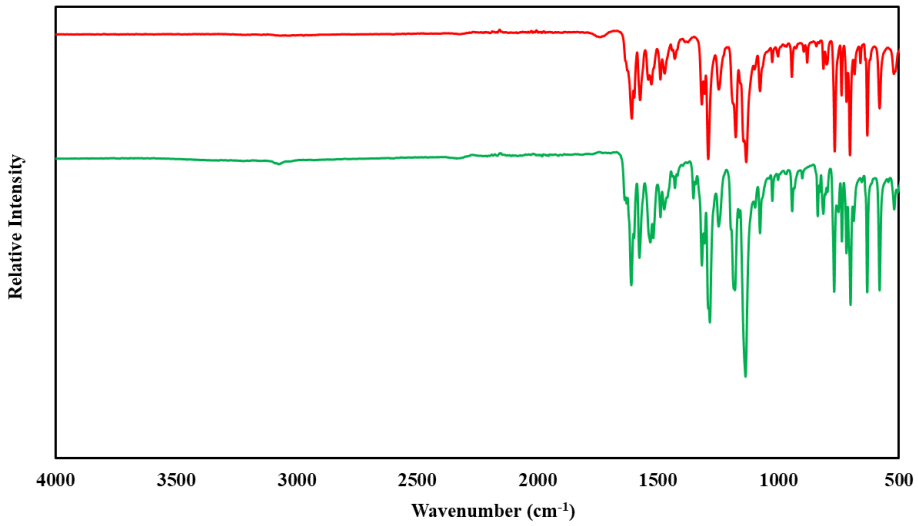


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Figure S16. FT-IR spectra of a) [Eu(**Me-phen**)(**BTA**)$_3$] (red line) b) [Eu(**Nitro-phen**)(**BTA**)$_3$] (green line)

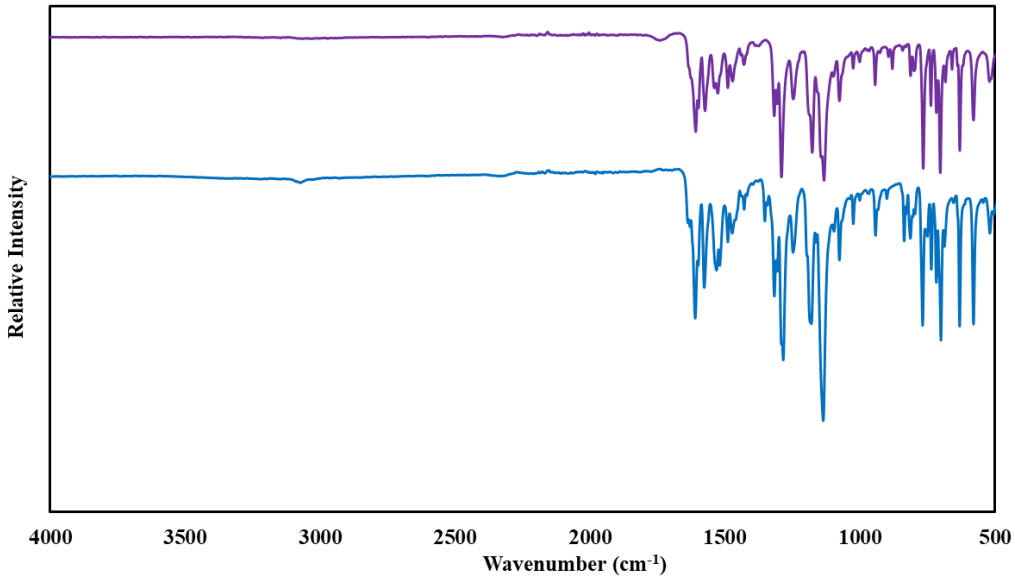

Figure S17. FT-IR spectra of a) [Eu(**One-phen**)(**BTA**)$_3$] (blue line) b) [Eu(**Epoxy-phen**)(**BTA**)$_3$] (orange line)

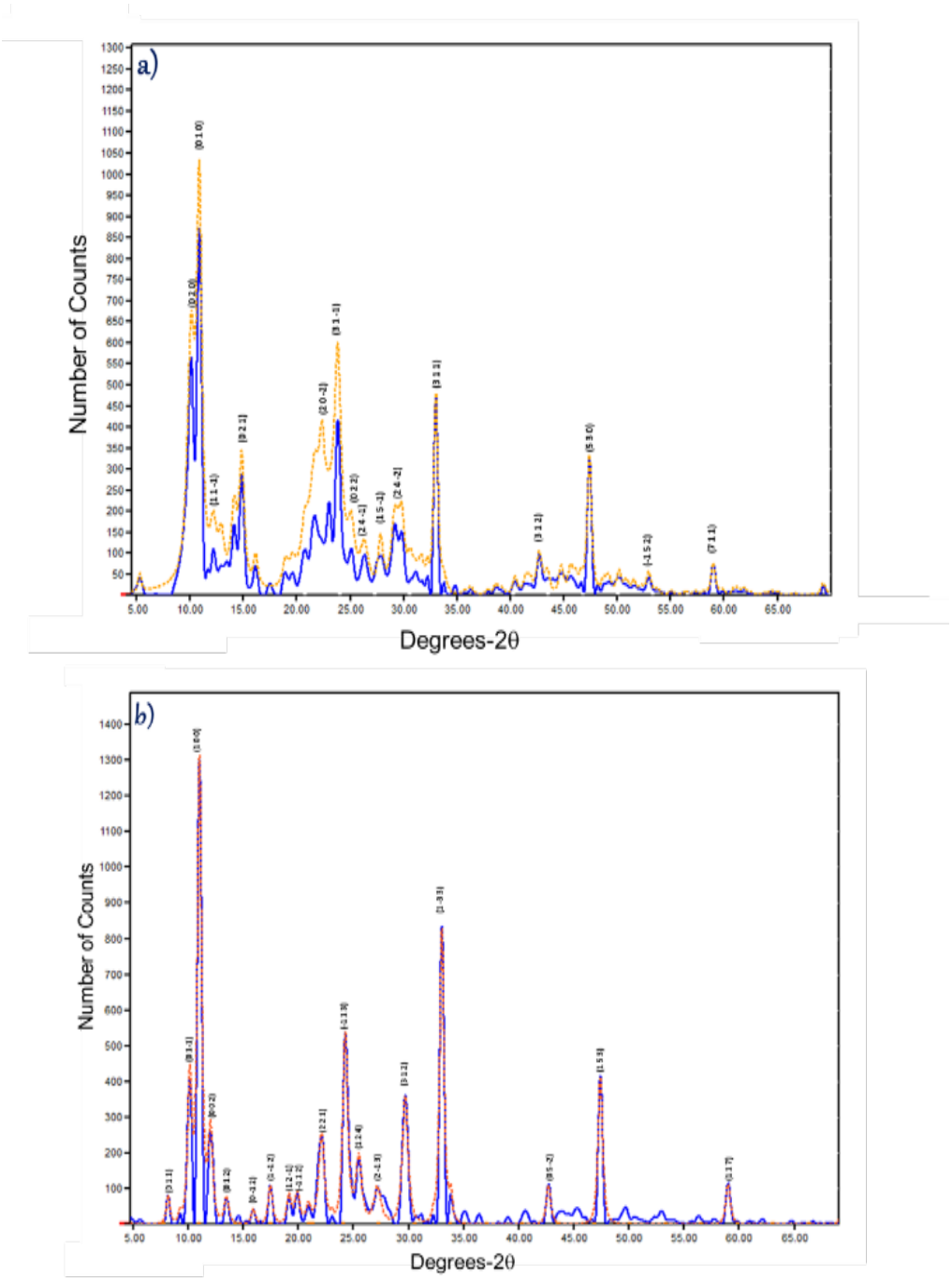

Figure S18. Simulated X -ray powder diffraction (λ= 1.54056 Å) pattern of a) Eu(**Me-phen**)(**BTA**)$_3$ b) Eu(**Nitro-phen**)(**BTA**)$_3$. Experimental (blue line), calculated (dashed line).

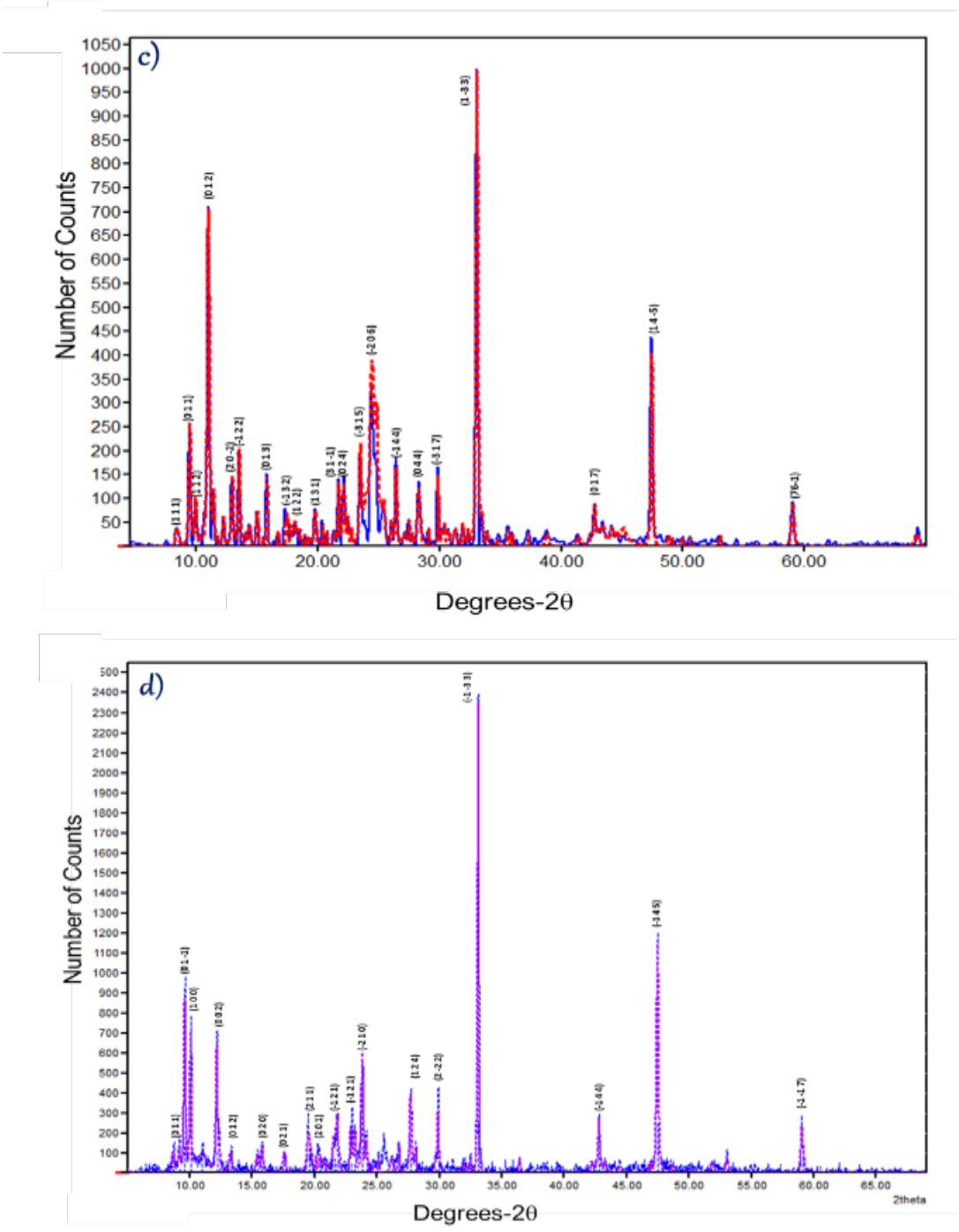

Figure S19. Simulated X-ray powder diffraction (λ= 1.54056 Å) pattern ofc) Eu(**One-phen**)(**BTA**)$_3$ d) Eu(**Epoxy-phen**)(**BTA**)$_3$. Experimental (blue line), calculated (dashed line).

References

(1) Martins, J. P.; Martín-Ramos, P.; Coya, C.; Silva, M. R.; Eusebio, M. E. S.; De Andrés, A.; Álvarez, Á. L.; Martín-Gil, J. Highly Luminescent Pure-Red-Emitting Fluorinated β-Diketonate Europium(III) Complex for Full Solution-Processed OLEDs. *J. Lumin.* **2015**, *159*, 17–25. https://doi.org/10.1016/j.jlumin.2014.10.020.