Supplementary Information

Highly luminescent Tb(III) cluster for sensitization of Eu(III) through $f \rightarrow f$ energy transfer for LED applications

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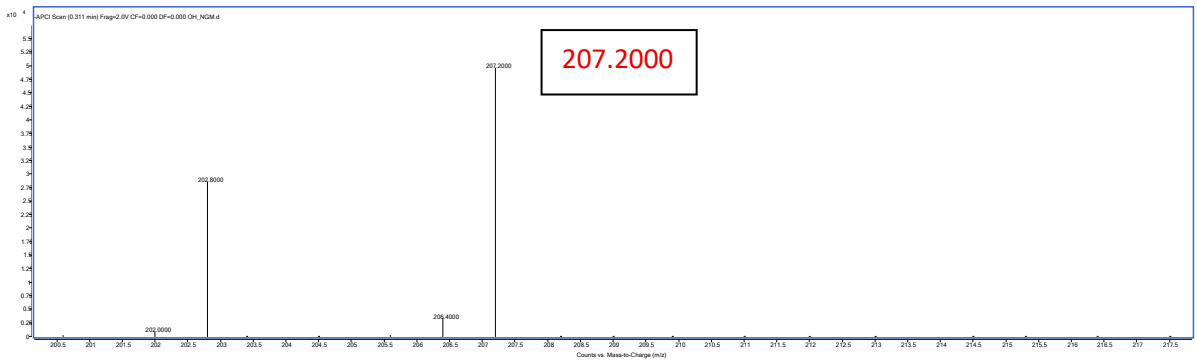
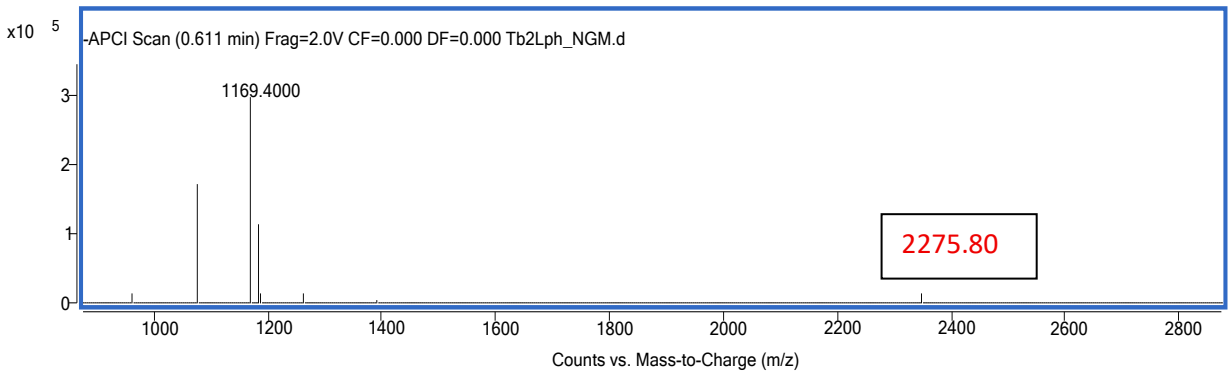
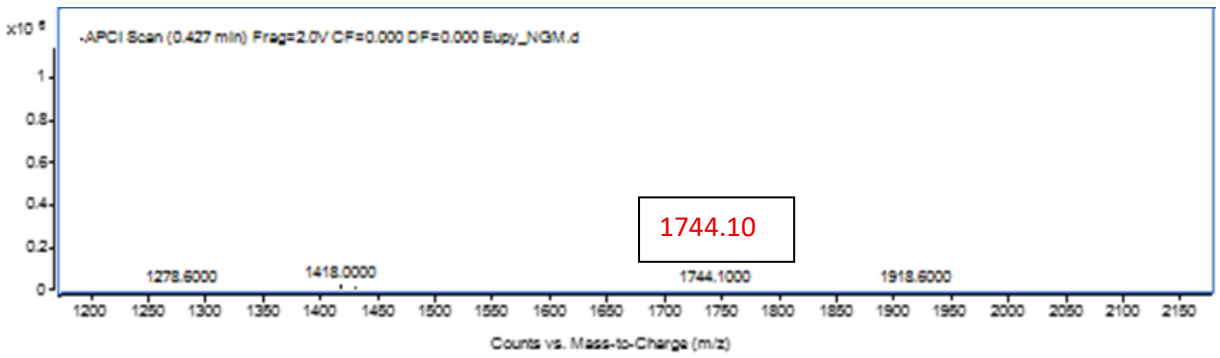


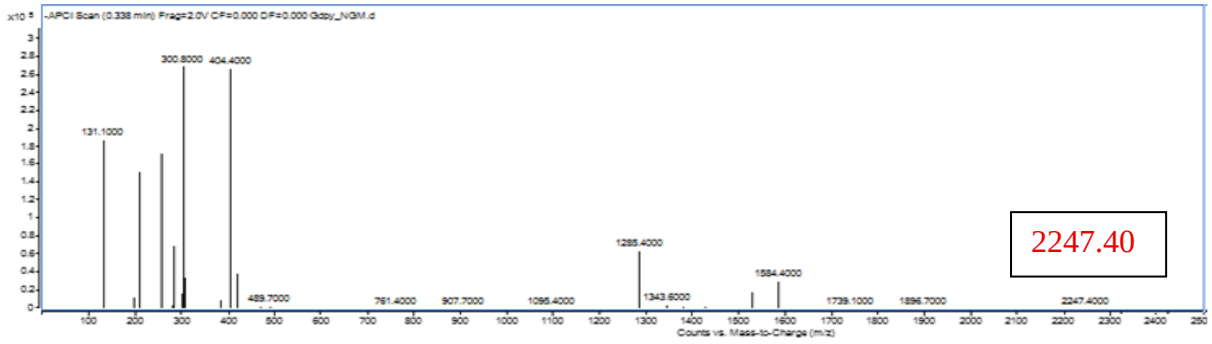
a) Ligand HL’.



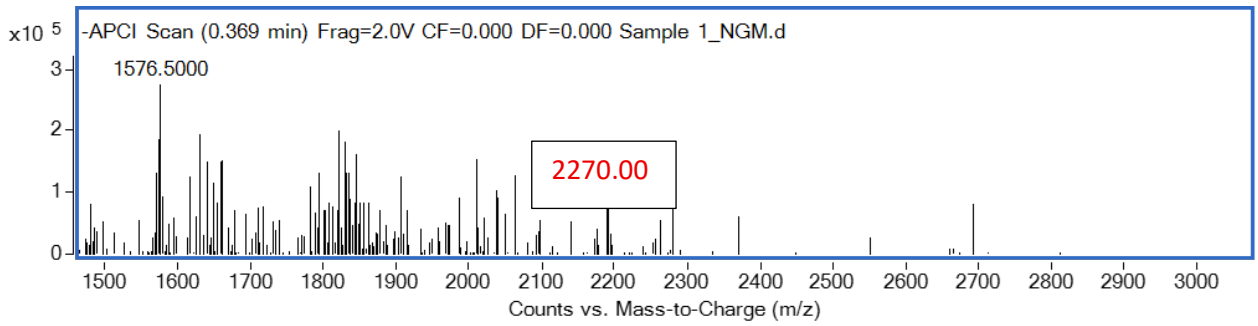
b) **TbC.**



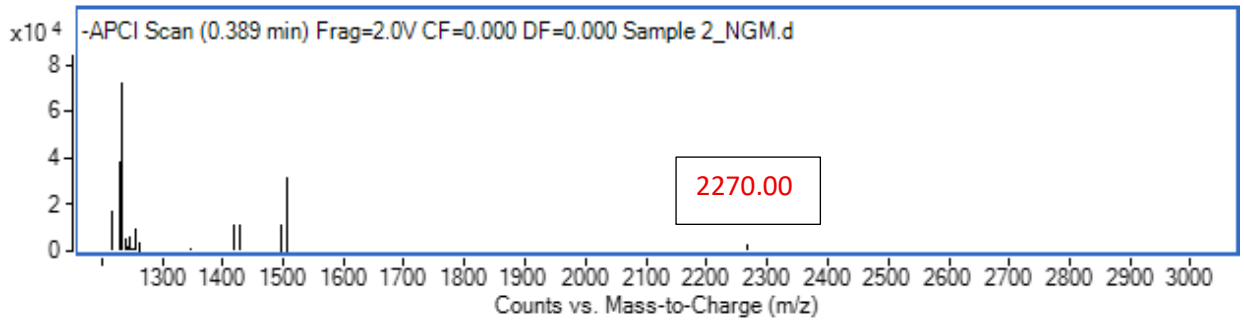
c) **EuC.**



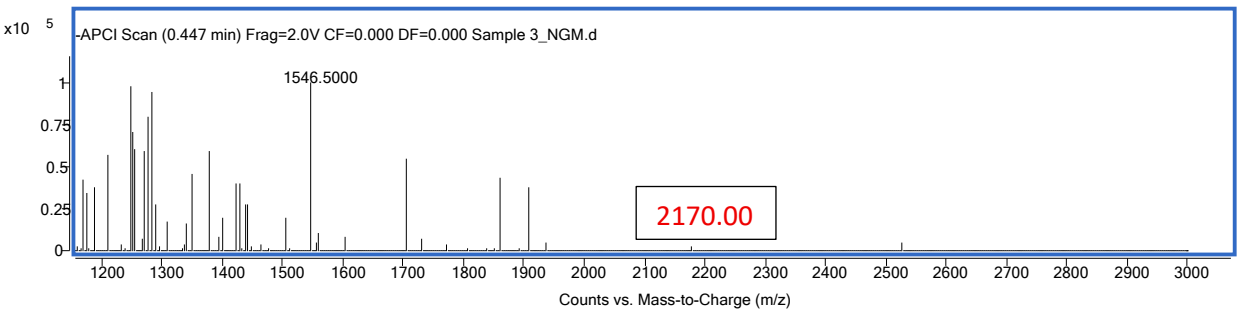
d) **GdC.**



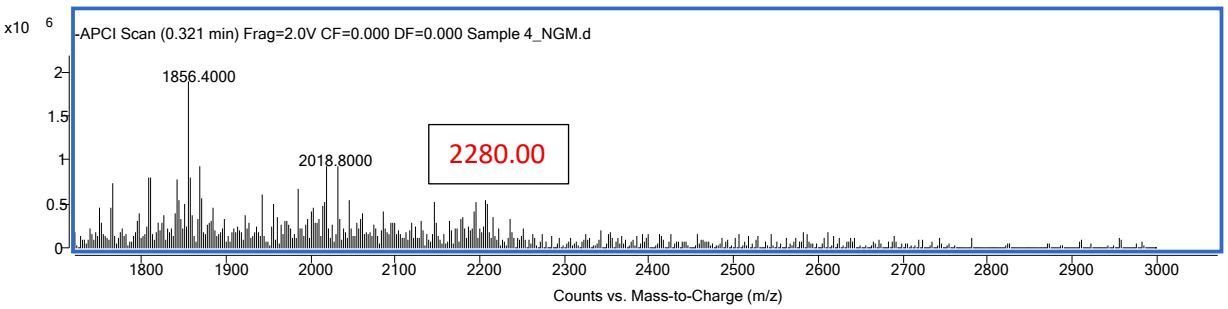
e) $Tb_{0.90}Eu_{0.10}$



f) $Tb_{0.92}Eu_{0.08}$



a) $Tb_{0.94}Eu_{0.06}$



a) $Tb_{0.96}Eu_{0.04}$

Figure S1: Mass spectrometry spectra for H**L'** and the **LnC** clusters in MeOH complexes.

Table S1: Mass to charge (*m/z*) of the fragments of Ln(III) clusters.

The complex	The fragments	*m/z* (found)	*m/z* (calculated)
TbC	$\{[Tb_2L'_2(hfac)_4(tfa)_2]\cdot Na_2L_2\}^-$	2275.80	2275.8
EuC	$\{[Eu_2L'_2(hfac)_4(tfa)_2]\}^-$	1744.10	1782.1
GdC	$\{[Gd_2L'_2(hfac)_4(tfa)_2]\cdot[Na_2L_2]\text{-}F\}^-$	2247.40	2249.4
$Tb_{0.90}Eu_{0.10}$	$\{[Tb_{0.9}Eu_{0.1}L'_2(hfac)_4(tfa)_2]\cdot Na_2L_2\}^-$	2280.00	2280.0
$Tb_{0.92}Eu_{0.08}$	$\{[Tb_{0.92}Eu_{0.08}L'_2(hfac)_4(tfa)_2]\cdot Na_2L_2\}^-$	2270.00	2274.68
$Tb_{0.94}Eu_{0.06}$	$\{[Tb_{0.94}Eu_{0.06}L'_2(hfac)_4(tfa)_1]\cdot Na_2L_2\}^-$	2170.00	2161.0
$Tb_{0.96}Eu_{0.04}$	$\{[Tb_{0.96}Eu_{0.04}L'_2(hfac)_4(tfa)_2]\cdot Na_2L_2\}^-$	2280.00	2275.24

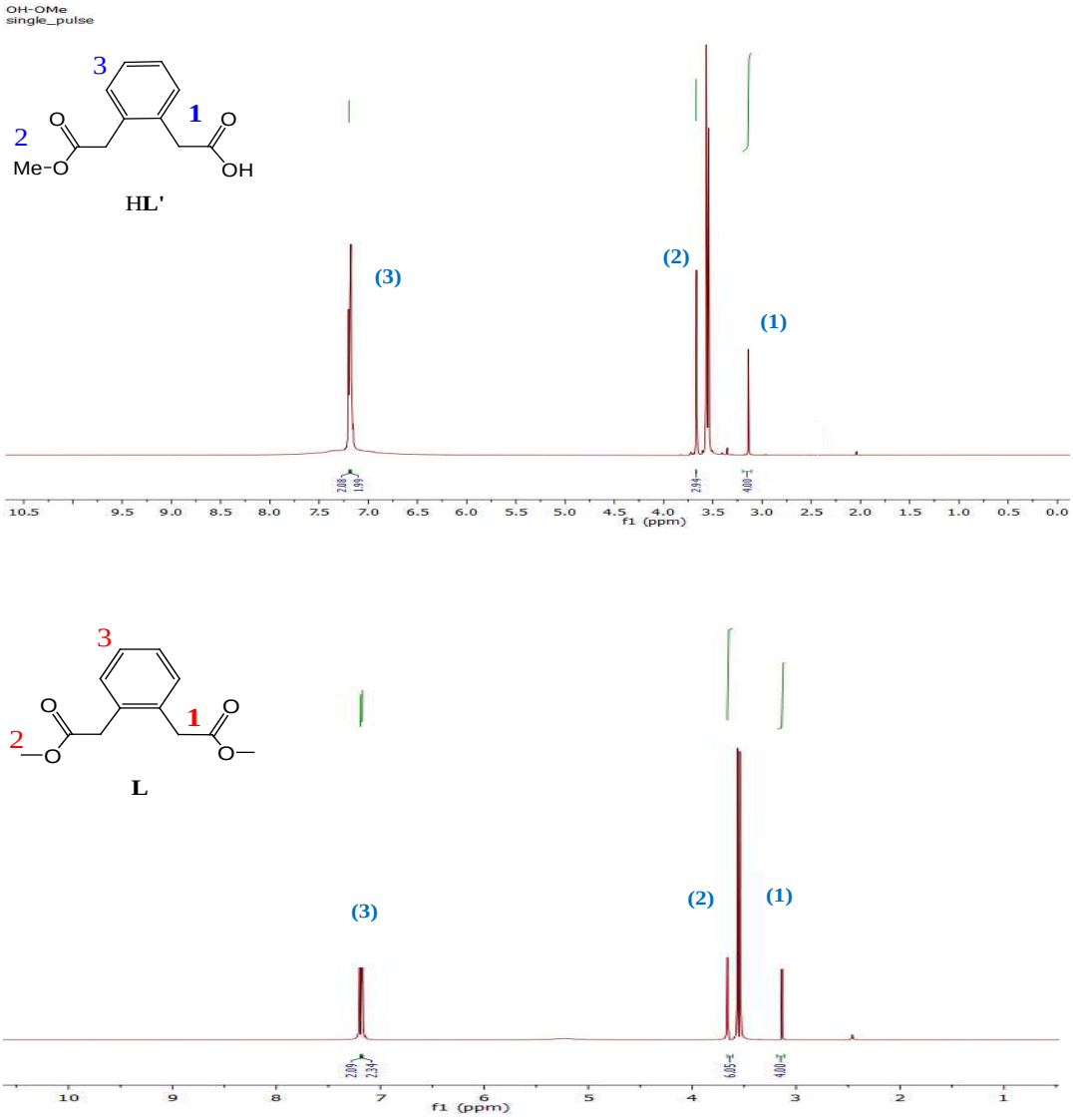


Figure S2: ^{1}H NMR (500 MHz) spectrum of ligand H**L'** in $CDCl_3$.

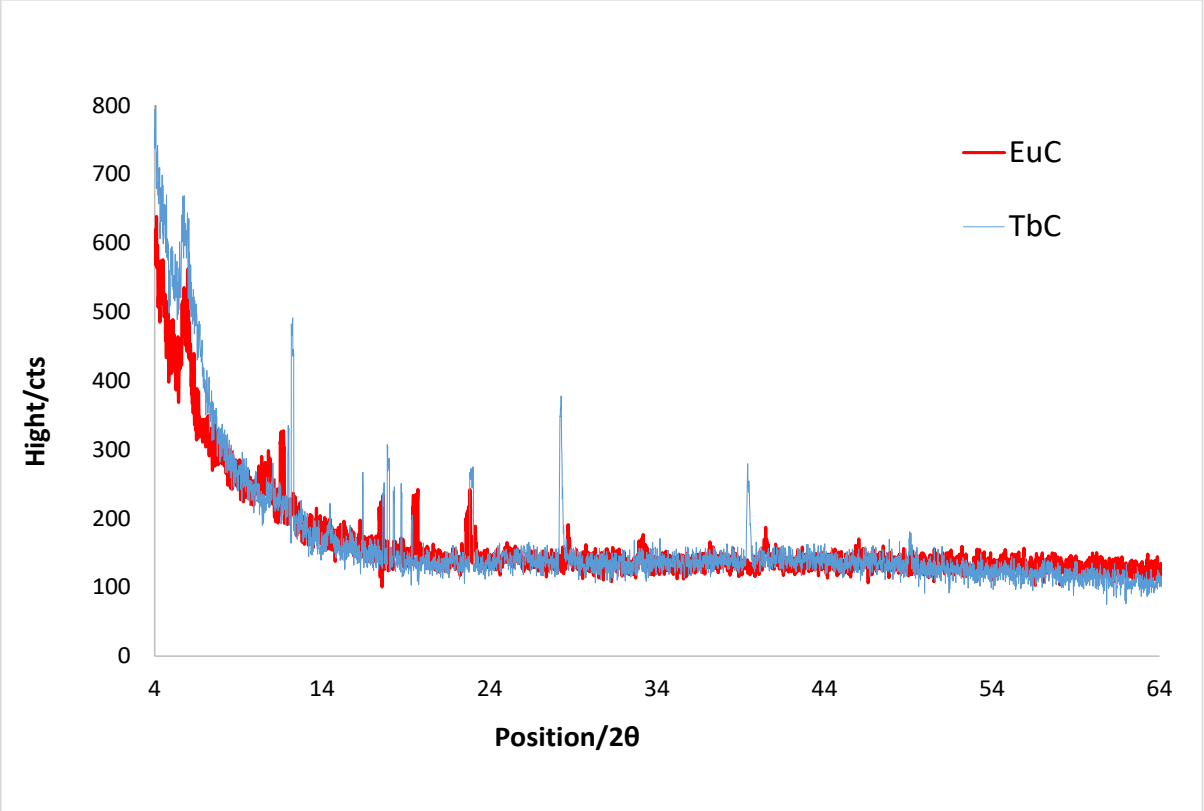


Figure S3. The powder X-ray diffraction (PXRD) patterns for **EuC** (top) and **TbC** (bottom).

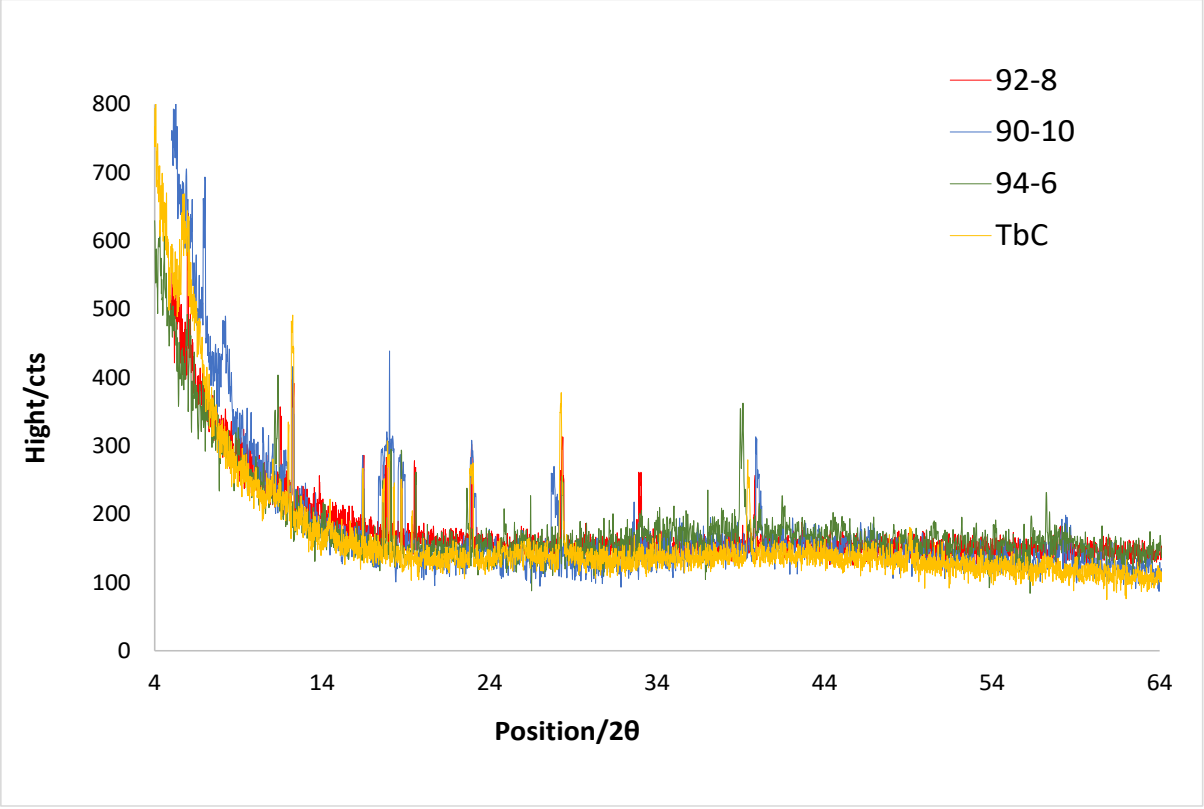


Figure S4. The powder X-ray diffraction (PXRD) patterns for **EuC** (top) and **TbC** (bottom).

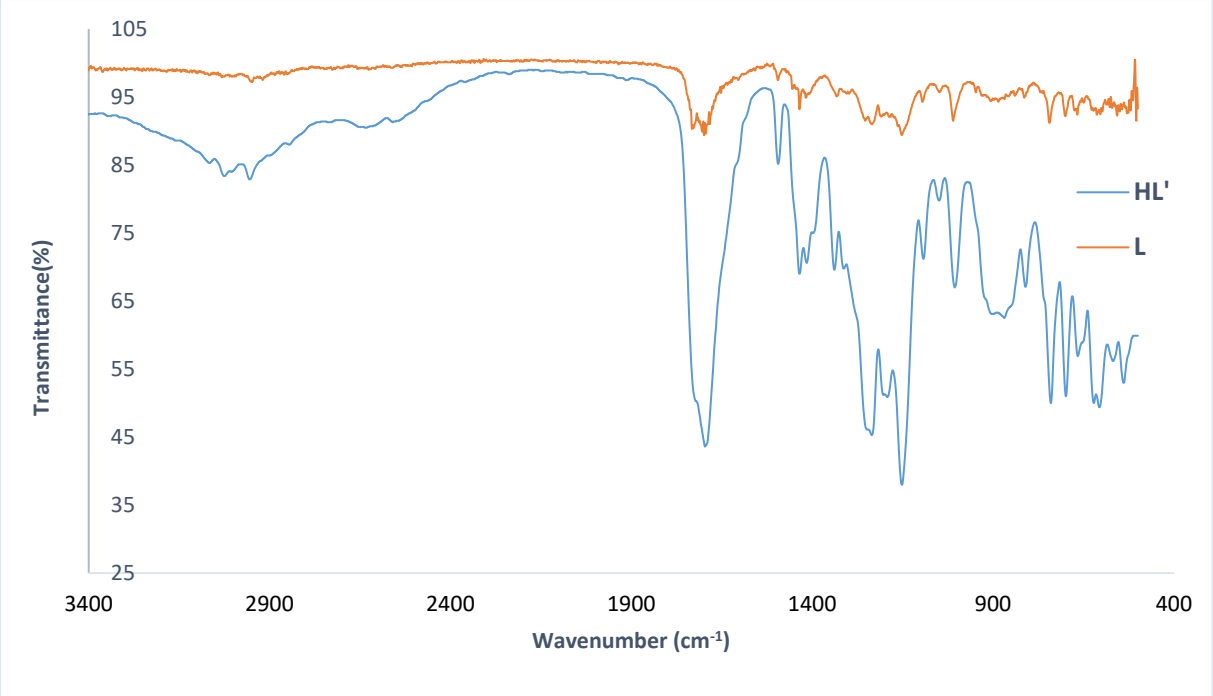


Figure S5: The IR spectra for the ligands and in the solid state at RT.

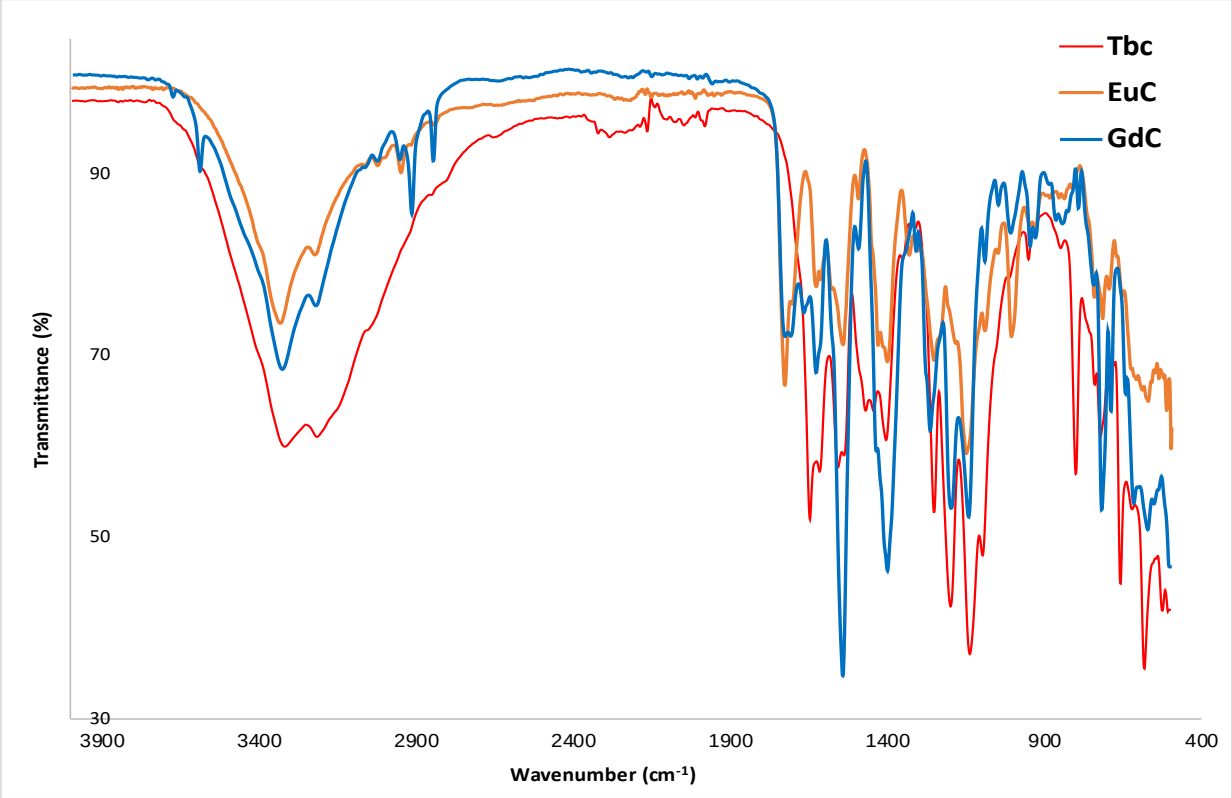


Figure S6: The IR spectra for the ligands and the **LnC** clusters, Ln = Tb, Eu and Gd in the solid state at RT.

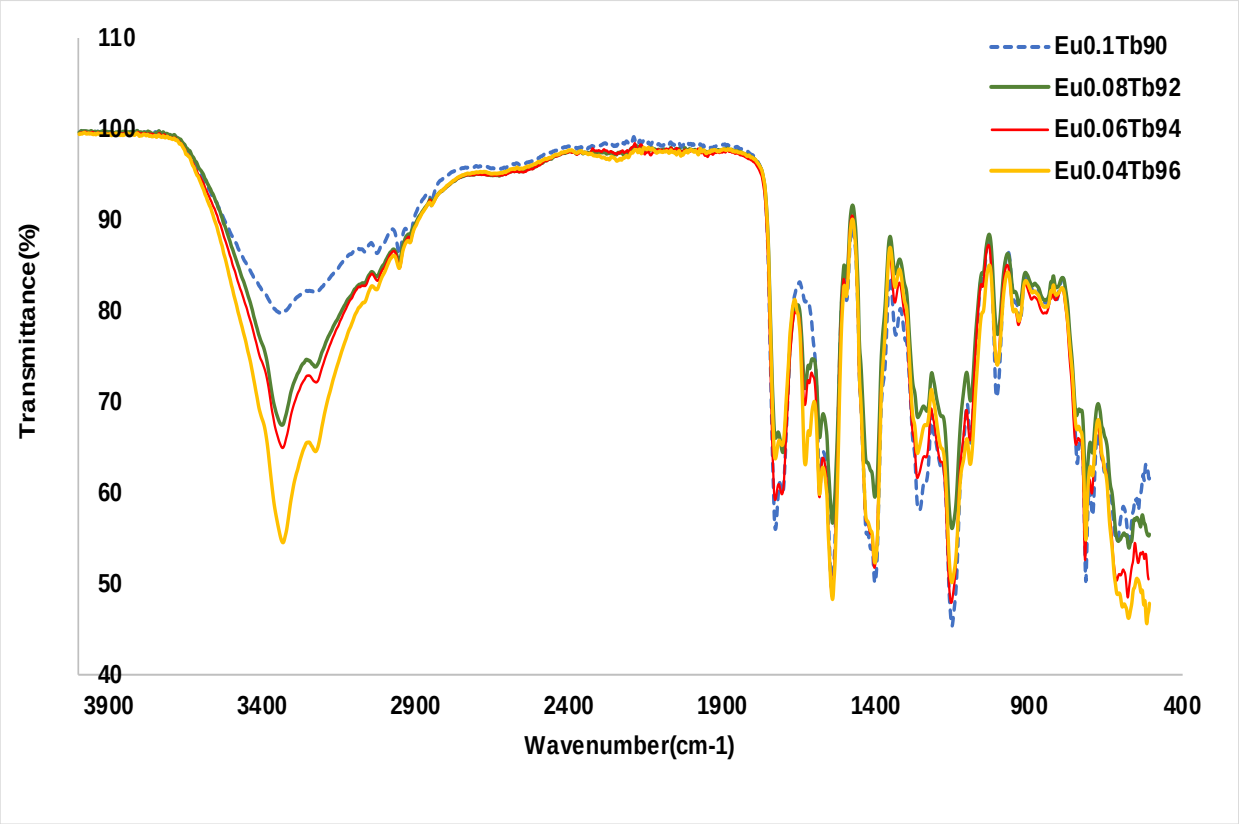


Figure S7: The IR spectra for the ligands and the $Tb_{1-x}Eu_x$ clusters (x = 0.04–0.10) in the solid state at RT.

Table S2: Summary of the important IR stretching frequencies for the Ln(III) clusters.

IR absorption (cm^{-1})						
Bond	**O–H (COOH)**	**C=O (COOMe)**	**C=O (hfac)**	**C–C/C=C**	**C–F**	**Ln(III)–O**
TbC	---	1647	1520	802/1403	1140	584
EuC	---	1631	1546	722/1401	1146	574
GdC	---	1631	1530	812/1415	1134	531
$Tb_{0.90}Eu_{0.10}$	---	1727	1534	718/1405	1007	582/572
$Tb_{0.92}Eu_{0.08}$	---	1717	1532	693/1393	1001	576/570
$Tb_{0.94}Eu_{0.06}$	---	1727	1534	717/1405	1005	582/578
$Tb_{0.96}Eu_{0.04}$	---	1727	1542	718/1401	1005	584/576
L	---	1668	---	988/1408	---	---
HL`	3002	1685	---	987/1391	---	---

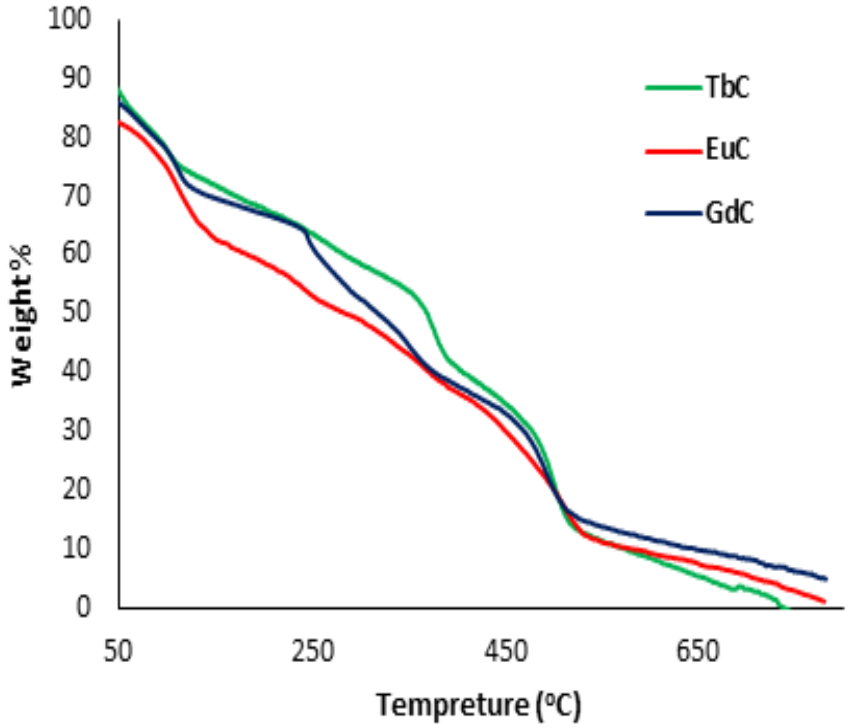


Figure S8. The TGA curves of **TbC**, **Eu1** and **GdC** recorded under an inert atmosphere of N_2.

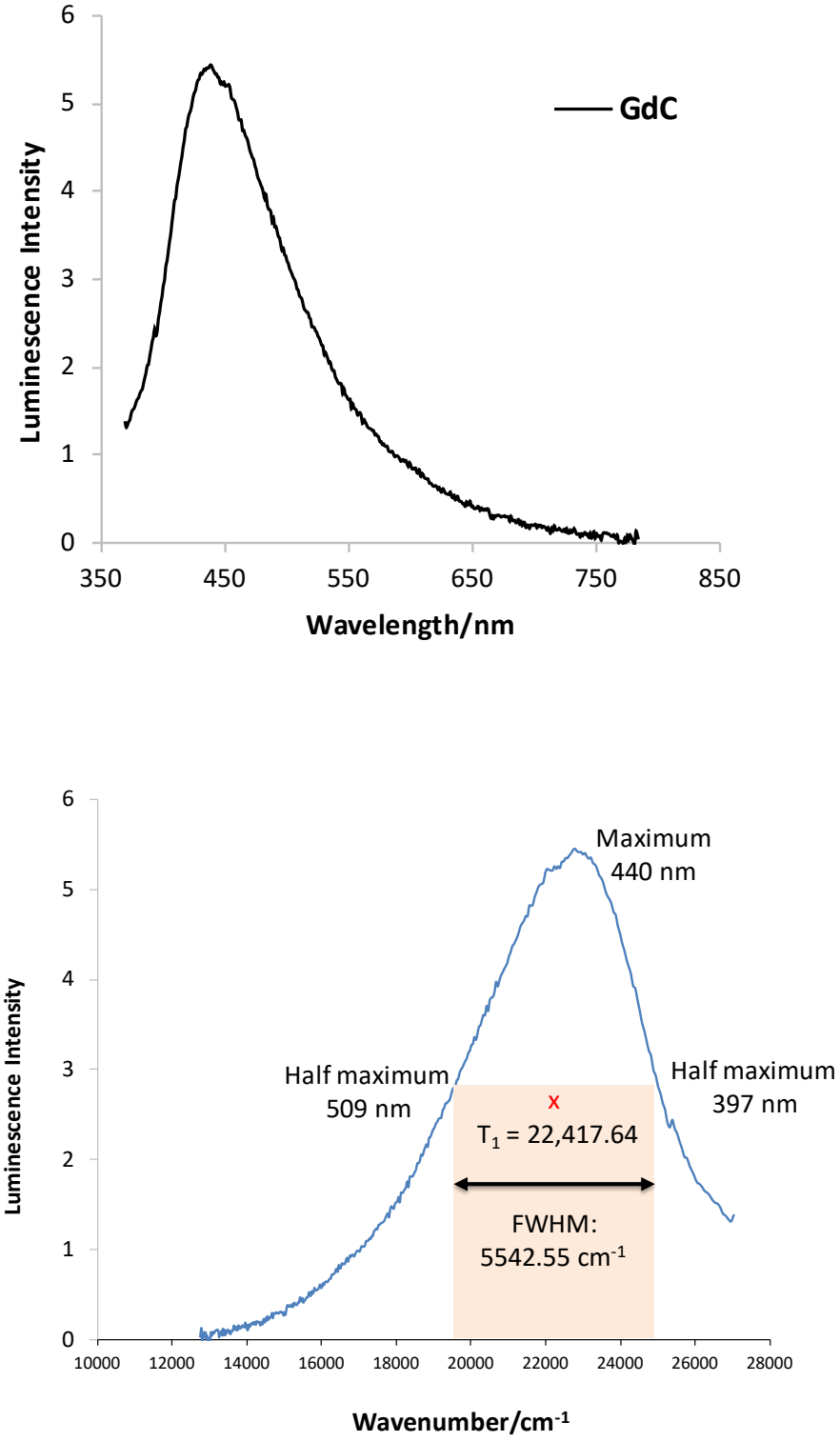


Figure S9: Above: The phosphorescence spectrum of **GdC** in ethanol (5 x10^{-5} M) at 77 K excited at 350 nm. Bottom: the corresponding phosphorescence spectrum processed via Jacobian transformation. The red mark indicates to the barycenter positions of the T_1 state, while the shaded orange regions represent the full width at half maximum (FWHM) of the emission bands.

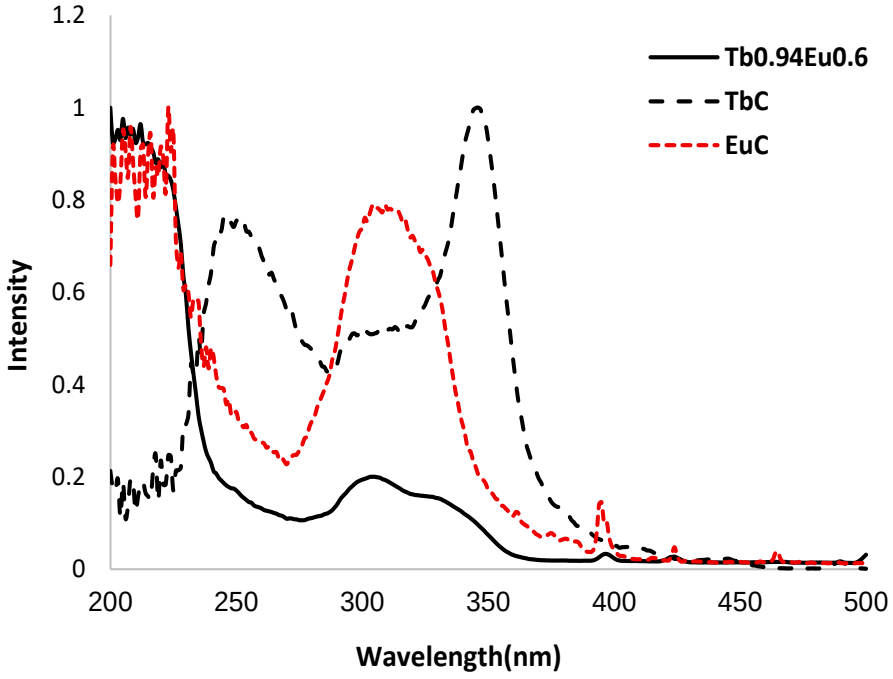


Figure S10. The excitation of the Ln(III) clusters: **TbC** (λ_{em} = 615), **EuC** (λ_{em} = 615) and $Tb_{0.94}Eu_{0.06}$ (λ_{em} = 615) in the solid state at room temperature.

Table S3: Summary of the CIE 1931 chromaticity coordinates of the Ln(III) clusters, the $Tb_{1-x}Eu_x$ clusters (where x = 0.04-0.10) and LED devices in the solid state at RT.

1931 Measurements	***x* Coord**	***y* Coord**	**Color**
TbC	0.34103	0.60148	Green
EuC	0.59978	0.31381	Red
GdC	0.26928	0.27636	Blue
$Tb_{0.90}Eu_{0.10}$	0.61664	0.32789	Red
$Tb_{0.92}Eu_{0.08}$	0.55982	0.41317	Orange
$Tb_{0.94}Eu_{0.06}$	0.52735	0.44016	Bright orange
$Tb_{0.96}Eu_{0.04}$	0.48005	0.46070	Yellow
LED devices:			
TbC LED	0.23291	0.49147	Green
$Tb_{0.90}Eu_{0.10}$ LED	0.47829	0.16216	Pink
$Tb_{0.96}Eu_{0.04}$ LED	0.36429	0.39198	Yellow

Table S4: Summary of the experimental photophysical parameters of the LED devices at RT.

Cluster	τ_{Ln}[a]/ms	Q_{Ln}[b]
TbC	1.10	33.5%
$Tb_{0.90}Eu_{0.10}$	1.43	81.3%
$Tb_{0.96}Eu_{0.04}$	0.54	30.8%

[a] In the solid state. [b] τ_{rad} = 3.28 ms for Tb(III) Ref. [45] and τ_{rad} = 1.76 ms for Eu(III) Ref. [21]

Summary of TD DFT results

The ligand **HL'** is optimized from ground state geometries at the UAPFD function 6-311+g(2d,p) basis in the gas-phase.

HOMO is 5	54					
No.	Energy (cm-1)	Wavelength	Osc. Stren	Symmetry	Major con	Minor contribs
1	28689.14104	348.5639387	0	3.000-A	H-2(A)->L(	H-3(A)->HOMO(A) (2%), H-3(A)->LUMO(A) (2%), H-2(A)->HOMO(A) (3%), H-1(A)->LUMO(A
2	36243.32982	275.9128383	0	3.000-A	H-2(A)->L(	H-3(A)->LUMO(A) (2%), H-2(A)->HOMO(A) (5%), H-1(A)->LUMO(A) (9%), H-1(A)->L+1(A) (2
3	36397.38172	274.7450374	0	3.000-A	H-2(A)->H	H-1(A)->HOMO(A) (5%), LUMO(B)->L+1(B) (5%)
4	38934.80195	256.8396267	0	3.000-A	H-2(A)->H	H-2(A)->LUMO(A) (4%), H-1(A)->HOMO(A) (2%), H-1(A)->L+1(A) (2%), HOMO(B)->L+2(B) (4
5	40812.46066	245.0232071	0	3.000-A	H-3(A)->H	HOMO(A) (5%), H-3(A)->L+1(A) (9%), H-3(A)->L+4(A) (7%), H-3(A)->L+5(A) (3%), H-1(A)->L+1(
6	41418.98959	241.4351508	0	3.000-A	H-4(A)->H	H-4(A)->L+2(A) (2%), H-3(A)->L+1(A) (2%), H-1(A)->L+1(A) (2%), H-2(B)->L+4(B) (2%), H-1(B
7	41623.85442	240.2468522	0.0006	1.000-A	H-2(A)->H	H-2(A)->LUMO(A) (3%), H-1(A)->HOMO(A) (4%), HOMO(B)->L+2(B) (3%), LUMO(B)->L+1(B)
8	43868.49539	227.9540228	0.0485	1.000-A	H-1(A)->H	H-4(A)->HOMO(A) (3%), H-4(A)->L+1(A) (2%), H-3(A)->L+1(A) (2%), H-2(A)->HOMO(A) (6%
9	45104.94333	221.7051893	0.0259	1.000-A	H-1(A)->L-	H-4(A)->HOMO(A) (2%), H-4(A)->L+1(A) (2%), H-3(A)->HOMO(A) (7%), H-3(A)->L+1(A) (4%
10	46339.77816	215.7973214	0.0458	1.000-A	H-1(A)->L(	H-4(A)->HOMO(A) (5%), H-4(A)->L+1(A) (2%), H-2(A)->HOMO(A) (4%), H-2(A)->LUMO(A) (
11	46644.65574	214.3868326	0	3.000-A	H-5(A)->L-	H-5(A)->HOMO(A) (3%), H-5(A)->L+3(A) (2%), H-5(A)->L+5(A) (6%), H-3(B)->L+1(B) (3%), H-
12	47114.87697	212.2471848	0	3.000-A	H-3(A)->H	H-3(A)->LUMO(A) (3%), H-1(A)->HOMO(A) (9%), H-1(B)->L+2(B) (3%), LUMO(B)->L+1(B) (9%
13	47577.03266	210.1854496	0	3.000-A	H-6(A)->H	H-12(A)->HOMO(A) (2%), H-12(A)->L+1(A) (2%), H-6(A)->L+2(A) (3%), H-6(A)->L+4(A) (2%),
14	48218.24343	207.3903836	0.0173	1.000-A	H-2(A)->L(	H-3(A)->HOMO(A) (9%), H-3(A)->LUMO(A) (2%), H-1(A)->HOMO(A) (3%), H-1(A)->LUMO(A
15	48593.29124	205.7897242	0	3.000-A	H-3(A)->L(	H-4(A)->HOMO(A) (2%), H-1(A)->LUMO(A) (5%), H-1(A)->L+1(A) (7%), H-2(B)->L+1(B) (2%),
16	49081.25667	203.7437645	0.064	1.000-A	H-3(A)->L(	H-4(A)->HOMO(A) (5%), H-4(A)->L+1(A) (3%), H-2(A)->HOMO(A) (8%), H-2(A)->LUMO(A) (
17	49352.25896	202.6249702	0	3.000-A	H-2(A)->L-	H-4(A)->HOMO(A) (5%), H-4(A)->L+1(A) (3%), H-3(A)->LUMO(A) (3%), H-2(A)->HOMO(A) (
18	50007.18115	199.9712795	0	3.000-A	H-3(A)->H	H-4(A)->HOMO(A) (2%), H-3(A)->LUMO(A) (4%), H-3(A)->L+1(A) (3%), H-3(A)->L+4(A) (2%)
19	50024.92535	199.9003483	0.0194	1.000-A	H-3(A)->H	H-4(A)->HOMO(A) (4%), H-4(A)->L+1(A) (2%), H-3(A)->LUMO(A) (4%), H-3(A)->L+1(A) (3%)
20	50883.90582	196.5257941	0.0027	1.000-A	H-4(A)->H	H-4(A)->L+1(A) (3%), H-3(A)->L+1(A) (3%), H-3(A)->L+4(A) (2%), H-2(A)->L+1(A) (4%), H-1(A
21	52107.44889	191.9111416	0	3.000-A	H-1(A)->L+2(A) (44%), LUMO(B)->L+4(B) (44%)	
22	52172.77979	191.6708299	0.1228	1.000-A	H-1(A)->L-	H-3(A)->HOMO(A) (4%), H-3(A)->L+1(A) (3%), H-3(A)->L+4(A) (2%), H-2(A)->LUMO(A) (7%)
23	52799.47259	189.3958313	0.2559	1.000-A	H-3(A)->L(	H-2(A)->HOMO(A) (7%), H-2(A)->L+2(A) (2%), H-2(A)->L+4(A) (2%), H-1(A)->LUMO(A) (4%)
24	53070.47487	188.4286889	0.1808	1.000-A	H-1(A)->L-	H-4(A)->LUMO(A) (3%), H-3(A)->HOMO(A) (3%), H-3(A)->L+1(A) (2%), H-2(A)->LUMO(A) (6
25	53558.4403	186.7119345	0	3.000-A	H-2(A)->L-	H-2(A)->L+3(A) (2%), H-2(A)->L+4(A) (2%), H-1(A)->L+3(A) (2%), HOMO(B)->L+5(B) (2%), HO

E T	-726.831	Eh		Eh_eV	27.21141
E S	-726.964	Eh		nm_eV	1239.8
DE	0.132676	Eh			
	2.99	eV			