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Supporting Information

Thiabendazole: A new class of antenna core structure for Multifunctional Trivalent Organo-Europium (Eu^{III}) Complexes†

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†Dedicated to Dr. V. Subramanian on the occasion of his 60th birthday.

General aspects of synthesis:

All reactions were carried out under an inert (nitrogen N_2) environment. Prior to the reaction, the usable Solvents tetrahydrofuran (THF), Dimethylformamide (DMF), Toluene, etc. were properly dried and carefully distilled by using appropriate drying agents (P_2O_5, sodium metal, Benzophenone. Commercially available chemicals TBZ, TTA, DBM, Carbazole, 1, 4 dibromo butane, Benzyl bromide, Europium (III) chloride hex hydrate (99.99%), were used for synthesis processes. $CdCl_3$, DMSO-d_6, poly (methyl methacrylate) (PMMA) and tetrabutylammonium perchlorate (nBu_4NClO_4) electrolyte were used for characterization process.

Characterization technique:

All the synthesized ligand and their corresponding Eu(III) complexes were synthesized and are characterized by different characterization techniques. ^1H and ^{13}C NMR spectra were recorded for the structural conformation of ligands as well as complexes in DMSO-d_6 and $CDCl_3$ solvents. All spectra were recorded with the help of the AV 400 Advance-III 400 MHz Fourier transform nuclear magnetic resonance (FT-NMR) spectrometer (Bruker Biospin International, Switzerland). To know electronic bond formation, the Fourier transforms infrared (FTIR) spectra (in 400-4000 cm^{-1} range) were recorded by using g KBr disc with the help of PerkinElmer, USA/RX-I FTIR, spectrophotometer.Mass spectra of all the synthesized fluorophores were recorded on High Resolution Mass Spectrometer (HRMS) Waters, USA, XEVO G2-XS QTOF model The thermal stability of the samples was investigated by TGA analytical technique (Nietzsche STA 449C, Germany) under N_2 atmosphere at 30° to 800°C temperature range of heating rate 10°C under ambient conditions. The UV-Vis absorption spectra using different solvents were performed. UV-Vis spectrophotometer (UV-2450 PerkinElmer).The photoluminescence (PL) excitation and emission spectra in solid, solution and thin film were measured by Edinburg Spectrofluorometer FS–5 instruments associated with SC – 10 modules and SC–5 modules. The photoluminescence quantum yield were recorded with the

with Edinburgh Instruments, Spectrofluorometer, FS5, Integrating Sphere SC-30. The CIE color coordinate for all emission spectra is calculated by MATLAB software. The electrochemical analysis was performed by using cyclic voltammeter (CV), AUTO LAB 302N Modular potentiostat. Basically, a calomel electrode was used as the reference electrode where as a platinum electrode was used as the working electrodes well as counter electrode. Measurement was performed in DMF solvents and tetrabutylammonium per chlorate was used as the supporting electrolyte, at a scanning speed of 50 mV/S. The computational study about ligand structure (ground state geometry) was optimized by density functional theory (DFT the B3LYP/6-31G (d, p) level of basis set in the G09W suite of programs.

General synthesis of ligands:

Synthesis of 4-(1-benzyl-1H-benzo[d]imidazol-2-yl) Thiazole (TBZ-CH_2-Ph

To begin the synthesis first, the DMF was dried and distilled properly. In a dried two necked Round bottom flask, 9.37 mmol of Thiabendazole (TBZ) and 22.8 mmol of K_2CO_3 were taken and dissolved in 30 mL of dry DMF. The reaction temperature was set to 600C and stirred for 30 minutes. To the above solution, 2.1 mmol of Benzyl bromide was added dropwise at the same temperature and left it for 12 hours. The progression of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was poured in ice-cold water. The organic compound was extracted in Ethyl acetate in a separating funnel. The purification was carried out by column chromatography packed with 200-300 mg silica gel by using Petroleum ether and Ethyl acetate as eluent. The white colour pure solid product was obtained. **^{1}H-NMR Data (400 MHz, $CDCl_3$, δppm):** δ 8.90 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.09 (m, 9H), 6.11 (s, 2H). **^{13}CNMR (400 MHz, $CDCl_3$, δppm)** δ 155.23 (s), 152.46 (s) 137.62 (s) 49.9 Hz(s), 131.60 (s), 129.16 (s), 127.22 – 113.89 (s), 97.74 (s), 79.41 – 70.45(s). HRMS: Mass Calculated m/z = 291.08 found m/z ratio = 291.12

Synthesis of 9-(4-bromobutyl)-9H-carbazole (Intermediate compound):

The synthesis was carried out first by dissolving 15 mmol of Carbazole in a minimum amount of THF. To the solution 60 mmol of 1, 4 dibromobutane was added dropwise. Another solution was prepared by taking 75 mmol of KOH and 1.5 mmol of TBAB in 100 mL water. Both the solution was mixed together and taken in a round bottom flask and allowed the reaction mixture to reflux for 18 hours. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was poured in ice-cold water and DCM. The organic layer was then separated. The purification was done by column chromatography and the white color product was collected and dried over vacuumed. **^{1}H-NMR Data (400 MHz, $CDCl_3$):** 1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.8 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.28 (dd, *J* = 9.9, 4.8 Hz, 2H), 4.39 (t, *J* = 6.9 Hz, 2H), 3.41 (t, *J* = 6.5 Hz, 2H), 2.14 – 2.04 (m, 2H), 1.94 3(dt, *J* = 13.1, 6.5 Hz, 2H). **^{13}C NMR (400 MHz, $CDCl_3$, δ ppm)** δ 140.30 (s), 125.73 (s), 123.52 – 122.95 (s), 120.44 (s), 118.96 (s), 108.54 (s), 80.75 – 71.12 (s), 42.18 (s), 33.14 (s), 30.25 (s), 27.67 (s).

Synthesis of 4-(1-(4-(9H-carbazol-9-yl)butyl)-1H-benzo[d]imidazol-2-yl)thiazole (TBZ-Bu-CBZ):

In a two necked round bottom flask CBZ-C_4-Br (2 mmol) was added in 25 mL of dry Toluene in N2 atmosphere. To the solution 2 mmol of TBZ was added in room temperature stirred for 15 minutes. Triethyl amine (Et_3N) of 3 mmol was taken as base. The reaction temperature was set upto 120°C and reflux for 24 hours. After completion of the reaction, the reaction mixture was poured in ice water and Ethyl acetate and organic layer was separated. Pure white color compound was obtained by column chromatography. 1H-NMR Data (**400 MHz, $CDCl_3$, δ ppm)**:δ 8.77 (d, J = 1.9 Hz, 1H), 8.34 (d, J = 1.7 Hz, 1H), 8.12 (d, J = 7.7 Hz, 2H), 7.81 (d, J = 5.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 3H), 7.30 (dd, J = 19.3, 14.8, 7.7 Hz, 6H), 4.75 (t, J = 6.6 Hz, 2H), 4.33 (t, J = 6.2 Hz, 2H), 2.01 – 1.97 (m,2 H), 0.91 (t, J = 6.7 Hz, 2H).**^{13}C NMR (400 MHz, $CDCl_3$. δ ppm)**: δ 152.86 (s), 152.86 (s), 140.32 (s), 140.32 (s), 125.70 (s), 130.58 102.58 (s), 84.04 – 69.83 (m), 43.61 (s,), 28.45 (s). HRMS: Mass Calculated m/z = 423.54 found m/z ratio = 424.16.

Synthesis root of Eu (III) complexes:

The synthesis of Eu (III) chloride ($EuCl_3.6H_2O$) from europium (III) oxide is carried out. Synthesis of four complexes **Eu-1, Eu-2, Eu-3, and Eu-4** are carried out in the N_2 atmosphere .In A 50 mL two-neck round-bottom flask $Eu(TTA)_3{\cdot}2H_2O$/Eu $(DBM)_3.2H_2O$ (0.161g, 0.189 mmol, 1 equiv) was taken and dissolved with 20 mL dry THF and stirred for 15 minutes. A condenser was fitted with N_2 containing a balloon to make the reaction condition inert. Another solution of ligand was prepared by taking 0.80 g, 0.189 mmol, of TBZ-CH_2-Ph/TBZ-Bu-CBZ with the same solvent (5 mL) and added dropwise to the above solution. The temperature was set up to 60°C and the reaction mixture (RM) was stirred for 12 hours. After overnight reaction minimum amount of THF and an excess amount of hexane was added to the resulting product to get the precipitate. It was then dried over vacuumed drier and the product was collected. The same procedure was followed for Eu $(DBM)_3L$. Finally, from the two ligands TBZ-CH_2-Ph and TBZ-Bu-CBZ four complexes $Eu(TTA)_3$-TBZ-Ch2-Ph **(Eu-1)**, $Eu(DBM)_3$-TBZ-CH_2-Ph **(Eu-2),** $Eu(TTA)_3$-TBZ-Bu-CBZ **(Eu-3),** and Eu(DBM $)_3$TBZ-Bu-cbz **(Eu-4)** have been synthesized from the above procedure.

NMR (^{1}H and ^{13}C)

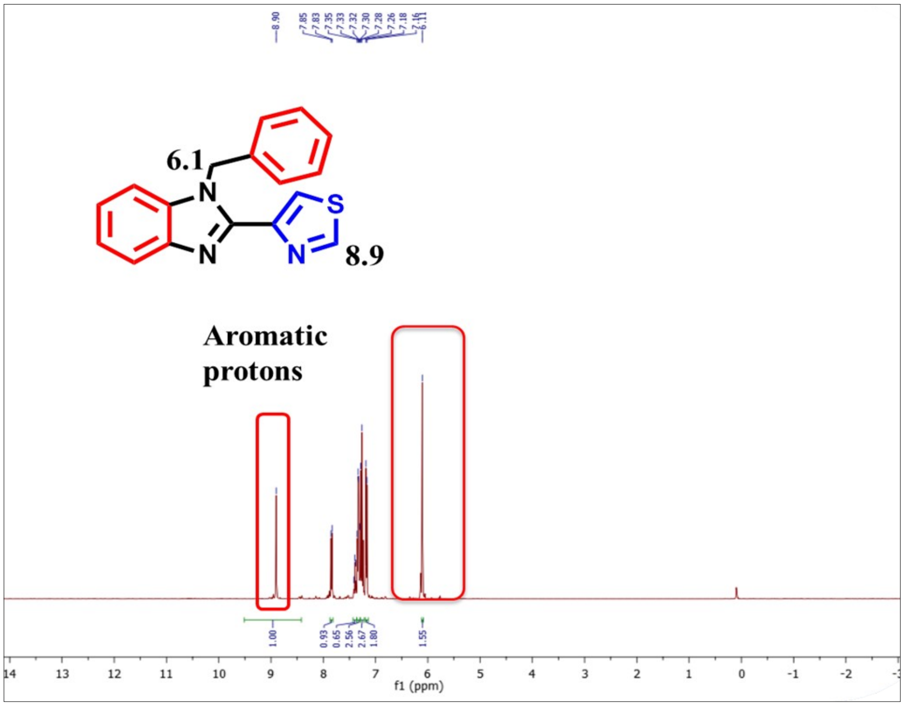


Fig S1. ^{1}H NMR spectroscopy of **TBZ-CH$_2$-Ph** in CDCl$_3$

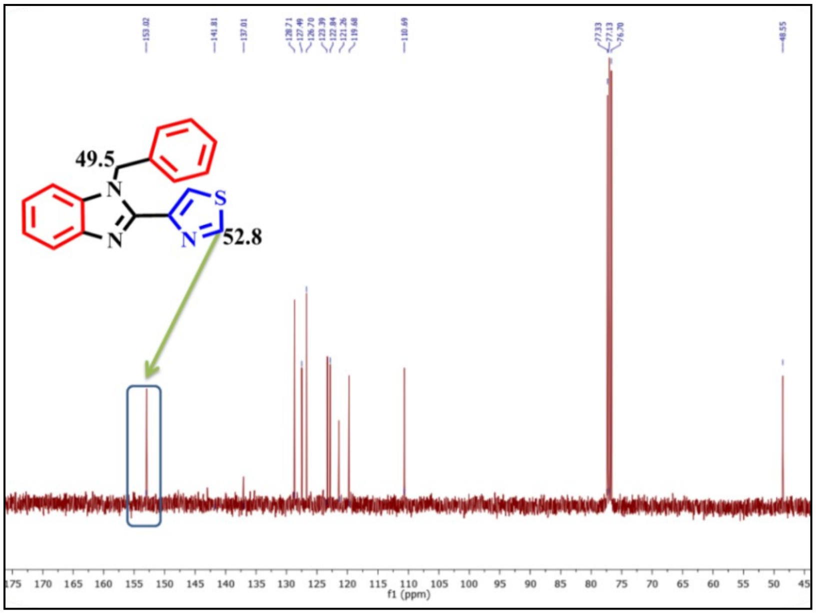


Fig S2. ^{13}C NMR spectroscopy of **TBZ-CH$_2$-Ph** in CDCl$_3$

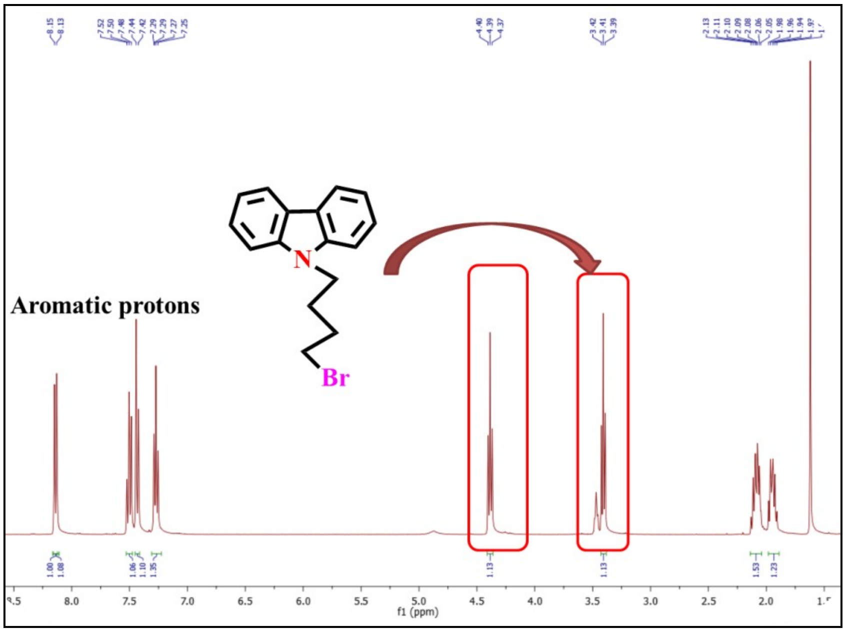


Fig S3. ^{1}H NMR spectroscopy of **CBZ-C$_4$-Br (Intermediate)** in CDCl$_3$

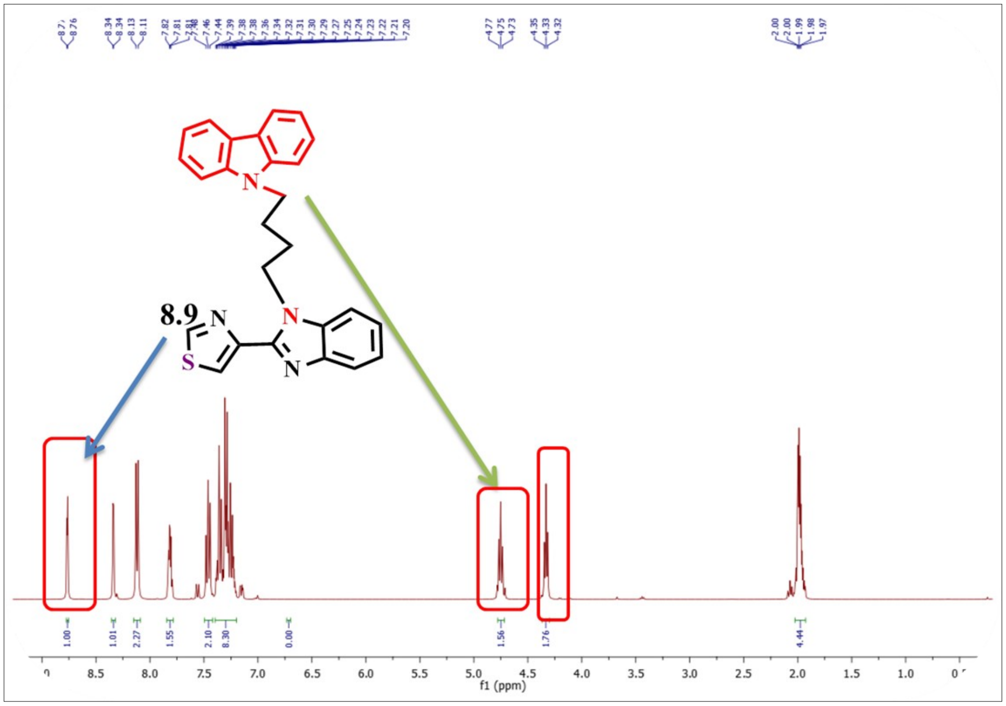


Fig S4. ^{1}H NMR spectroscopy of **TBZ-Bu-CBZ** in CDCl$_3$

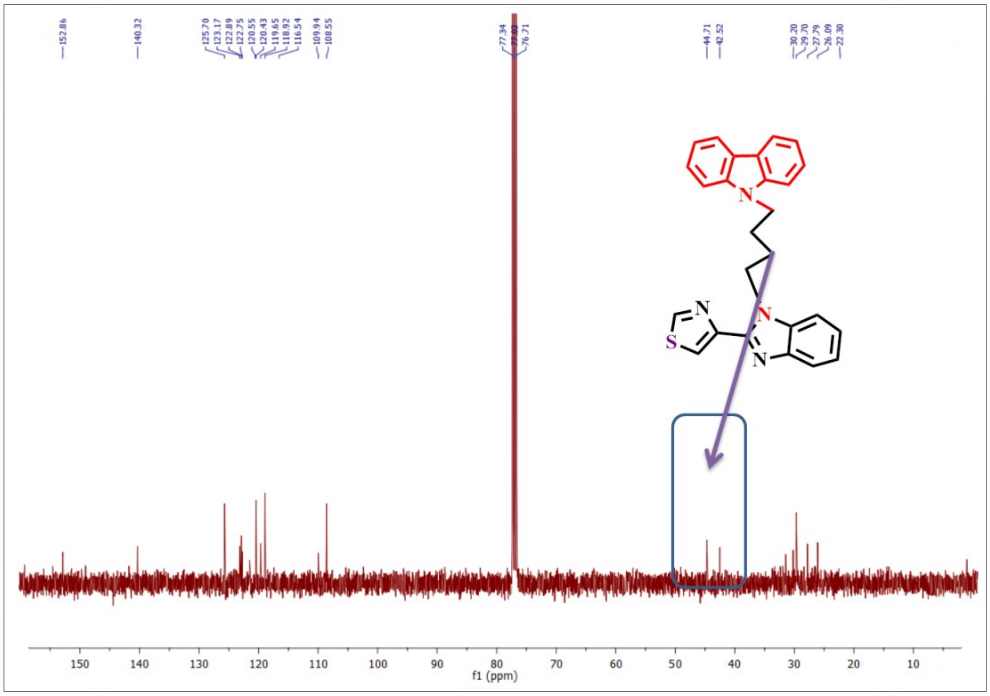


Fig S5. ^{13}C NMR spectroscopy of **TBZ-Bu-CBZ** in $CDCl_3$

^{1}H NMR of Eu-complexes

In 1H NMR, data of all the complexes are showing obvious changes relative to spectra of ligands due to paramagnetic nature of europium (III) ion. The proton signal of keto –CH_2 protons peak at 4.22-4.5 ppm are disappeared from complexes spectra suggesting that the enolic –OH from β-diketone ligands involved in coordination process. The enolic –CH proton of all β-diketone have been a shifted to upfield at 3.30–2.50 ppm in complexes, suggesting the paramagnetic behavior of lanthanide ion. In addition to this multiplate peaks arise due to the overall aromatic protons present in ligand (ancillary and diketones) is now moved toward higher field as compared to free ligand. The obtained data giving obvious result of coordination of ligands with the metal ion

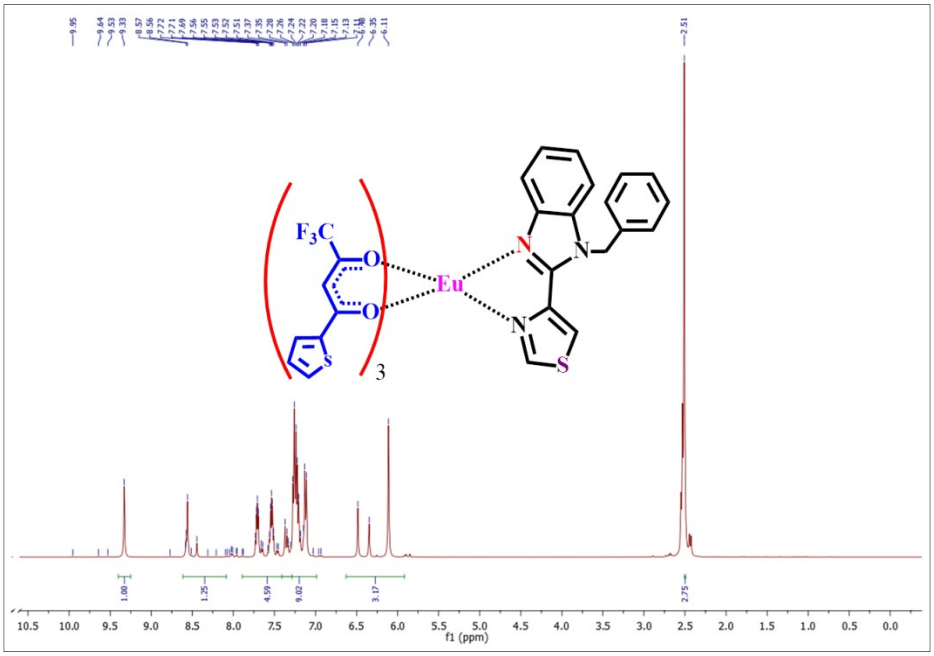


Fig S6. ^{1}H NMR spectroscopy of **Eu(TTA)$_3$TBZ-CH$_2$-Ph** in **DMSO-d$_6$**

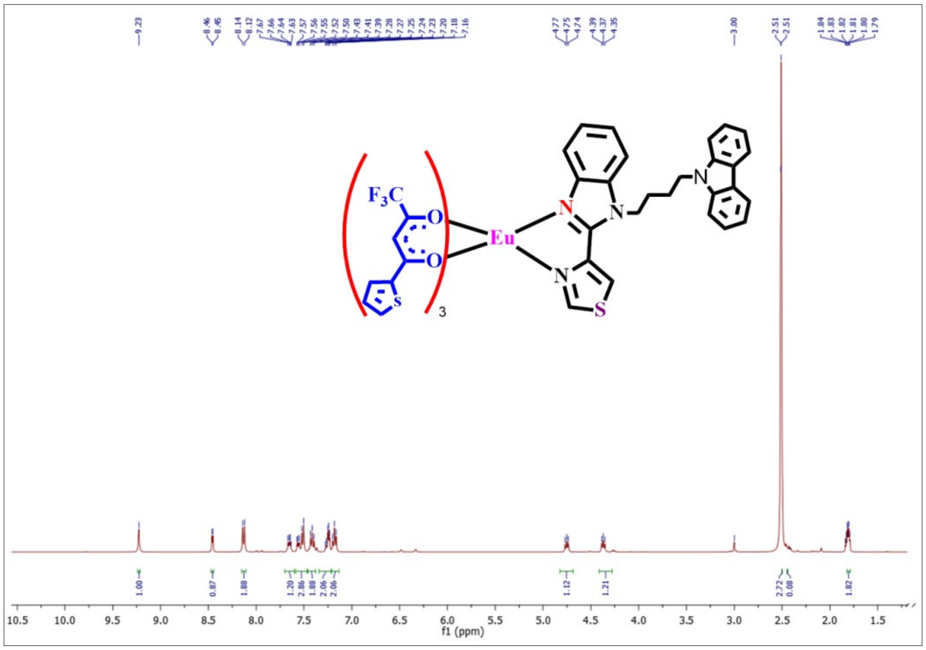


Fig S7. ^{1}H NMR spectroscopy of **Eu(TTA)$_3$TBZ-Bu-CBZ** in DMSO-d$_6$

Mass (HRMS) spectra:

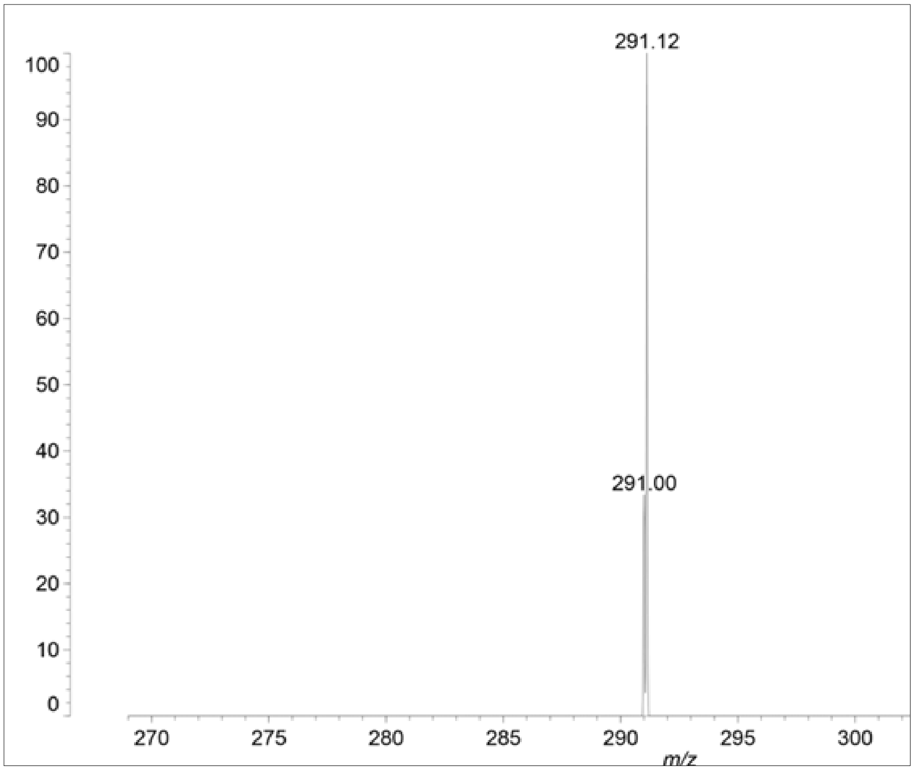


Fig S8 Mass spectral data of **TBZ-CH$_2$-Ph**

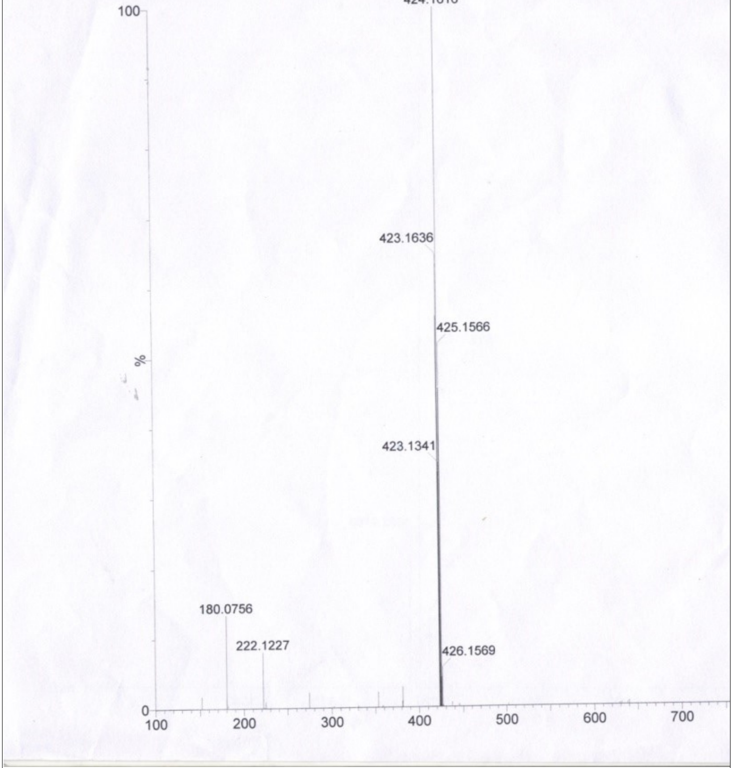


Fig S9. Mass spectral data of **TBZ-Bu-CBZ**

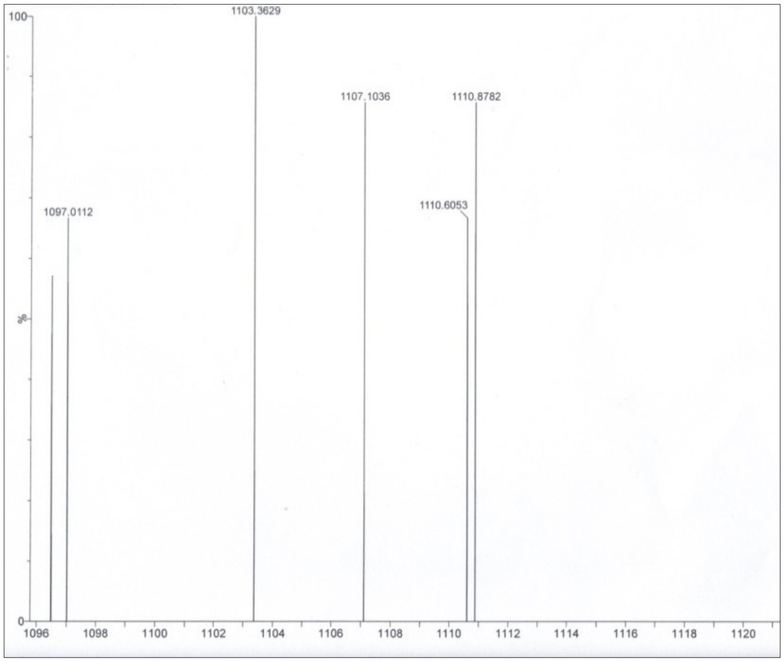


Fig S10. Mass spectral data of **Eu(TTA)$_3$TBZ-CH$_2$-Ph**

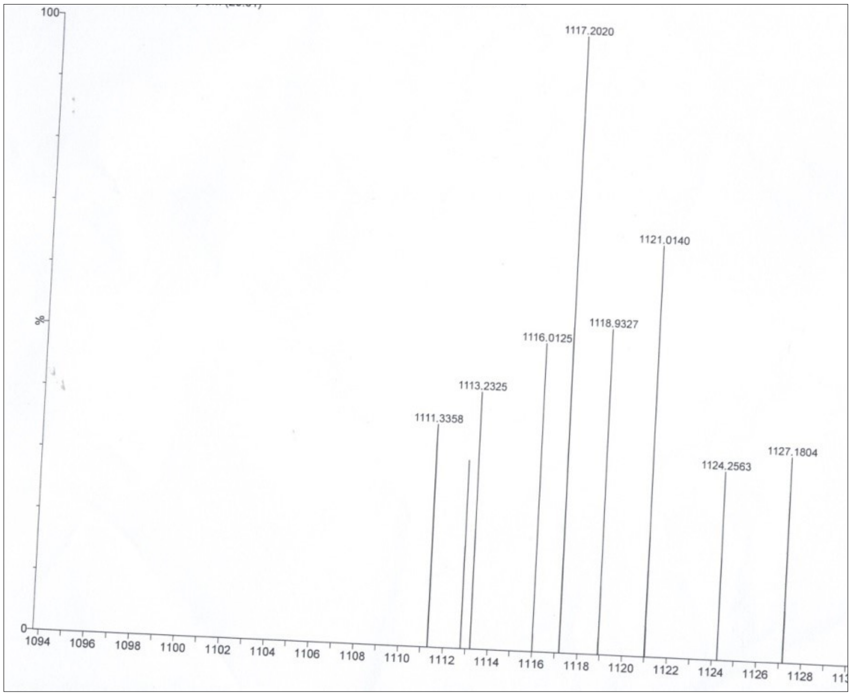


Fig S11 . Mass spectral data of **Eu(DBM)$_3$TBZ-CH$_2$-Ph**

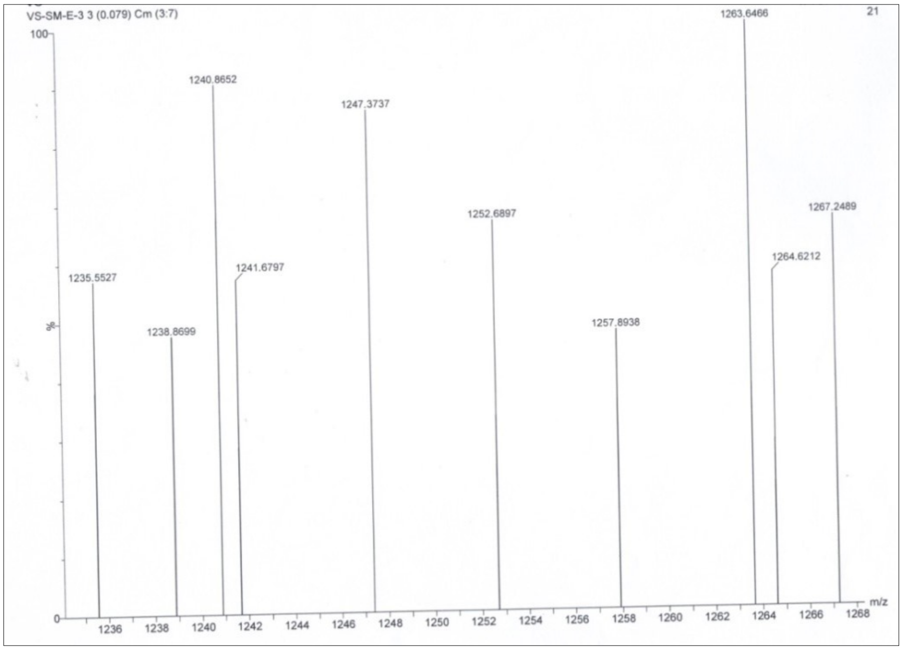


Fig S12 . Mass spectral data of **Eu(TTA)$_3$TBZ-Bu-CBZ**

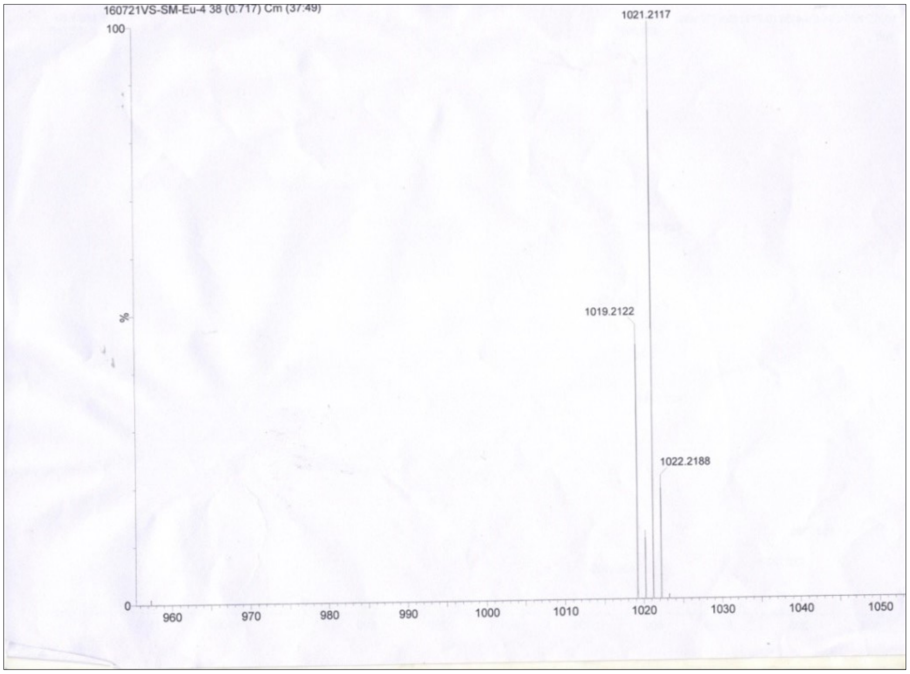


Fig S13 . Mass spectral data of **Eu(DBM)$_3$TBZ-Bu-CBZ**

FT-IR Spectra

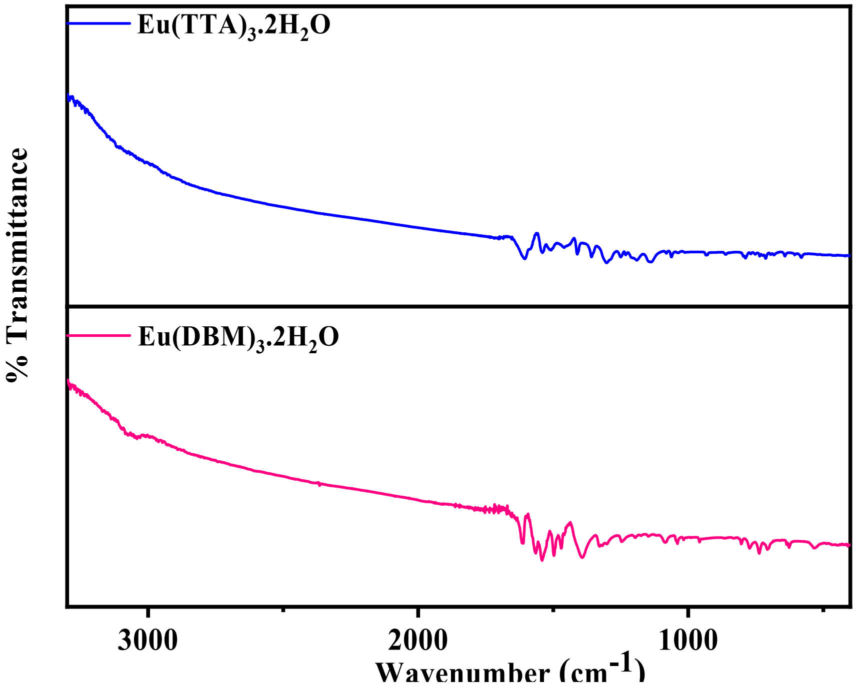


Fig S14. FTIR Spectra of Eu(TTA)$_3$.2H$_2$O and Eu(DBM)$_3$.2H$_2$O.

PL spectra:

Solvatochromism study of ligands:

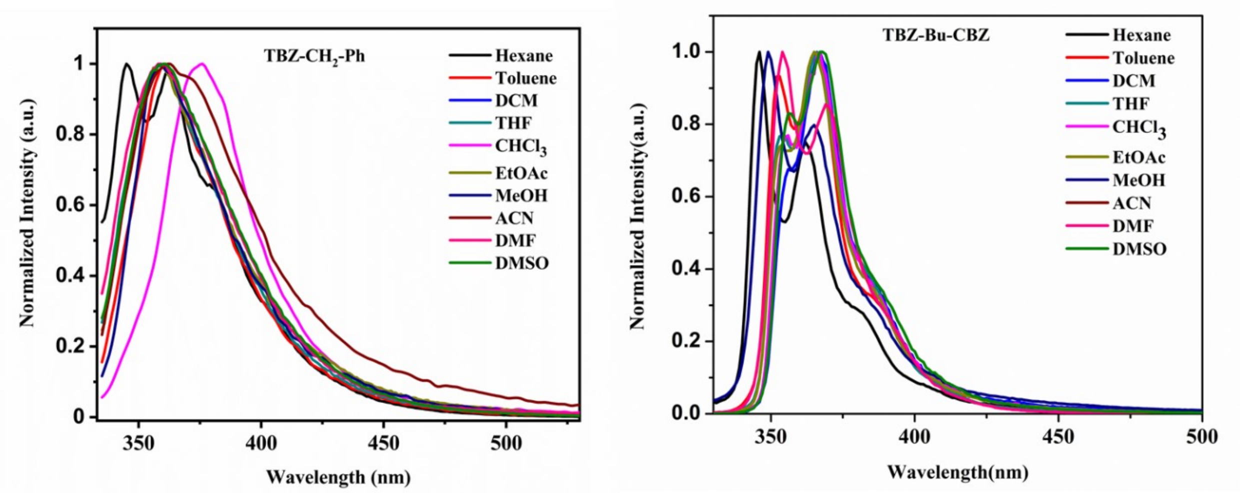


Fig S15. Solvatochromism PL emission spectra of all ligands

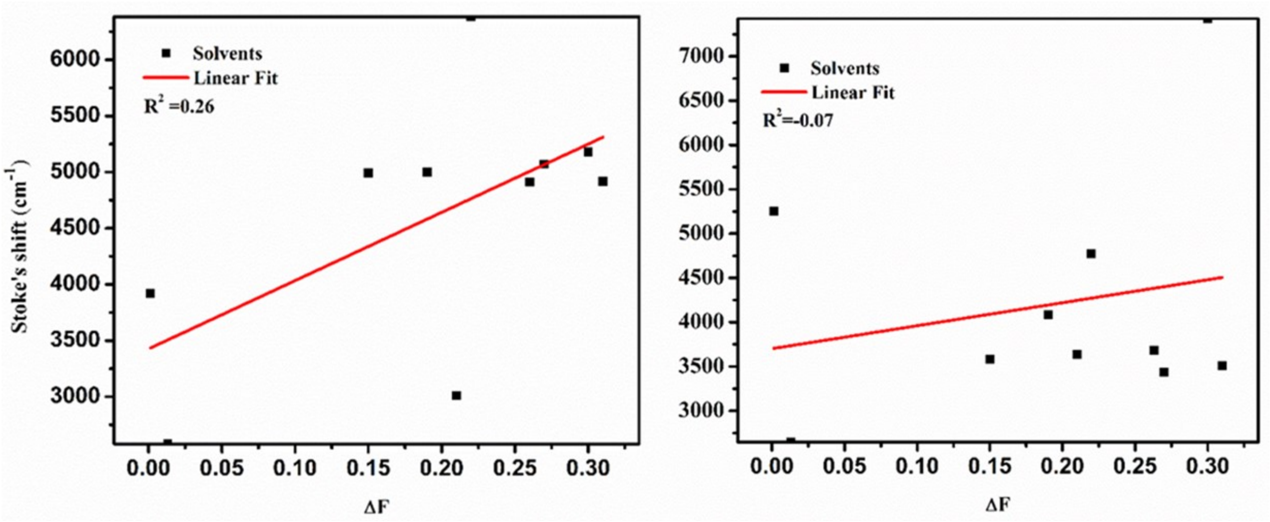


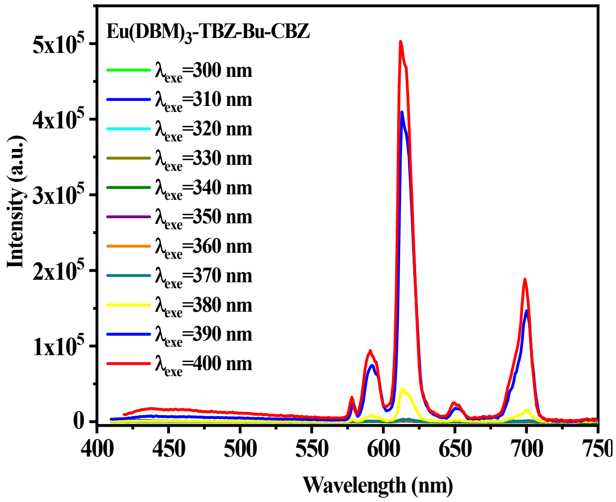
Fig S16 Stokes shift of ligands Δυ versus the Lippert solvent parameter Δf = f(ε) – f(n2) (The numbers refer to the solvents in Table S5). The straight line represents the linear fit to the 10 data points.

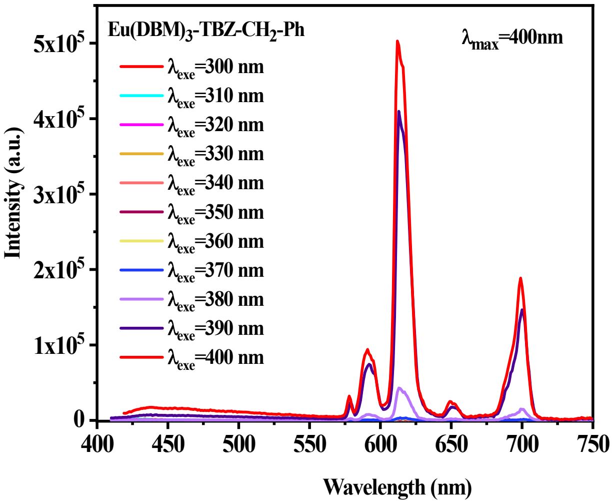
Table ST1: PL spectral data of TBZ-CH$_2$-Ph in various solvents

S.No.	Solvent	λ_{abs} (max) in nm	λ_{em} (max) in nm	Stoke's shift (Δν□) in cm^{-1}
1	**Hexane**	304.29	345.48	3918
2	**Toluene**	300.41	352.63	2578
3	**DCM**	297.30	366.93	6382
4	**THF**	319.62	353.64	3009
5	**CHCl$_3$**	301.74	355.23	4991
6	**EtOAc**	3.01.18	355.23	5000
7	**MeOH**	297.74	348.81	4918
8	**ACN**	300.74	356.23	5180
9	**DMF**	301.74	356.24	5071
10	**DMSO**	301.18	353.36	4912

Table ST2: PL spectral data of TBZ-Bu-CBZ in various solvents

Sl.No.	Solvent	λ_{abs} (max) in nm	λ_{em} (max) in nm	Stoke's shift (Δν□) in cm^{-1}
1	**Hexane**	292.74	345.85	5250
2	**Toluene**	322.62	352.63	2646
3	**DCM**	303	355	4772
4	**THF**	315	355	3632
5	**$CHCl_3$**	315	355	3580
6	**EtOAc**	308	353	4082
7	**MeOH**	294	349	3505
8	**ACN**	281	355	7425
9	**DMF**	317	352	2646
10	**DMSO**	313	354	3682





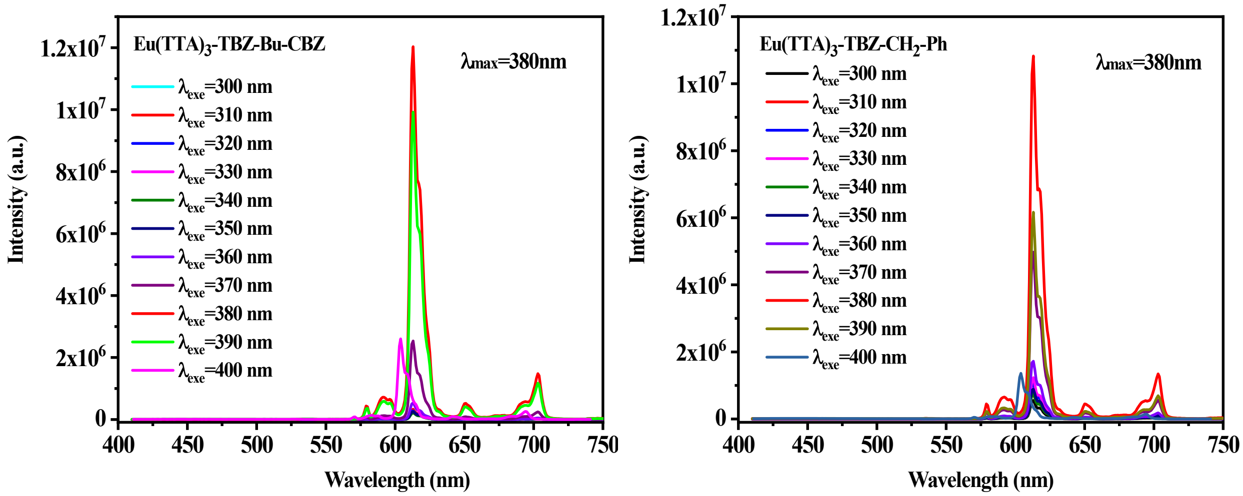


Fig S17. Emission Spectra of all the complexes (Eu-1-4) under excitation range 300 - 400

Table ST3 CIE coordinates and color purity of complexes

Code	**x**	**y**	**Color Purity (%)**
Eu-1	0.6692	0.3294	96.62
Eu-2	0.6692	0.3297	96.66
Eu-3	0.6695	0.3295	96.70
Eu-4	0.6570	0.3298	93.35

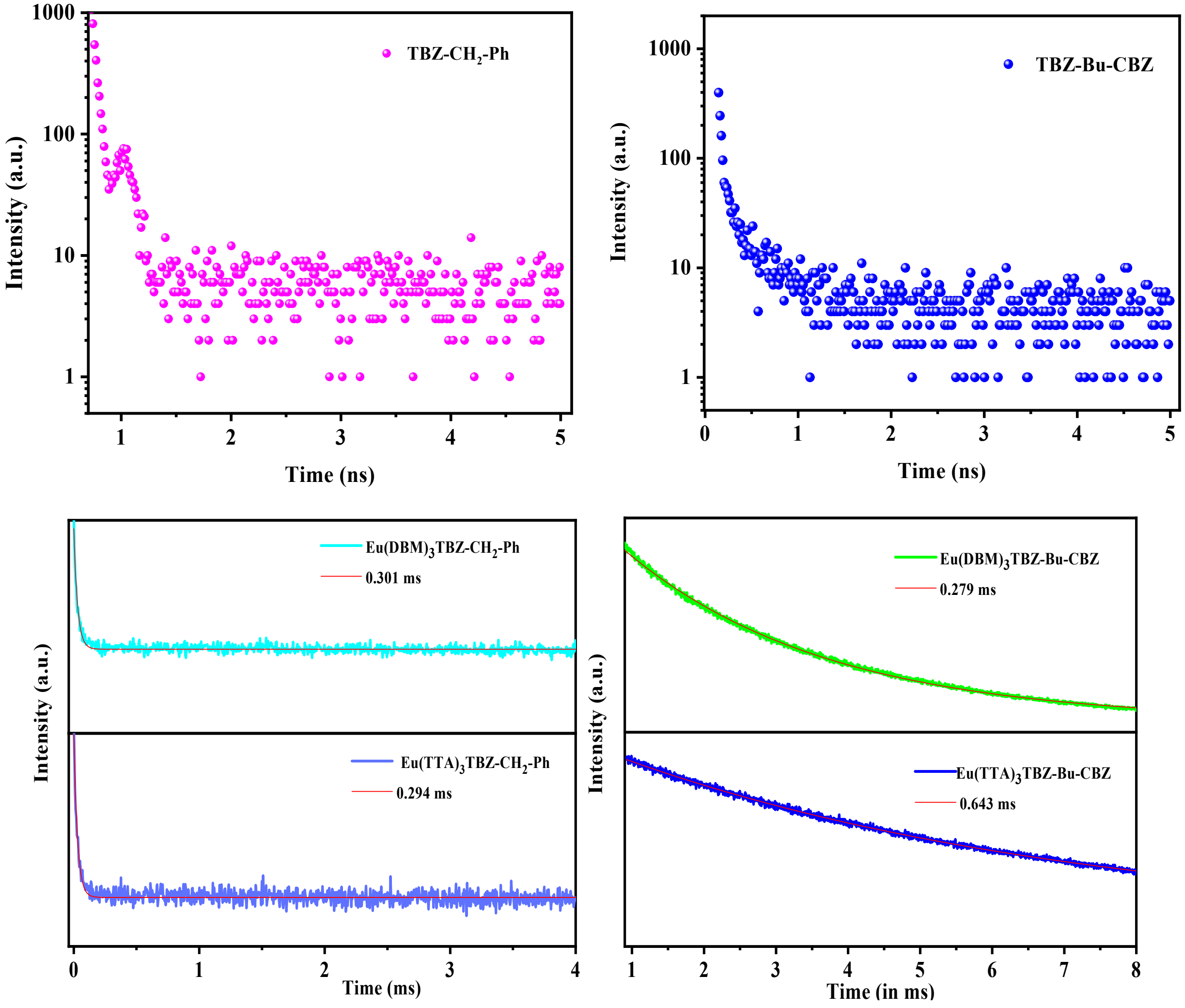


Fig S18 Lifetime decay profile of ligands and therir respective Eu(III) complexes

Table ST4. The calculated CIE from the PL emission data of Eu(III) complexes in different solvents and corresponding asymmetric ratio

SOLVENT	Eu-1		Eu-2		Eu-3		Eu-4	
	(x, y)	AR	(x, y)	AR	(x, y)	AR	(x, y)	AR
Hexane	(0.612, 0.301)	4.68	(0.451, 0.229	4.85	(0.600, 0.294)	4.52	(0.349, 0.173)	4.27
Toluene	(0.666, 0.326)	11.22	(0.644, 0.324)	14.88	(0.590, 0.288)	9.16	(0.631, 0.316)	3.56
DCM	(0.664, 0.330)	10.83	(0.638, 0.334)	8.93	(0.661, 0.330)	6.22	(0.656, 0.328)	6.27
THF	(0.664, 0.324)	8.49	(0.638, 0.318)	4.51	(0.597, 0.290)	7.22	(0.383, 0.195)	4.61
CHCl3	(0.664, 0.329)	3.50	(0.406, 0.362)	3.63	(0.329, 0.205)	3.39	(0.596, 0.312)	3.19
EtOAc	(0.665, 0.326)	4.9	(0.627, 0.312)	4.01	(0.417, 0.224)	2.52	(0.226,0.130)	4.03
MeOH	(0.666, 0.327)	9.98	(0.596, 0.307)	7.84	(0.643, 0.320)	5.39	(0.478, 0.247)	4.47
ACN	(0.666, 0.326)	14.02	(0.658, 0.330)	6.81	(0.630, 0.319)	5.37	(0.504, 0.267)	3.02
DMF	(0.670, 0.327)	13.95	(0.660, 0.327)	5.99	(0.664, 0.326)	6.59	(0.659, 0.324)	4.28
DMSO	(0.668, 0.327)	4.83	(0.656, 0.325)	4.48	(0.650, 0.320)	4.24	(0.649, 0.320)	4.82

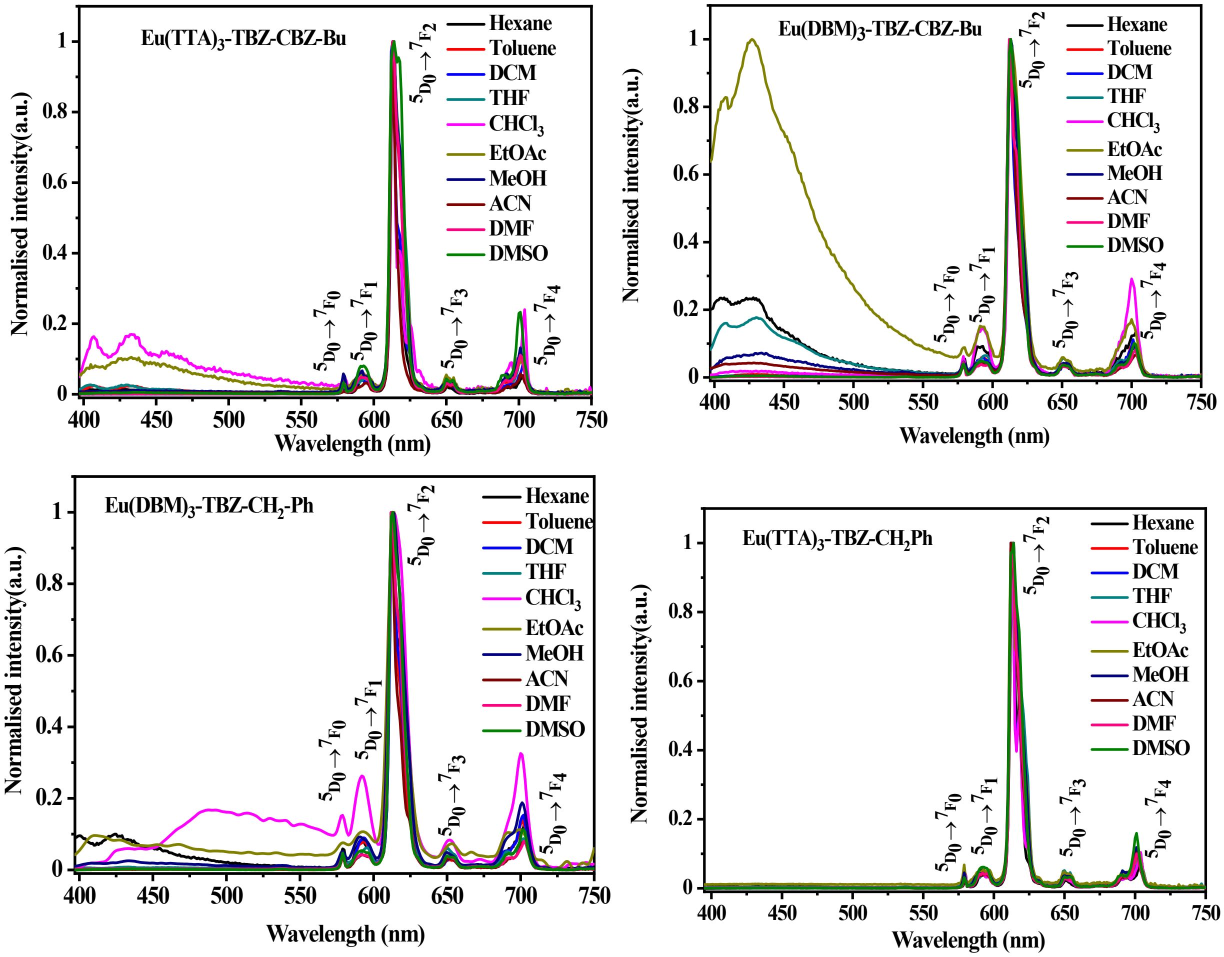


Fig S19 Solvatochromism study of complexes

Table ST5: Cyclic voltammetry study of ligands and complexes

Sl. No.	Compound name	Voltage oxi$_{onset}$[V] (E$_{HOMO}$ [eV])	Voltage red$_{onset}$[V] (E$_{HOMO}$ [eV])	Energy gap [eV]
1	**TBZ-CH$_2$-Ph**	1.71 (-5.875)	-1.81 (-2.69)	3.12
2	**CBZ-Bu-TBZ**	1.49 (-5.89)	-1.72 (-2.68)	3.21
3	**Eu-1**	1.32 (-5.72)	-1.85 (-2.55)	3.0
4	**Eu-2**	1.64 (-6.04)	-1.39 (-3.01)	3.03
5	**Eu-3**	1.56 (-5.96)	-1.34 (-3.06)	2.9
6	**Eu-4**	1.39 (-5.79)	-1.46 (-2.94)	2.85

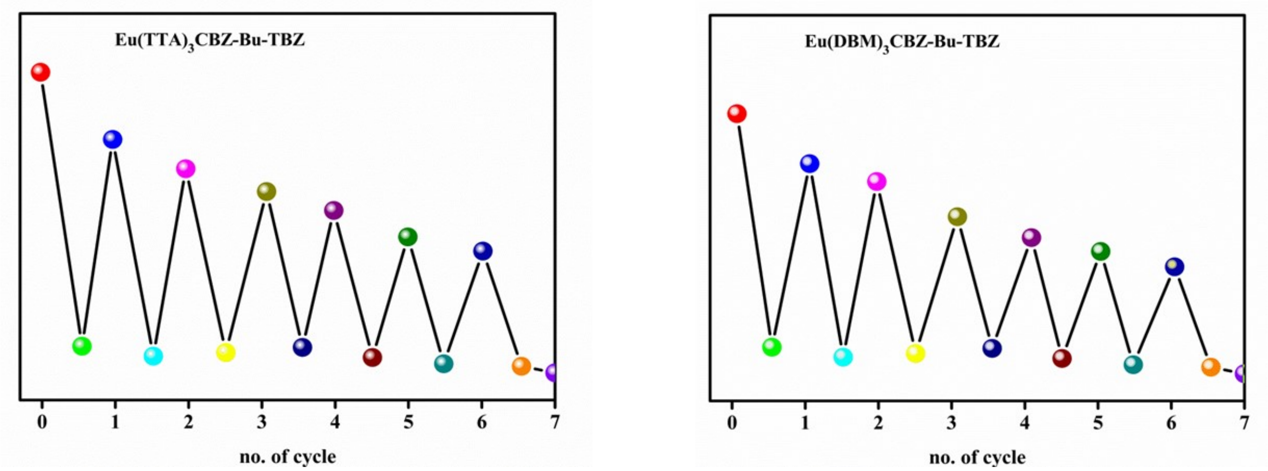


Fig S20 The reversible cycle for luminance switches are shown in

Judd-Ofelt (J –O) analysis:

The Judd-Ofelt parameters investigation of the emission spectrum is a potent tool for calculating the parity forbidden electric-dipole radiative transition rates between the different levels of the lanthanide ions. To study the chemical environment impact on the luminescent characteristics of the Eu3+ ions, it is probable to analyze the Ω_λ (λ =2, 4) parameters from the emission spectra by the standard calculation method. The experimental intensity parameters were calculated for the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions by maintaining $^5D_0 \rightarrow {}^7F_1$ transition as a reference. The following equation explains the relationship between the radiative emission rate and integrated emission intensity. [1]

$$\frac{A_{0-2,4}}{A_{0-1}} = \frac{I_{0-2,4}\, h\vartheta_{0-1}}{I_{0-1}\, h\vartheta_{0-2,4}} \qquad (1)$$

Where I_{0-J} is the area under the spectral curve and $h\upsilon_{0-J}$ is the energy related to the $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 4) transition of Eu^{3+}. The magnetic dipole radiative ($^5D_0 \rightarrow {}^7F_2$) transition rate A_{0-1} was considered as $50 s^{-1}$. The above relation was given the probability of the electric dipole transition. The radiative transition probability of forced electric dipole transitions ($^5D_0 \rightarrow {}^7F_2$) as a function of Judd–Ofelt intensity parameter is expressed as:

$$A = \frac{64\pi^4(\vartheta_{0-2,4})^3}{3hc^3} e^2 \sum_{\lambda=2,4} \chi \; \Omega_\lambda \; |\langle {}^5\boldsymbol{D_0} \parallel \mathbf{U}^{(\lambda)} \parallel {}^7\boldsymbol{F_{2,4}} \rangle|^2 \; \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where χ is the Lorentz local field correction factor which is a function of refractive index n = 2.02 of the host and is given by the relation $\chi = n\,(n^2 + 2)^2/9$. $|\langle {}^5\boldsymbol{D_0} \parallel \mathbf{U}^{(\lambda)} \parallel {}^7\boldsymbol{F_2} \rangle|^2$ is the square reduced matrix elements, independent of the chemical environment of the Eu^{3+} ion. The values of non-zero square reduced matrix $\mathbf{U}^{(2)} = 0.0032$ for $^5D_0 \rightarrow {}^7F_2$ transition and $\mathbf{U}^{(4)} = 0.0023$ for $^5D_0 \rightarrow {}^7F_4$ transition were taken for the present calculations. The Ω_2 parameter is more sensitive towards symmetry and angular part in spherical harmonics and Ω_4 is more sensible to the distance between ligand and metal ion. Inclusion of chemical bond overlap polarizability (α_{OP}) in dynamic coupling (DC) mechanism helps to quantify covalency of Eu(III) - ligand bond. α_{OP} contribution to DC mechanism is 1% for Ω_2 and 2-8% for Ω_4. Therefore, Ω_4 parameter is a better probe to measure the covalency in Eu(III) - ligating atom bond than that of Ω_2 intensity parameter

Phosphorescence spectra in 77k

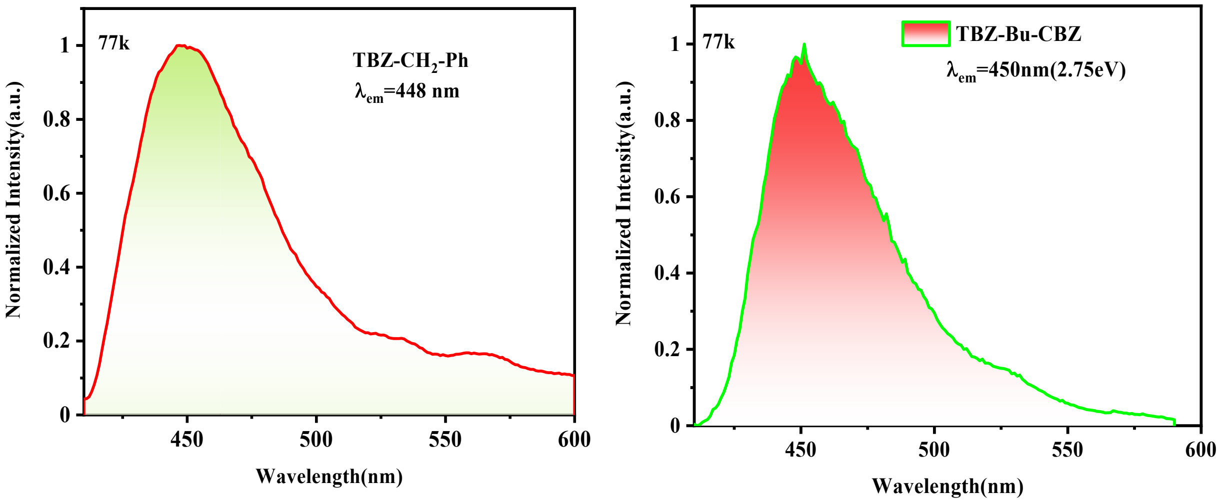


Fig S21 Phosphorescence emission spectra of ligands in 77k.

Cytotoxicity assay

The MTT assay was performed on the human lung cancer cell (A549) line to determine the cytotoxic potential of Eu- complexes. Initially, the A549 cells at the concentration of (10^6 cells/well) were seeded into 96 well plates and kept for starvation for the period of 1 hr at 37C. Various concentration of (100, 50, 25, 12, 6 µm/100µl) Eu-1, Eu-2, Eu-3, Eu-4 complexes and as well as two ligands alone were treated with cells for 24 hr at 37°C. After the incubation period, the cells were treated with 0.5mg/ml MTT with plain media and incubated at 37C for 4 hr. Then, the solution was removed and mixed with 200 µl DMSO to dissolve the formazan crystal. The optical density was read at 570 nm using microplate reader (Multiskan SkyHigh Microplate Spectrophotometer).

MTT assay

A549 Cell line

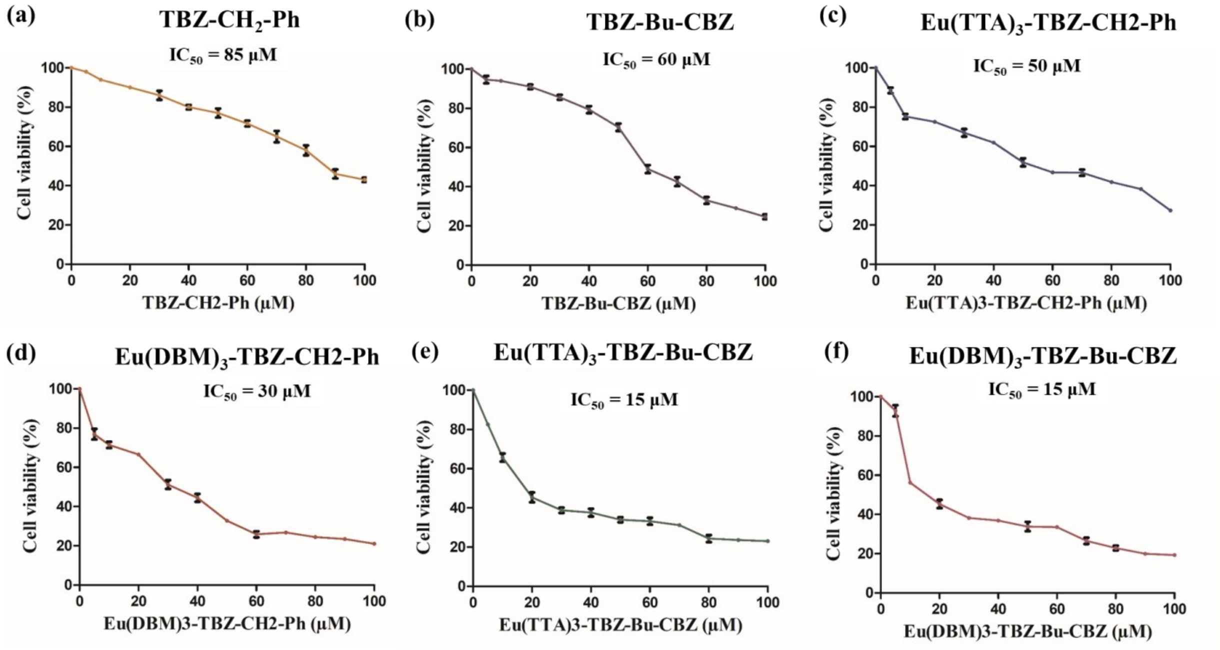


Fig S22(a). Cytotoxicity study of ligands and complexes in A549 with I$_{C50}$ values

HacaT Cell line

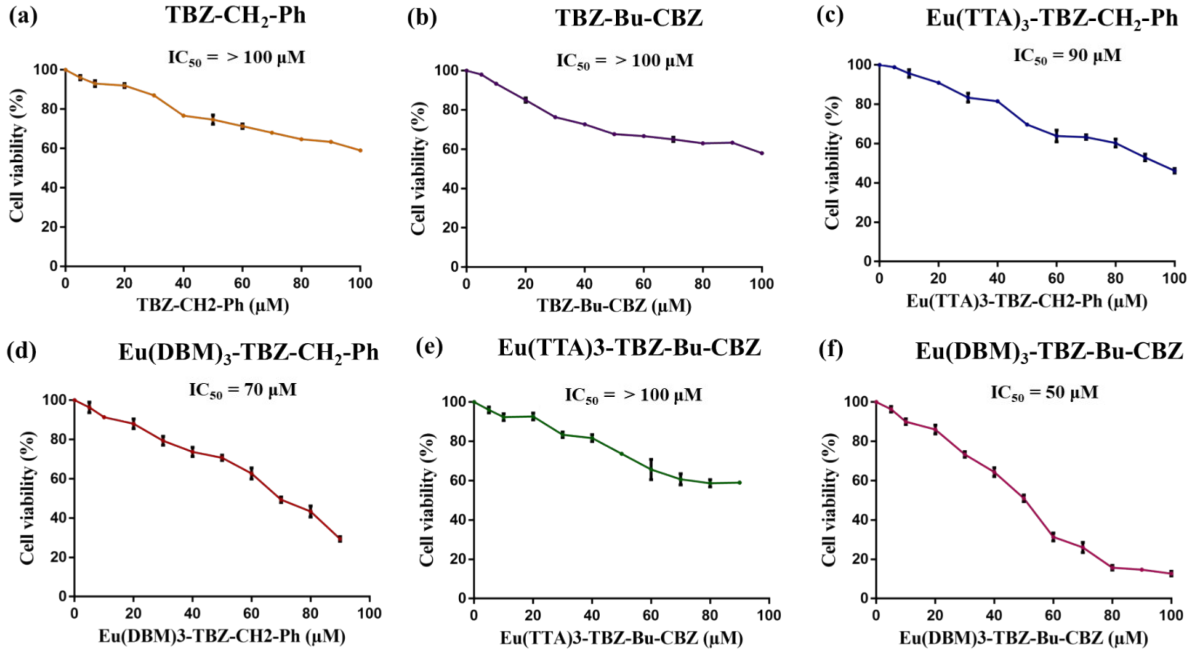


Fig S22(b). Cytotoxicity study of ligands and complexes in A549 with I$_{C50}$ values

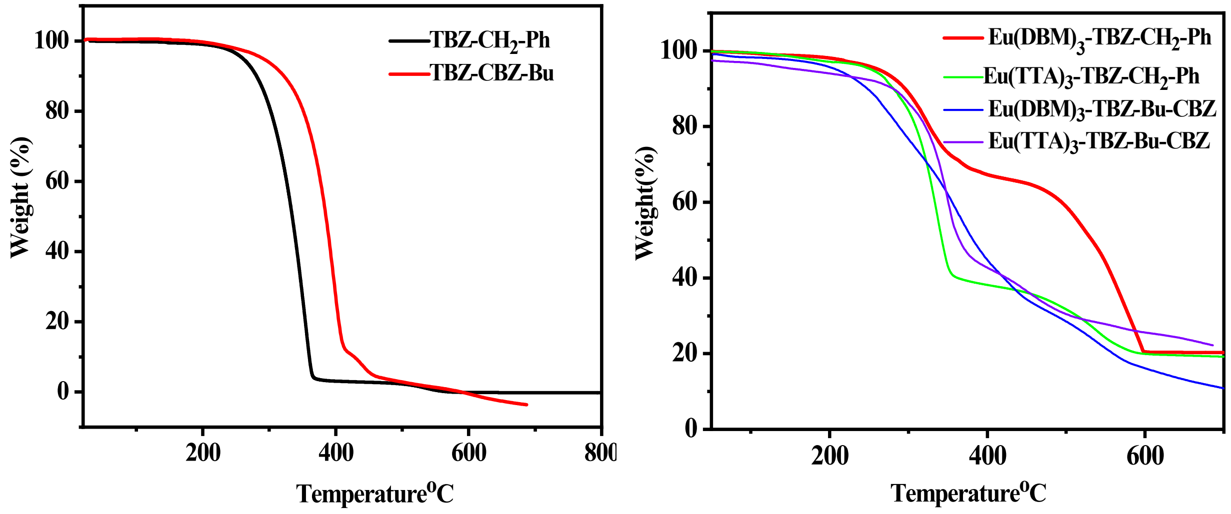


Fig S23. Thermograms of ligands and complexes

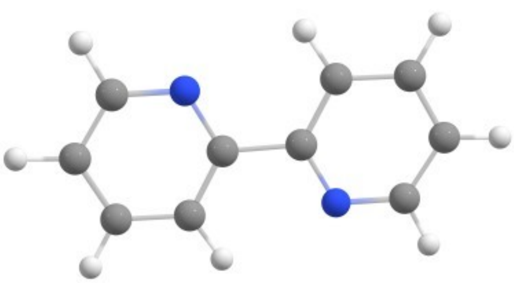
Table ST6(a).The input and output of on-of –of switches mechanisim.

Input-1 HCl Vapors	**Input-2 Et_3N Vapors**	**Output Ligands Emission**	**Output Eu(III) Emission**
0	**0**	**0**	**1**
1	**0**	**1**	**0**
0	**1**	**0**	**1**
1	**1**	**0**	**1**

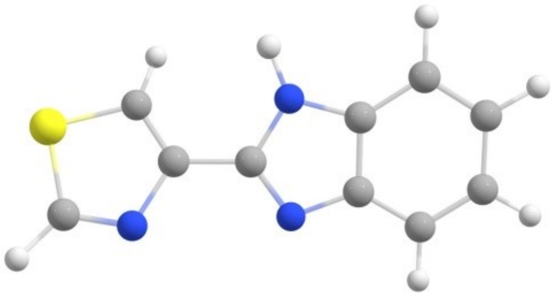
Table ST6(b). The Eu-complex response time for acid-base interaction

Complexes	**Response Time For HCl**	**Response Time For base**
Eu-3	**53 sec**	**41 sec**
Eu-4	**48 sec**	**35 sec**

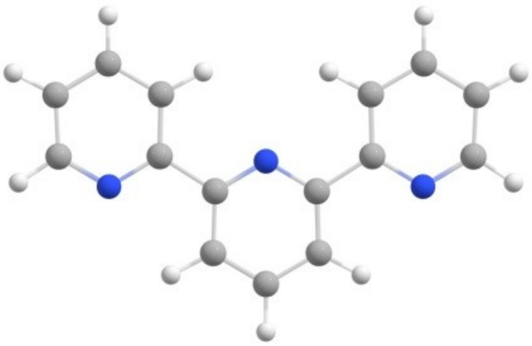
DFT Study:



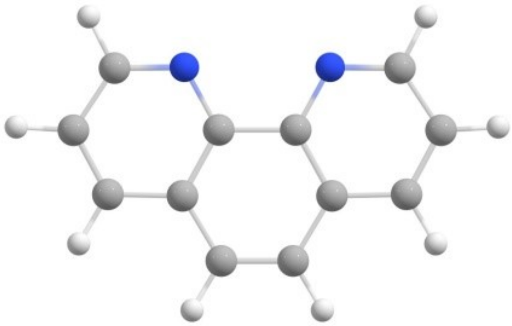
Bipyridyl
T_1 = 25164 cm^{-1}
S_1 = 34037 cm^{-1}



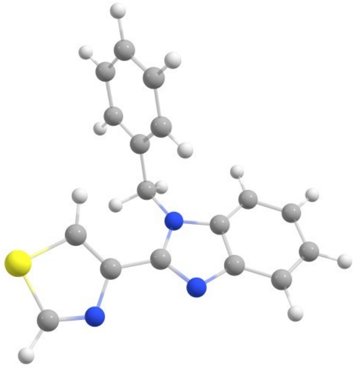
TBZ
T_1 = 23229 cm^{-1}
S_1 = 33880 cm^{-1}



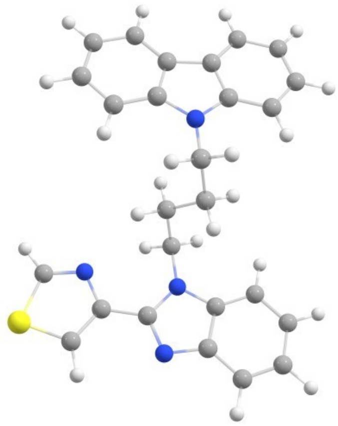
Terpyridyl
T_1 = 23713 cm^{-1}
S_1 = 33909 cm^{-1}



Phen
T_1 = 21777 cm^{-1}
S_1 = 29197 cm^{-1}



TBZ-CH2-Ph



Tbz-Bu-CBZ

Fig S24. Optimized Structures of presently ligands

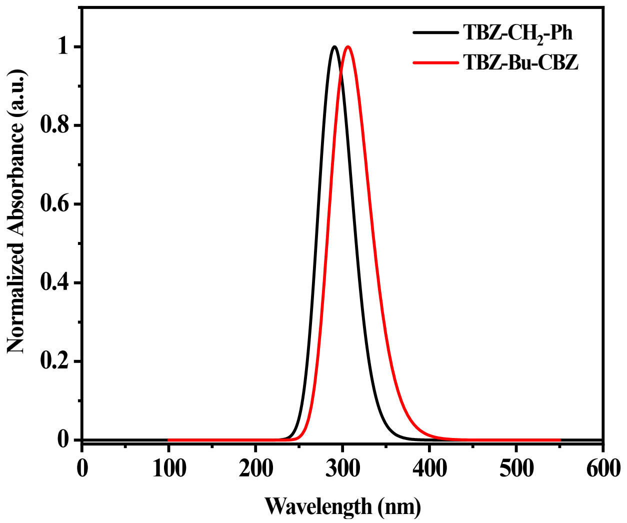


Fig S25. UV obtained from theoretical analysis by DFT study.

Table ST7 Singlet triplet energy values, vertical transition, and oscillatory strength of ligands obtained from DFT

Ligands	State	Energy (eV)	λmax (nm)	*f*	Configuration
TBZ-CH2-Ph Triplet	Gas	3.04 (T_1)	407.00	0	HOMO-1→LUMO+2(10.05%) HOMO→LUMO (61.8)
		3.49 (T_2)	339.75	0	HOMO-1→LUMO (45.01%) HOMO→LUMO+25(15.70%) HOMO→LUMO+2(27.81%)
		3.76 (T_3)	329.18	0	HOMO-4→LUMO+1 (24.53%) HOMO-3→LUMO+25(24.53%) HOMO-3→LUMO+3(31.94%) HOMO-2→LUMO+1(40.74%) HOMO-2→LUMO+3(28.39%)
Singlet	Gas	4.25 (S_1)	291.60	0.2718	HOMO→LUMO (69.05%)
		4.32 (S_2)	286.71	0.0367	HOMO-1→LUMO (69.01%) HOMO→LUMO+5 (11.13%)
		3.1722 (S_3)	262.57	0.0033	HOMO→LUMO+1 (70.09%)

Tbz-Bu-CBZ Triplet	Gas	2.79 (T$_1$)	442.91	0	HOMO-6→LUMO(19.79%) HOMO-1→LUMO (64.53%)
		3.17 (T$_2$)	390.72	0	HOMO-7→LUMO+8 (12.72%) HOMO-4→LUMO+1 (15.26%) HOMO-4→LUMO+6 (10.45%) HOMO-2→LUMO+1 (61.41%) HOMO→LUMO+4 (11.74%)
		3.28 (T$_3$)	377	0	HOMO-1→LUMO+1(68.51%)
Singlet	Gas	3.679 (S$_1$)	336.99	0.0010	HOMO→LUMO (70.67%)
		3.95 (S$_2$)	313.70	0.00382	HOMO-2→LUMO+3(14.19%) HOMO-1→LUMO+1(48.81%)
		(S$_3$)	308.30	0.1827	HOMO-1→LUMO (67.83%)

XYZ Coordinates

TBZ-CH$_2$-Ph

C	2.061756000	-0.243529000	-0.322255000
C	2.324574000	-1.487352000	0.293125000
C	3.638789000	-1.839066000	0.620467000
C	4.650348000	-0.939104000	0.316427000
C	4.371428000	0.295250000	-0.300295000
C	3.072978000	0.667422000	-0.629412000
C	0.205259000	-1.420540000	-0.010207000
H	3.843055000	-2.791994000	1.093219000
H	5.677783000	-1.186558000	0.557591000
H	5.187691000	0.974152000	-0.519065000
H	2.865550000	1.626310000	-1.089731000

C	-1.216804000	-1.782921000	-0.005702000
C	-0.017651000	0.806372000	-1.273257000
H	-0.885355000	0.336021000	-1.740781000
H	0.641571000	1.120715000	-2.088803000
N	0.688677000	-0.211305000	-0.512099000
N	1.150579000	-2.189891000	0.471849000
C	-0.461605000	2.029382000	-0.482182000
C	-0.151923000	2.203419000	0.866820000
C	-1.206144000	3.016136000	-1.138847000
C	-0.579156000	3.344380000	1.547533000
H	0.426717000	1.450359000	1.388069000
C	-1.631682000	4.153389000	-0.460741000
H	-1.455266000	2.892324000	-2.188728000
C	-1.318525000	4.321107000	0.888176000
H	-2.208194000	4.908387000	-0.983422000
H	-1.649313000	5.206780000	1.418387000
N	-1.562899000	-3.110453000	-0.169939000
C	-2.273966000	-0.930796000	0.194236000
C	-2.842474000	-3.268852000	-0.100181000
S	-3.762209000	-1.804871000	0.176499000
H	-2.259968000	0.129010000	0.392193000
H	-3.345333000	-4.220499000	-0.209259000
H	-0.329295000	3.466288000	2.595452000

TBZ-Bu-CBZ

C	-2.847545000	-1.999518000	-0.380624000
C	-4.093605000	-1.919955000	0.283078000
C	-4.753822000	-3.089346000	0.679977000
C	-4.152421000	-4.306578000	0.398468000
C	-2.913404000	-4.372030000	-0.267768000
C	-2.239825000	-3.224266000	-0.666931000
C	-3.500802000	0.099482000	-0.127860000
H	-5.708496000	-3.027001000	1.188204000
H	-4.641843000	-5.227886000	0.692799000
H	-2.473872000	-5.341183000	-0.474254000
H	-1.286661000	-3.290771000	-1.177055000
C	-3.568973000	1.560035000	-0.192691000
C	-4.640282000	2.266559000	0.293924000
C	-2.866307000	3.592623000	-0.695409000
H	-5.522985000	1.865892000	0.763669000
H	-2.231868000	4.382895000	-1.072744000
C	-1.241380000	-0.283350000	-1.319684000
H	-1.479580000	0.539311000	-1.990332000
H	-0.929624000	-1.134119000	-1.930058000
C	-0.109899000	0.146006000	-0.378304000
H	0.721029000	0.481180000	-1.007965000
H	-0.443886000	1.023118000	0.183306000
C	0.375317000	-0.946140000	0.579372000
H	0.708835000	-1.819590000	0.008853000
H	-0.451715000	-1.285539000	1.211893000

C	1.511383000	-0.493089000	1.509500000
H	1.735228000	-1.287501000	2.228391000
H	1.195401000	0.373832000	2.093946000
N	-2.476537000	-0.687734000	-0.636164000
N	-4.467806000	-0.604520000	0.424352000
N	-2.570491000	2.331820000	-0.750552000
S	-4.400934000	3.953409000	0.049909000
C	3.680486000	-1.057852000	0.352015000
C	3.226322000	1.141833000	0.581965000
C	3.651510000	-2.454079000	0.392002000
C	4.775673000	-0.357429000	-0.215944000
C	2.655478000	2.380149000	0.885550000
C	4.485497000	1.051833000	-0.067736000
C	4.732899000	-3.142146000	-0.148617000
H	2.819288000	-2.992679000	0.828879000
C	5.846943000	-1.074415000	-0.755102000
C	3.360861000	3.526484000	0.535402000
H	1.692800000	2.458107000	1.375539000
C	5.170186000	2.220309000	-0.412106000
C	5.819752000	-2.463479000	-0.719796000
H	4.733126000	-4.226188000	-0.127823000
H	6.691671000	-0.553669000	-1.192589000
C	4.605151000	3.452775000	-0.108423000
H	2.936385000	4.497522000	0.764723000
H	6.133026000	2.165593000	-0.908232000

H	6.645079000	-3.030357000	-1.134503000
H	5.127296000	4.365918000	-0.369228000
N	2.747860000	-0.142127000	0.825290000

References:

1 R. T. Moura, A. N. Carneiro Neto, R. L. Longo and O. L. Malta, *J. Lumin.*, 2016, **170**, 420–430.