White light emissive Europium complex and their versatile applications

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Experimental section:

General information for synthesis:

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All the commercially obtained chemicals were used directly without any further modifications unless stated otherwise. All the reaction was done in the inert atmosphere. Solvent THF is dried and distilled by using Na metal. All the commercially available reagents (Sigma Aldrich and Alfa Aesar) were used without further refinement unless otherwise needed. 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione (TTA, 99.99%), tetrabutylammonium perchlorate (n-Bu_4NClO_4, 99.9%) electrolyte were purchased from Sigma-Aldrich chemicals company. Europium (III) oxide (99.99%), 1, 10-Phenanthroline, aniline and benzaldehyde were purchased from Alfa Aesar and 4-(trifluoromethyl)benzenamine, 3-(trifluoromethyl)benzenamine were purchased from Avra chemicals. Thin layer chromatography with silica gel 60 F_{254} Aluminium plates (Merk) was used to monitor the reactions. Column chromatography was conducted using 100-200 mesh silica to get the pure compound. Diphenylamine (DPA) was purchased from the Sigma-Aldrich.

Measurements:

Nuclear magnetic resonance (^{1}H-, ^{13}C-, ^{19}F NMR) spectra were recorded with an AV 400 Avance-III 400MHz Fourier Transform nuclear magnetic resonance (FT-NMR) Spectrometer Bruker Biospin International, Switzerland, in deuterated chloroform($CDCl_3$) or dimethyl sulfoxide solution (based on the solubility nature). Chemical shifts were estimated relative to the tetramethylsilane (TMS) standard reference. Fourier Transform Infrared (FT-IR) spectra were recorded with a Perkin Elmer, USA/ RX-I FTIR spectrophotometer and elemental analyses were measured by Elementar Analysen Systeme, Germany/Vario EL spectrometer. The mass spectra were recorded by LC–MS (Perkin–Elmer, USA/Flexer SQ 300 M). DSC-TGA (thermal decomposition) was performed by using Netzsch, Germany, STA449C/4/MFC/G.

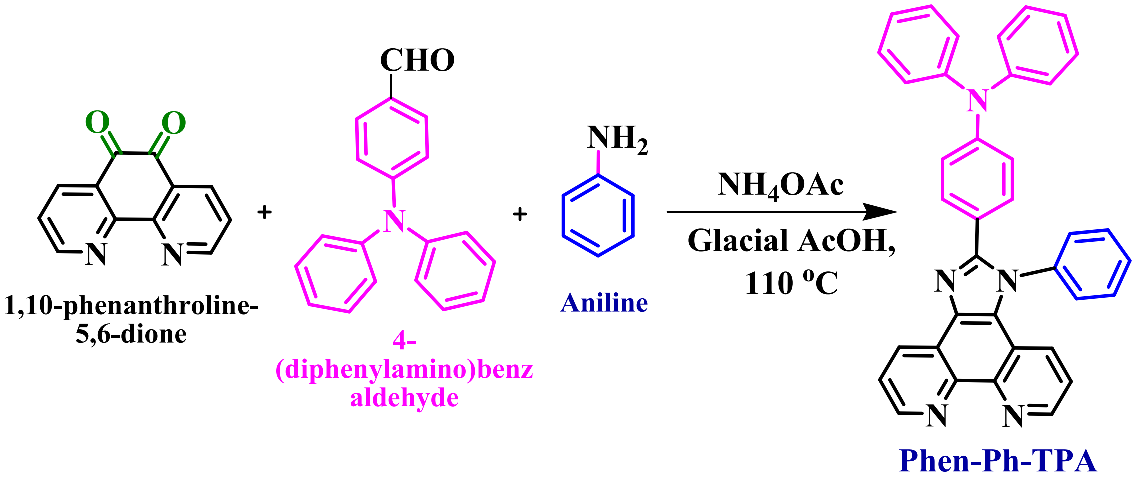
Absorption analysis was done by using the UV-Visible spectrometer (Shimadzu Corporation, Japan or UV-2450 Perkin Elmer, USA/Lamda 25 and Lamda Perkin Elmer) for a solution and solid form diffuse reflectance spectra (DRS). The PL excitation and emission spectrum in both solid and solution phase for all the samples were recorded with a Horiba Jobin Yvon, USA/Fluoromax 4P spectrophotometer with a 150W xenon lamp as an excitation source. Thin films were prepared by a spin coating method using a spin NXG P1A instrument and measured the PL by spectrofluorimetry. The PL quantum yield (PLQY) of the complex in the form of a solution, a thin film (with a different ratio (PMMA Vs Eu-complexes) and solid were measured with Edinburgh spectrofluorometer FS5, integrating sphere S30. A life time of the Eu^{III} complexes and ligands were measured at 298 K with Edinburgh Instruments FLS 980 based on the time correlated single photon counting technology upon the excitation at a suitable wavelength for ligands and complexes, respectively. A pulsed xenon lamp was used as the excitation source and the signals were detected with a photomultiplier. The triplet energy of the ligand was measured with the corresponding Gd-complex at 77 k and liquid nitrogen quartz Dewar was used to record the phosphorescence spectra of the ligand with FLS920 spectrofluorimeter (Edinburgh Instruments Ltd., UK).

Cyclic voltammetry was carried out using AUTOLAB 302N Modular potentiostat at room temperature in N, N-dimethylformamide (DMF) with glass-carbon rod as working, Pt wire as auxiliary and Ag/AgCl wire as reference electrodes. Bu_4NClO_4 (0.1 M) in DMF was used as the supporting electrolyte and scan rate was maintained as 100 mV s^{-1}. All the ligand structures were optimized using density functional theory (DFT) and their respective theoretical UV-Vis spectra were computed using B3LYP/6-31(G) level of theory [2]. The ground state geometry of the ligand structures was confirmed and the ligands were excited vertically to estimate the first excited state using time-dependent DFT (TD-DFT). The same procedure was followed to obtain the triplet excited states from which PL spectra of the compounds were derived. The HOMO and LUMO levels were also been calculated.

Synthesis:

The compounds aldehyde (TPA-CHO) [1,2] and 1,10-phenanthroline-5,6-dione [3], were synthesized by reported literatures. The metal complex tris(thenoyltrifluoroacetone) europium(III) ($Eu(tta)_3(H_2O)_2$) was synthesized by using the well-known method, $EuCl_3$. $6H_2O$ (1 eq) treated with alcoholic solution of TTA (3 eq.) in presence of 1N sodium hydroxide solution (3.1 eq.) to get $Eu(TTA)_3(H_2O)_2$.

- **Synthesis of *N,N-diphenyl-4-(1-phenyl-1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)benzenamine*) *(1l, Phen-Ph-TPA):***



To a stirred solution of 1,10-phenanthroline-5,6-dione (1g, 4.761 mmol, 1 eq) in acetic acid (15 mL), aniline (0.532g, mmol 5.714, 1.2 eq) and TPA-CHO (1.560g, mmol 5.714, 1.2 eq) were added turn wise followed by ammonium acetate (3.66g, mmol 47.61, 10 eq) and the mixture was stirred for 12 hours at 110 °C under nitrogen atmosphere. The reaction was monitored with TLC (MeOH:DCM = 1 : 9). The obtained reaction mixture was then neutralized with ammonium hydroxide solution and extracted with DCM followed by drying with sodium sulphate. It was then concentrated and purified through column chromatography using silica bed (100-200 mesh) with 5% MeOH in DCM as the eluent. The purified product was dissolved in minimal amount of THF and excess amount of hexane was added to it. The solid was allowed to settle down and then the solvent was decanted. The above process was repeated till a fine powder like sediment was obtained (1.50 g compound 1L (58.3 %) solid). ^{1}H-NMR Data (400 MHz, $CDCl_3$): δ (ppm): 9.19 (dd, J= 2 Hz, J= 2 Hz,1H), 9.15 (dd, J= 2 Hz, J= 2 Hz, 1H), 9.04 (dd, J= 1.6 Hz, J= 1.5 Hz, 1H), 7.67 (m, 1H), 7.57 (m, 3H), 7.45 (d, J = 2 Hz, 2H), 7.42 (m, 3H), 7.28 (m, 5H), 7.04 (m, 6H), 6.8 (d, J= 6.8 Hz, 2H). ^{13}C-NMR Data ($CDCl_3$, 100MHz): δ 151.6, 148.4, 148.3, 147.2, 146.5, 144.2, 143.8, 137.7, 135.6, 130.0, 129.8, 129.4, 128.8, 128.3, 127.3, 126.2, 124.7, 123.4, 123.2, 122.9, 122.1, 121.5, 121.1, 119.3. Elemental Analysis: Anal. Calc. for. $C_{37}H_{25}N_5$; C, 82.35; H, 4.67; N, 12.98 %, Found: C, 82.30; H, 4.61; N, 12.99%. EI-MS: m/z exp (calc). 539.63 m/z found 541.33 $[M + H]^+$. FT-IR (KBr, ν in cm^{-1}): 3419, 3055, 3034, 1589, 1525, 1491, 1465, 1442, 1391, 1378, 1313, 1290, 1281, 1191, 1181, 1151, 1120, 1073, 1063, 1031, 975, 933, 900, 858, 838, 831, 812, 799, 782, 760, 744, 698, 670, 638, 618.

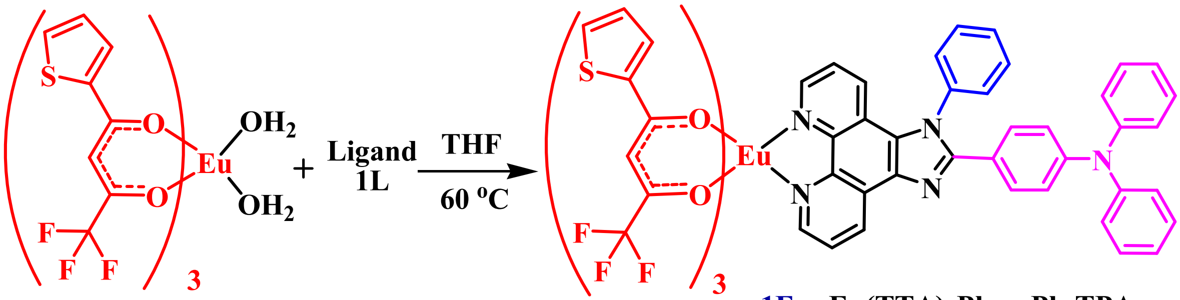
- **Synthesis of** ***(4-(1-(3-(trifluoromethyl)phenyl)-1H imidazo[4,5f][1,10] phenanthroline-2-yl)-n,n-diphenylbenzenamine (2L, Phen-mCF$_3$-TPA):***

The above procedure was followed for synthesis of Phen-mCF_3-TPA. After minimum amount of THF solution and an excess of hexane solvent, the pale yellow color solid was formed. After settled of solid, decant and repeated this process three more times and get 1.54 g compound 2L (55.0 %) solid. ^{1}H-NMR Data (400 MHz, $CDCl_3$): δ (ppm): 9.19 (dd, J = 1.2 Hz, 1H), 9.12 (dd, J = 1.6 Hz, J = 1.2 Hz, 1H), 9.05 (dd, J = 1.6 Hz, J = 1.2 Hz, 1H), 7.95 (d, J = 4 Hz, 1H), 7.79 (m, 4H), 7.39 (dd, J =1.6 Hz, J=1.6 Hz, 1H), 7.30 (m, 7H), 7.08 (m, 6H), 6.97 (d, J = 8.8 Hz, 2H). ^{13}C-NMR Data ($CDCl_3$, 100 MHz): δ (ppm): 151.8, 148.6, 147.4, 146.4, 144.2, 144.7, 138.3, 135.9, 132.7, 132.3, 131.9, 130.6, 130.1, 129.6, 128.9, 126.9, 126.4, 126.4, 125.7, 125.5, 125.4, 124.7, 123.3, 123.2, 123.1, 121.6, 121.3, 121.2, 118.9. Elemental Analysis: Anal. Calc. for. $C_{38}H_{24}F_3N_5$; C, 75.11; H, 3.98; N, 11.53%, Found: C, 75.06; H, 3.95; N, 11.56 %. EI-MS: m/z exp (calc). 607.63, m/z found 608.36 $[M + H]^+$. FT-IR (KBr, ν in cm^{-1}): 3421, 3012, 1592, 1490, 1467, 1451, 1388, 1377, 1327, 1298, 1280, 1176, 1129, 1073, 1031, 897, 842, 807, 756, 736, 721, 693, 618.

- **Synthesis of** ***4-(1-(4-(trifluoromethyl)phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline-2-yl)-n,n-diphenylbenzenamine) (3L, Phen-pCF_3-TPA):***

The above procedure was followed for synthesis of Phen-pCF_3-TPA and get the 1.51 g compound 3L (54.0 %) solid. ^{1}H-NMR Data (400 MHz, $CDCl_3$): δ (ppm): 9.21 (dd, J = 2 Hz, J = 1.6 Hz, 1H), 9.46 (dd, J = 1.6 Hz, J = 2 Hz, 1H), 9.07 (dd, J = 1.6 Hz, J = 1.6 Hz, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.45 (m, 3H), 7.34 (m, 8H), 7.05 (m, 6H), 6.96 (d, J = 2 Hz, 2H). ^{13}C-NMR Data ($CDCl_3$, 100MHz): δ (ppm): 151.7, 149.8, 148.6, 148.6, 147.4, 146.3, 144.3, 143.8, 140.9, 136.0, 130.1, 129.5, 129.0, 128.9, 127.1, 127.1, 127.0, 125.9, 124.8, 123.4, 123.3, 123.1, 122.5, 121.7, 121.3, 121.9, 118.9. Elemental Analysis: Anal. Calc. for. $C_{38}H_{24}F_3N_5$; C, 75.11; H, 3.98; N, 11.53 %, Found: C, 75.05; H, 3.92; N, 11.58 %. EI-MS: m/z exp (calc). 607.63, m/z found 609.35 $[M + H]^+$. FT-IR (KBr, ν in cm^{-1}): 3449, 3319, 3059, 3040, 1591, 1514, 1491, 1468, 1441, 1417, 1379, 1321, 1294, 1271, 1166, 1132, 1120, 1066, 1058, 1028, 977, 881, 836, 807, 757, 738, 618.

Synthesis of Eu(TTA)$_3$Phen-Ph-TPA (1Eu)**:**



Eu (TTA)$_3$.2H$_2$O

1Eu: Eu(TTA)$_3$Phen-Ph-TPA

In a round-bottom flask, a solution of Eu(TTA)$_3$(H$_2$O)$_2$ (0.230 g, 0.27 mmol) in dry THF (5 mL) was taken and to its mixture of Phen-Ph-TPA ligand in THF (5 mL) was added. The mixture was then stirred for 6 hours at 60 °C in nitrogen atmosphere. The obtained product was dissolved in minimum amount of THF and added an excess of hexane to get a solid product (repeated several times) and get pale yellow color solid with 120 mg (50.0 %). Elemental Analysis: Anal. Calc. for. $C_{61}H_{37}EuF_9N_5O_6S_3$; C, 54.07; H, 2.75; N, 5.17; S, 7.10 %; Found: C, 53.98; H, 2.70; N, 5.20; S, 7.05 %. EI-MS: m/z exp (calc). 1355.12, m/z found 1354.62 [M - H]$^+$. FT-IR (KBr, ν in cm^{-1}): 3406, 3088, 2955, 2927, 2870, 1598, 1537, 1509, 1494, 1469, 1447, 1411, 1349, 1306, 1244, 1230, 1187, 1140, 1061, 934, 858, 840, 786, 721, 695, 637.

***Synthesis of Eu(TTA)$_3$Phen-mCF$_3$-TPA (2Eu)*:**

The complex was synthesised in the above mentioned procedure using Phen-mCF$_3$-TPA as the ligand. The obtained product was dissolved in minimum amount of THF and added an excess of hexane to get a solid product (repeated several times) and get pale yellow color solid with 713 mg (60.1 %). Elemental Analysis: Anal. Calc. for. $C_{62}H_{36}EuF_{12}N_5O_6S_3$; C, 52.33; H, 2.55; N, 4.92; S, 6.76 %; Found: C, 52.30; H, 2.51; N, 4.98; S, 6.79 %. EI-MS: m/z exp (calc). 1423.12, m/z found 1444.53 [M + Na]$^+$. FT-IR (KBr, ν in cm^{-1}): 3419, 3092, 1693, 1598, 1537, 1511, 1493, 1445, 1413, 1329, 1303, 1190, 1193, 1066, 931, 837, 808, 786, 720, 698, 640.

***Synthesis of Eu(TTA)$_3$Phen-pCF$_3$-TPA (3Eu)*:**

The complex was synthesised in the above mentioned procedure using Phen-pCF$_3$-TPA as the ligand. The obtained product was dissolved in minimum amount of THF and added an excess of hexane to get a solid product (repeated several times) and get pale yellow color solid with 689 mg (58.0 %). Elemental Analysis: Anal. Calc. for. $C_{62}H_{36}EuF_{12}N_5O_6S_3$; C, 52.33, H, 2.55; N, 4.92; S, 6.76 %; Found: C, 52.29; H, 2.51; N, 4.95; S, 6.79 %. EI-MS: m/z exp (calc). 1423.12, m/z found 1422.51 [M - H]$^+$. FT-IR (KBr, ν in cm^{-1}): 3441, 2926, 1691, 1606, 1536, 1470, 1444, 1411, 1322, 1307, 1248, 1230, 1193, 1138, 1064, 1402, 983, 957, 935, 861, 839, 787, 758, 735, 721, 690, 676, 639.

NMR SPECTRA of Ligands:

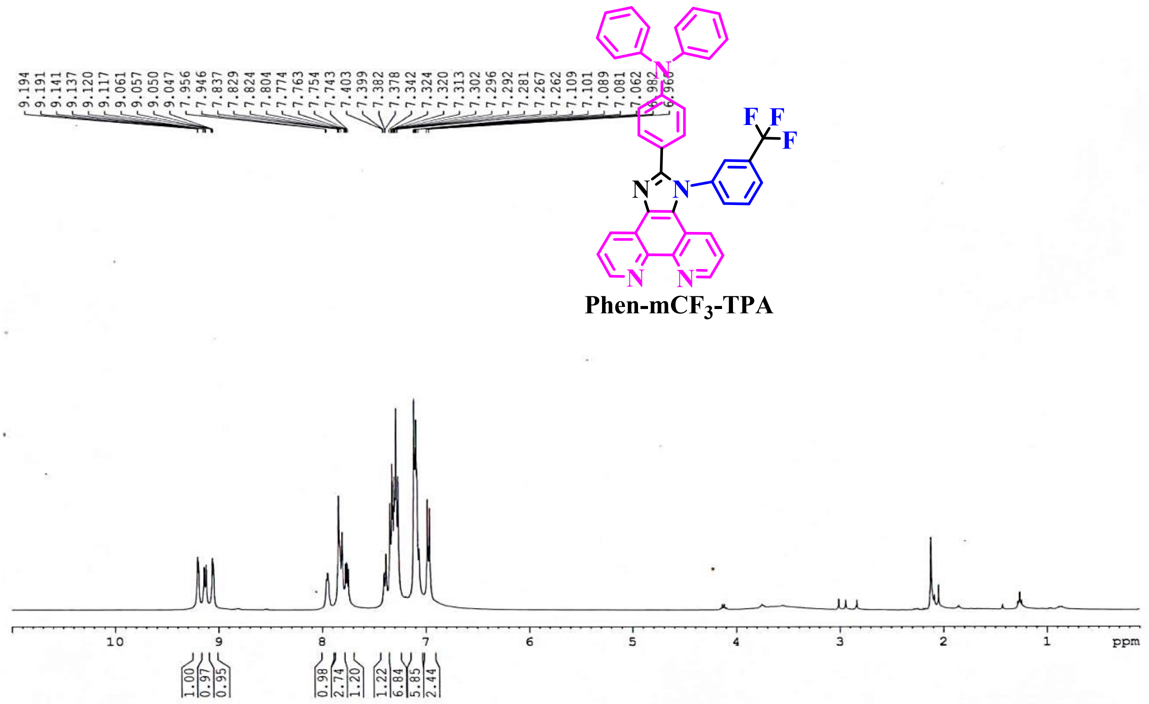


Figure S1. The ^{1}H-NMR spectra of the ligand, Phen-mCF$_3$-TPA.

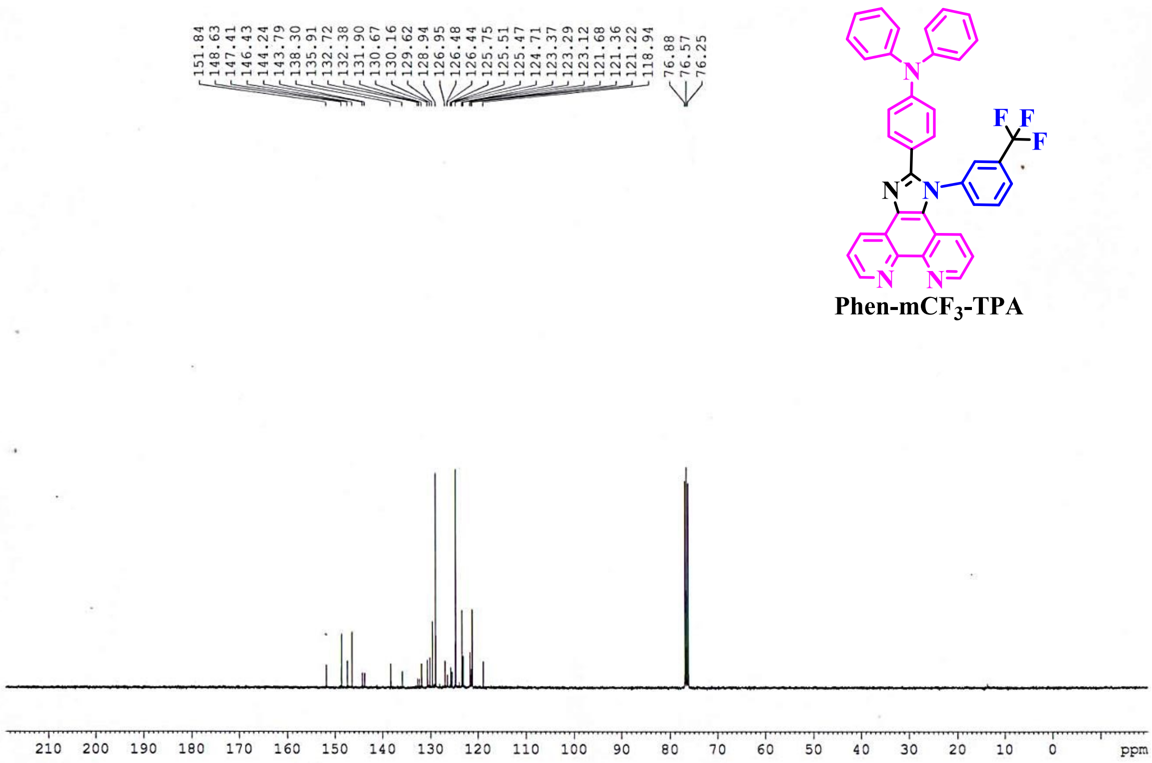


Figure S2. The ^{13}C-NMR spectra of the ligand, Phen-mCF$_3$-TPA.

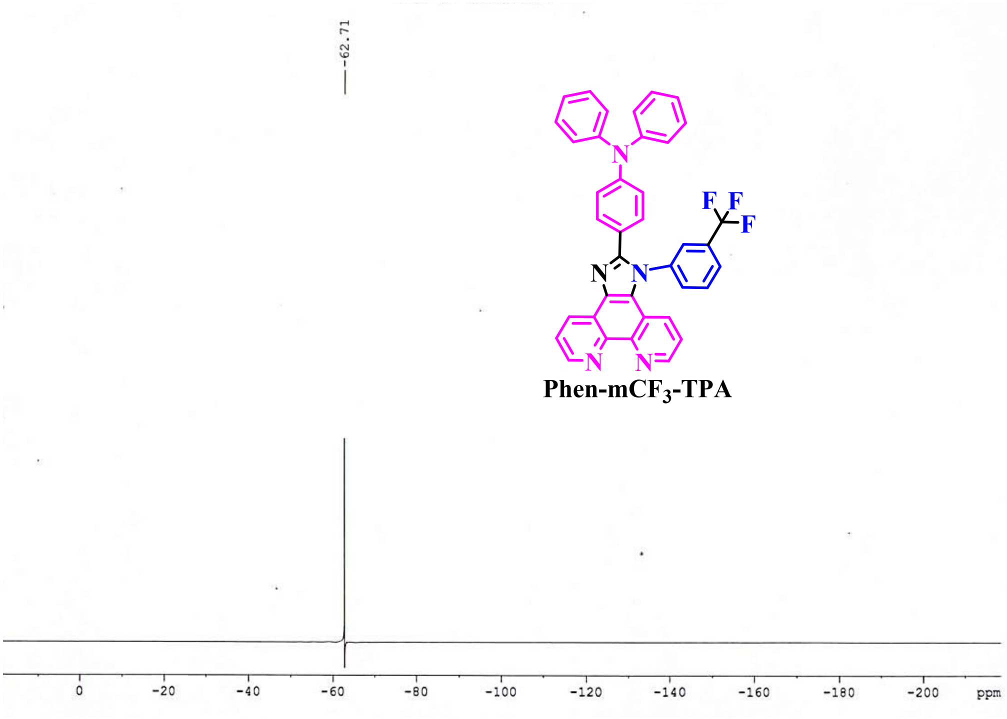


Figure S3. The ^{19}F-NMR spectra of the ligand, Phen-mCF$_3$-TPA.

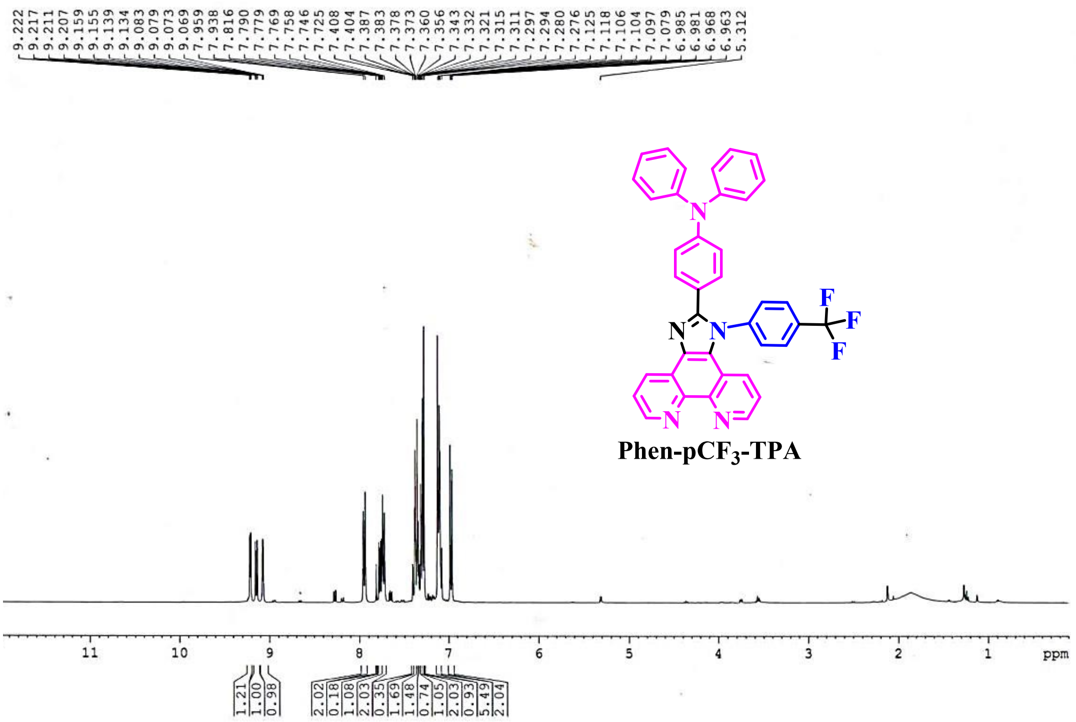


Figure S4. The ^{1}H-NMR spectra of the ligand, Phen-pCF$_3$-TPA.

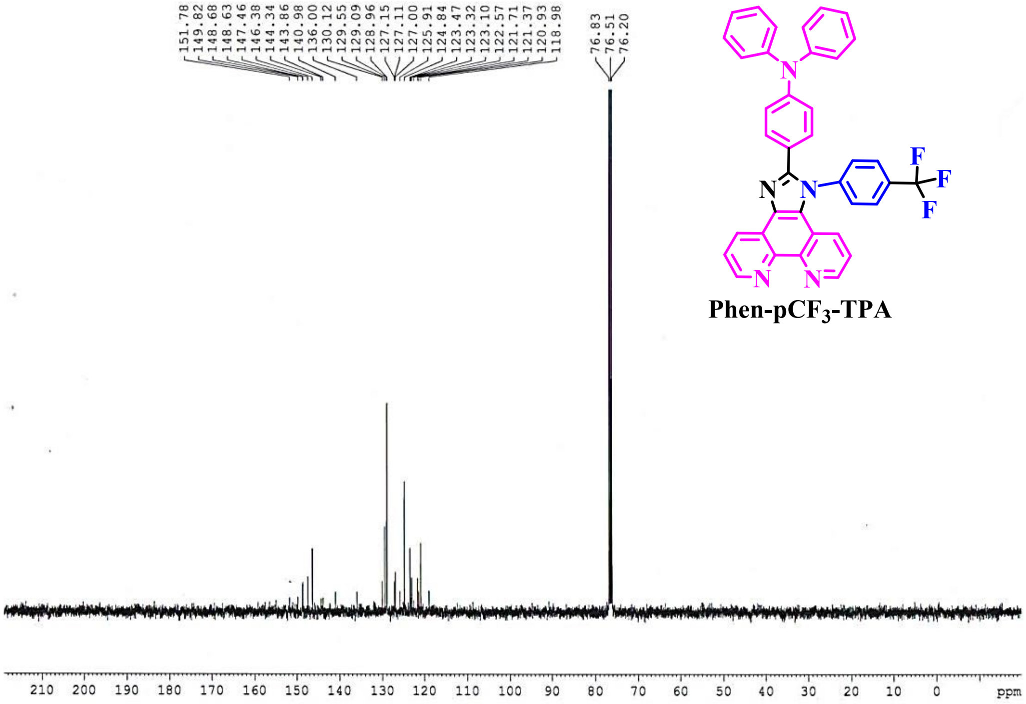


Figure S5. The ^{13}C-NMR spectra of the ligand, Phen-pCF_3-TPA.

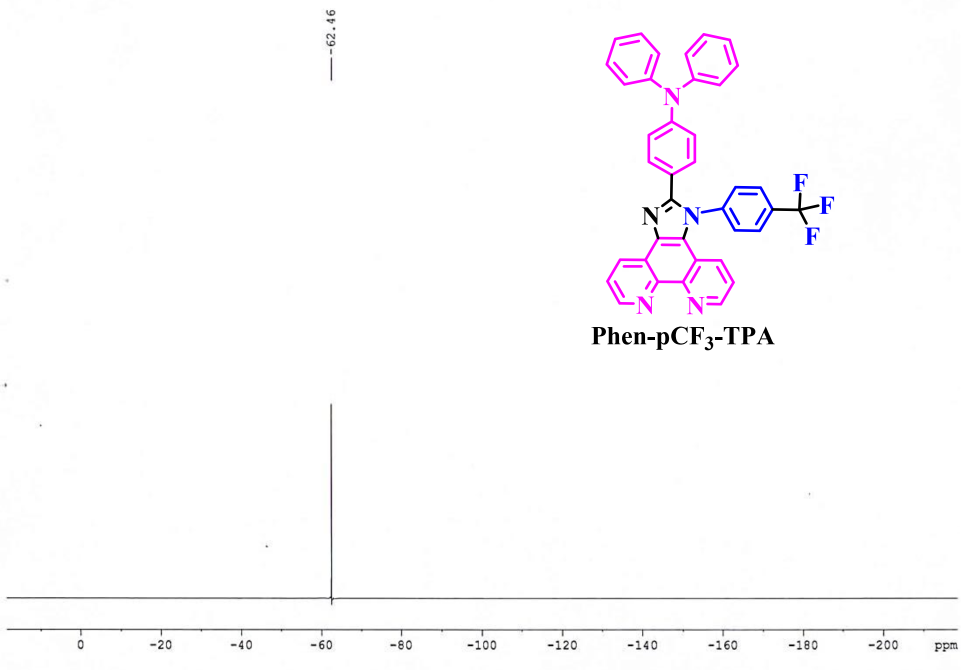


Figure S6. The ^{19}F-NMR spectra of the ligand, Phen-pCF$_3$-TPA.

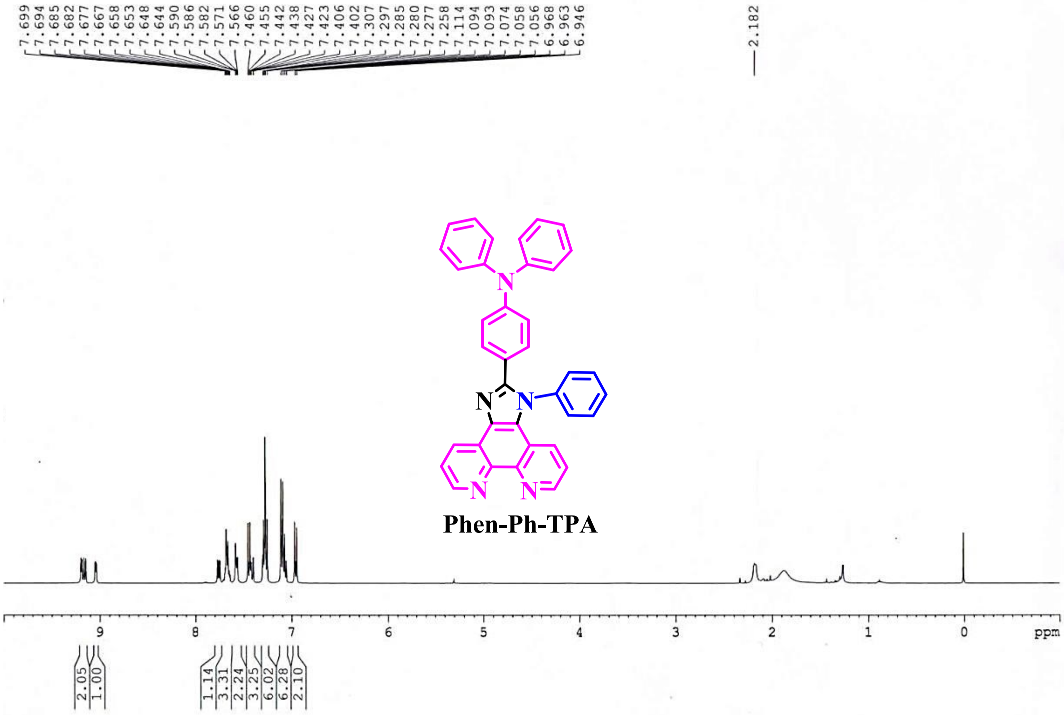


Figure S7. The ^{1}H-NMR spectra of the ligand, Phen-Ph-TPA.

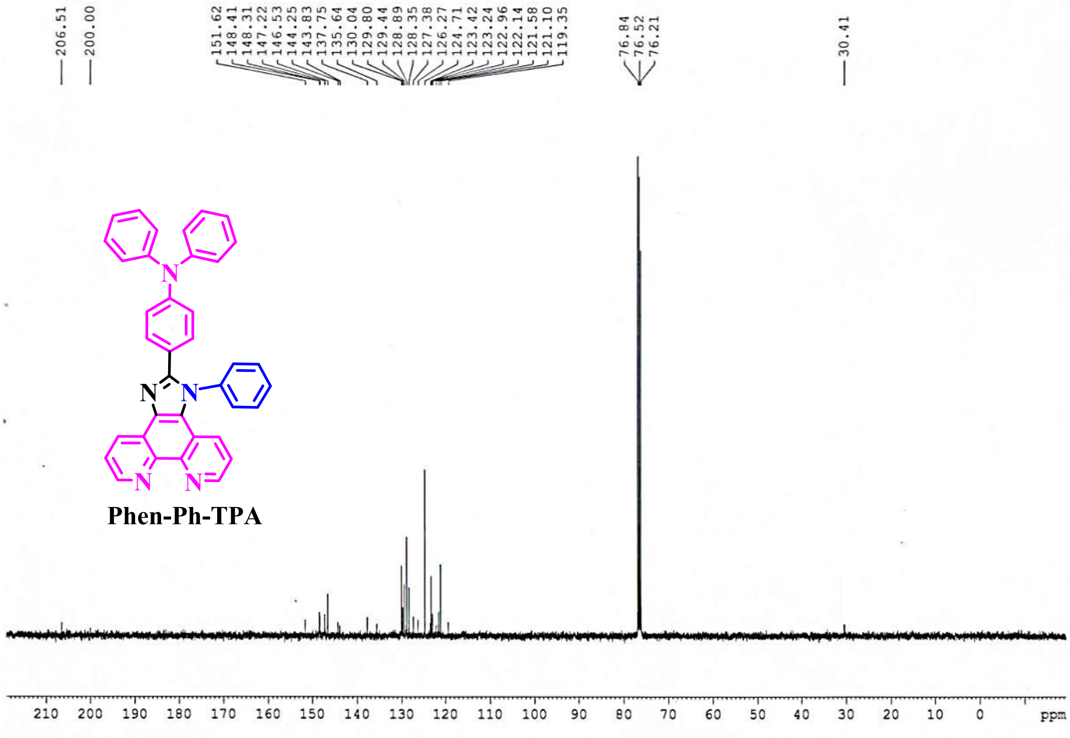


Figure S8. The ^{13}C-NMR spectra of the ligand, Phen-Ph-TPA.

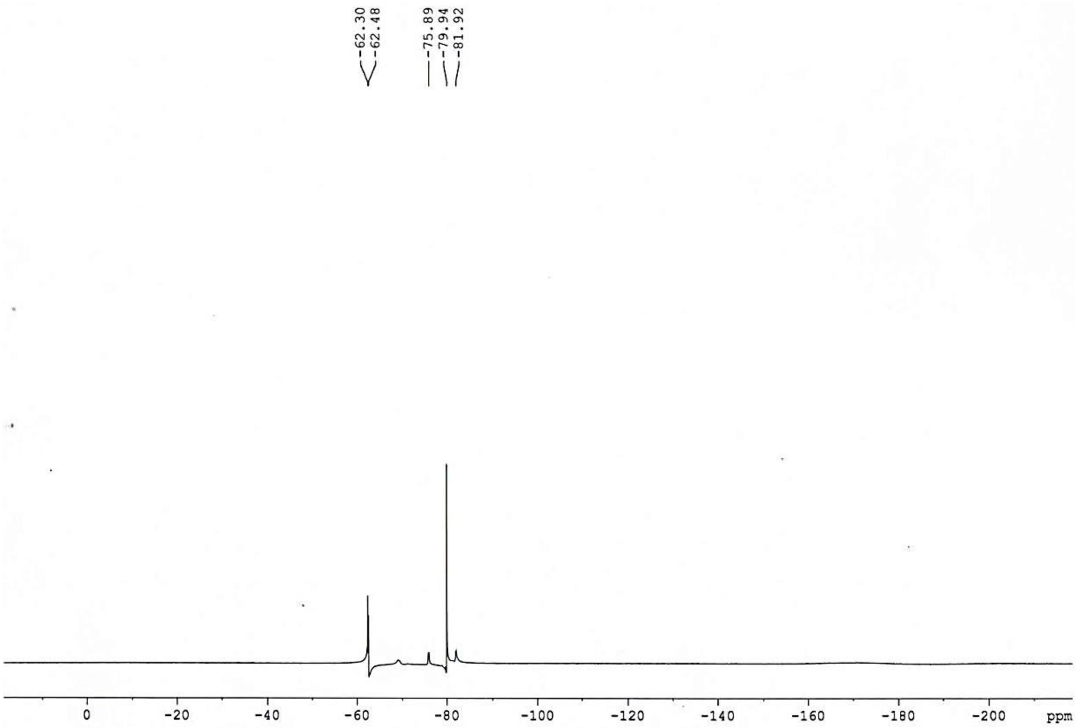


Figure S9. The ^{19}F-NMR spectra of the Eu-complex, Eu(TTA)$_3$Phen-mCF$_3$-TPA.

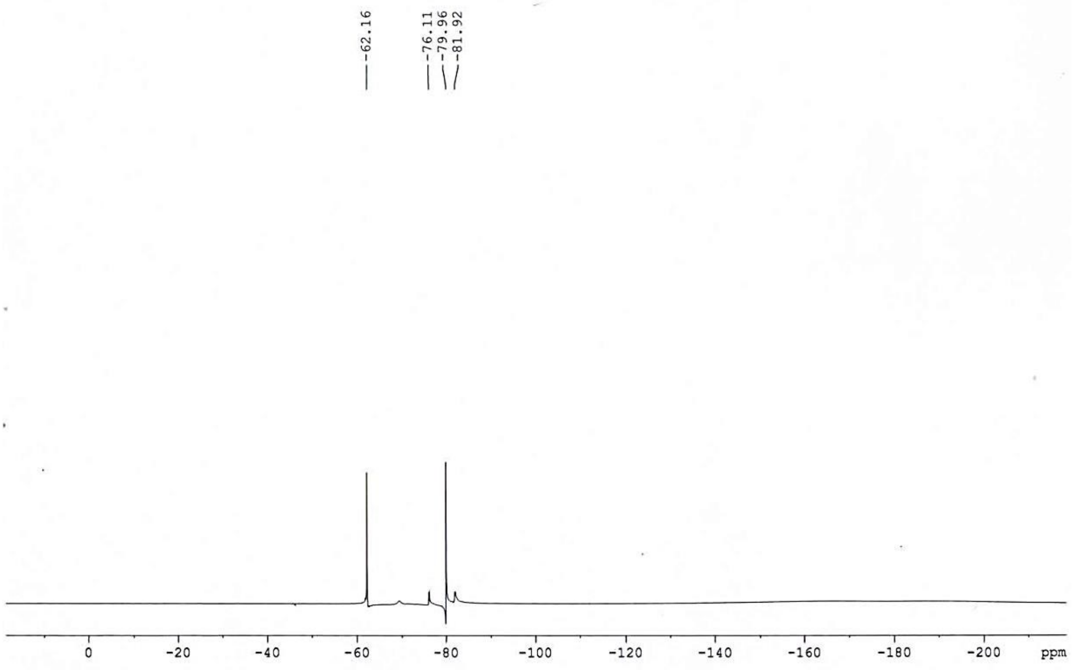


Figure S10. The ^{19}F-NMR spectra of the Eu-complex, Eu(TTA)$_3$Phen-pCF$_3$-TPA.

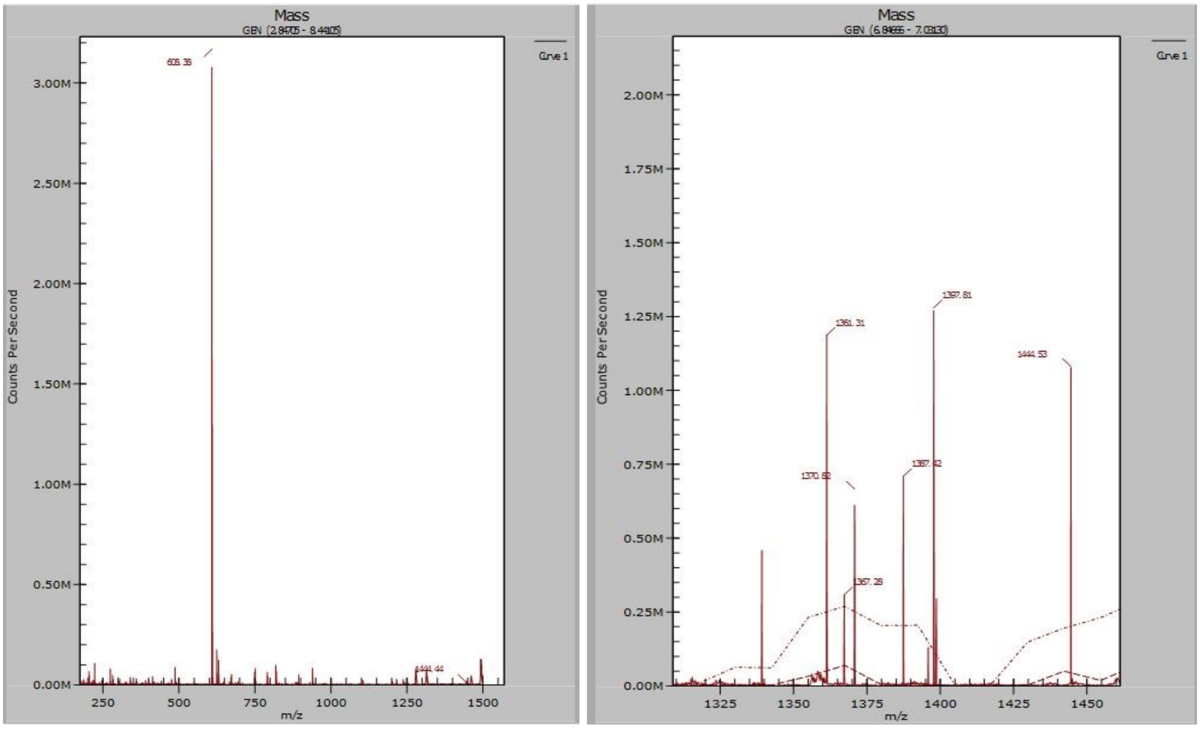


Figure S11. The mass spectra of the ligand (left) and Eu-complex, Eu(TTA)$_3$Phen-mCF$_3$-TPA (right).

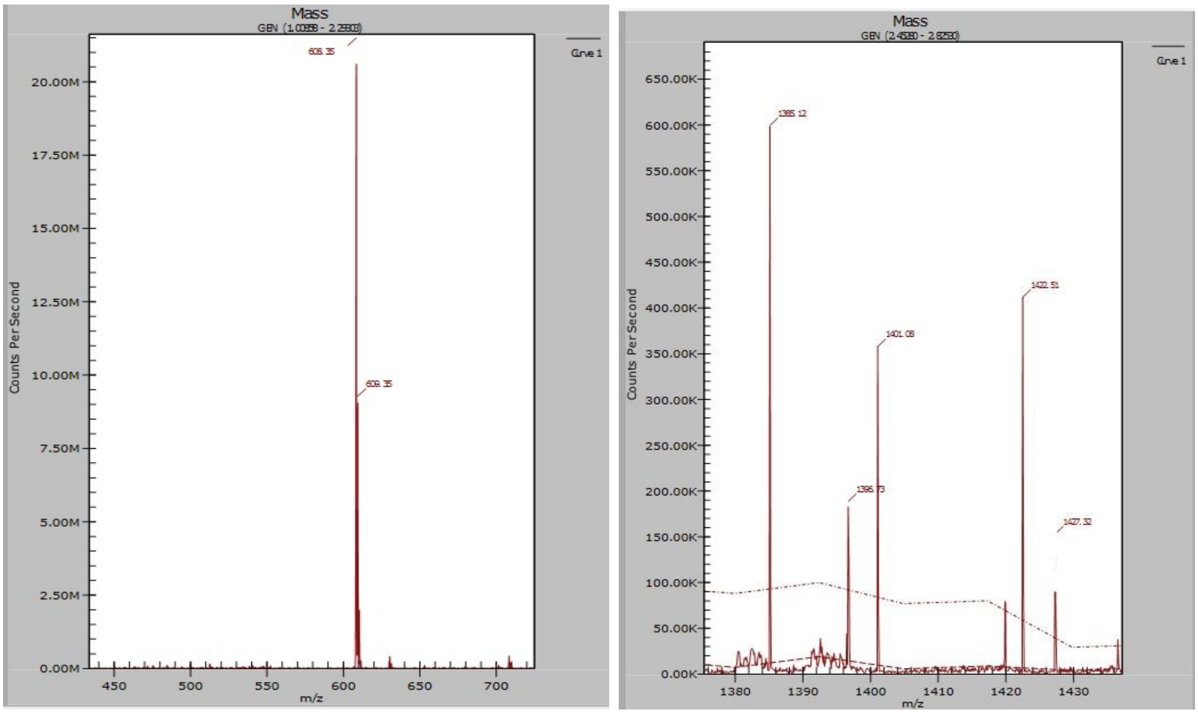


Figure S12. The mass spectra of the ligand (left) and Eu-complex, Eu(TTA)$_3$Phen-pCF$_3$-TPA (right).

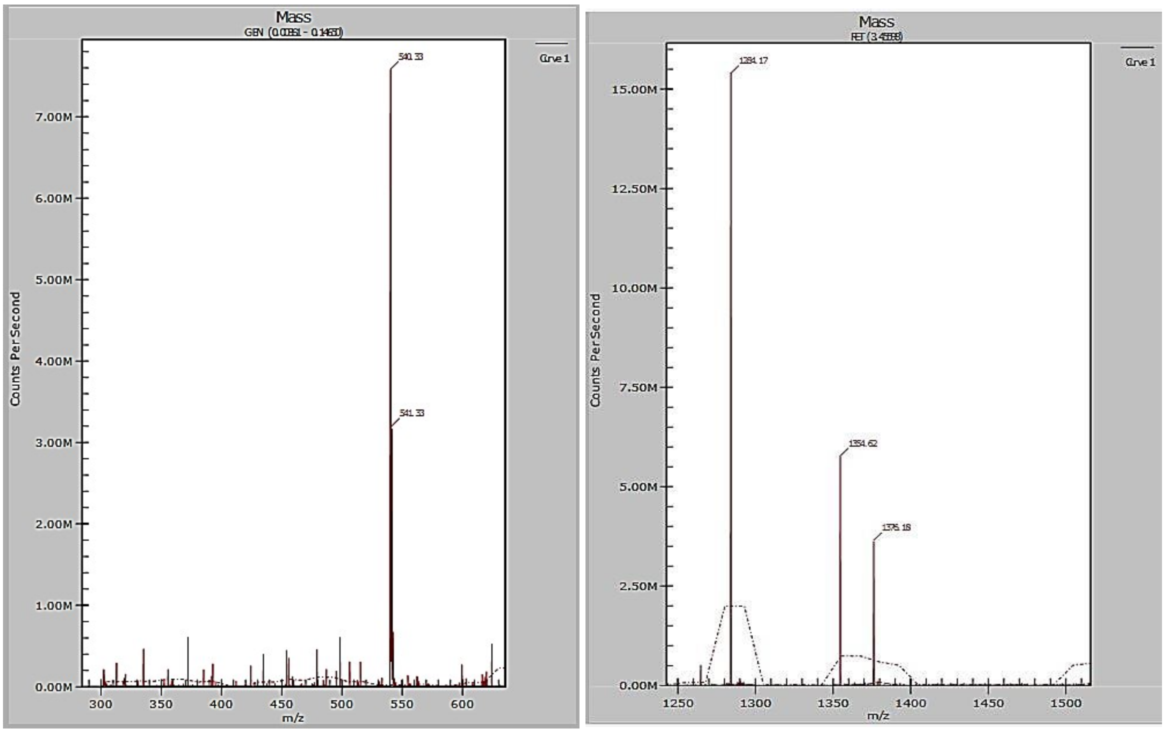


Figure S13. The mass spectra of the ligand (left) and Eu-complex, Eu(TTA)$_3$Phen-Ph-TPA (right).

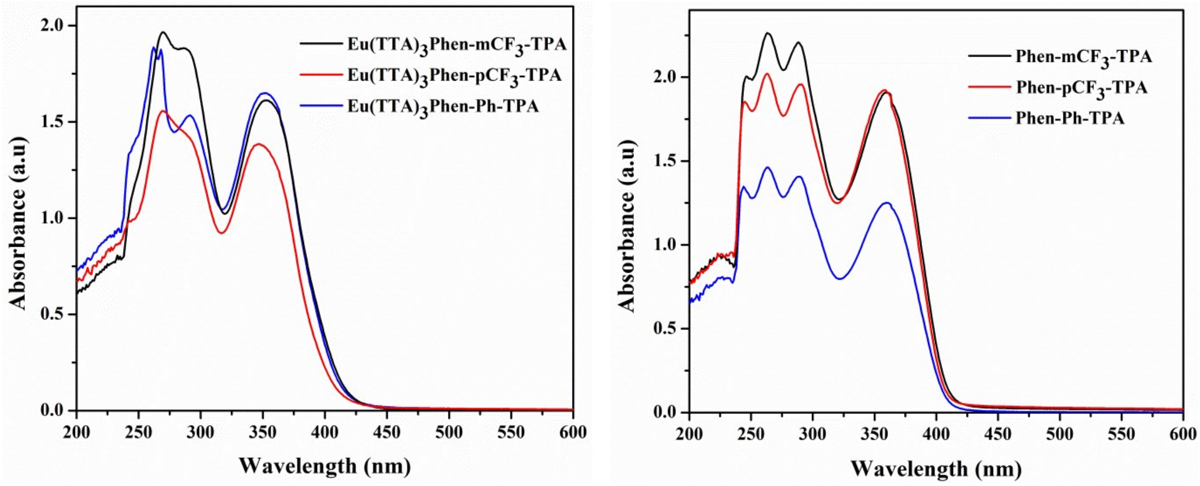


Figure S14. The absorption spectra of the Eu(III) complexes (left) and ligands (right) without normalization.

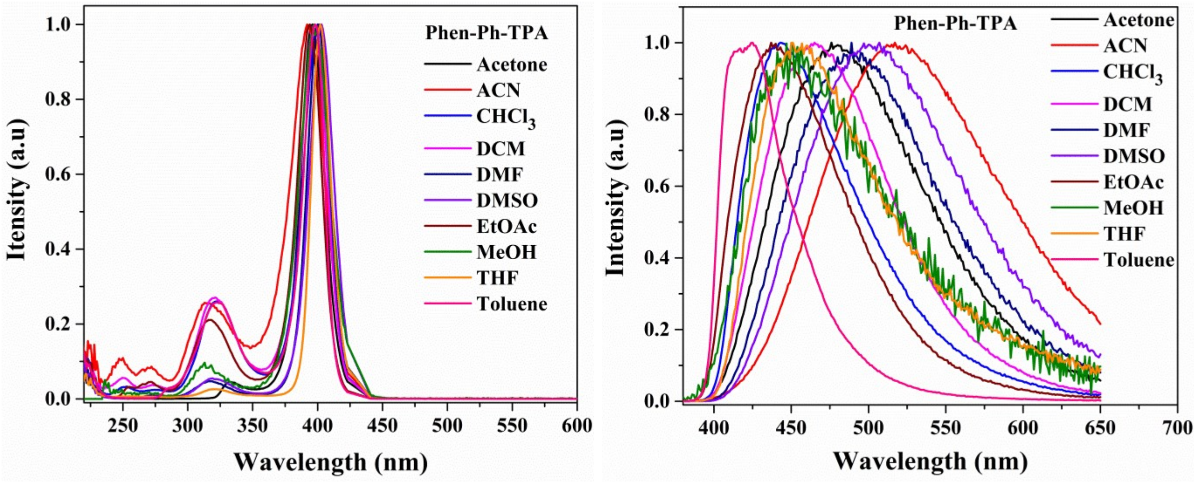


Figure S15. The PL excitation (left) and emission (right) spectra of the ligand (1L) in different solvents.

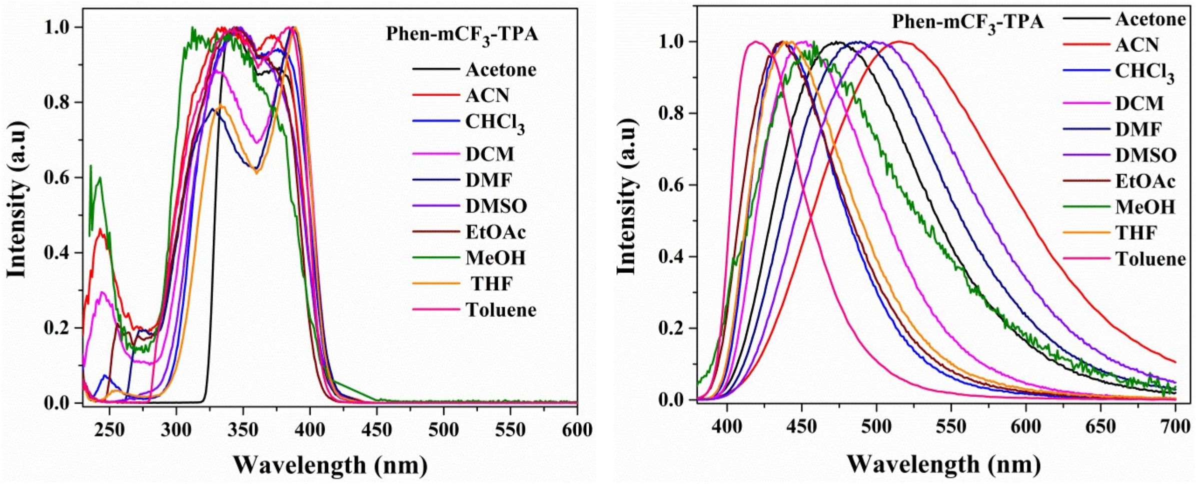


Figure S16. The PL excitation (left) and emission (right) spectra of the ligand (2L) in different solvents.

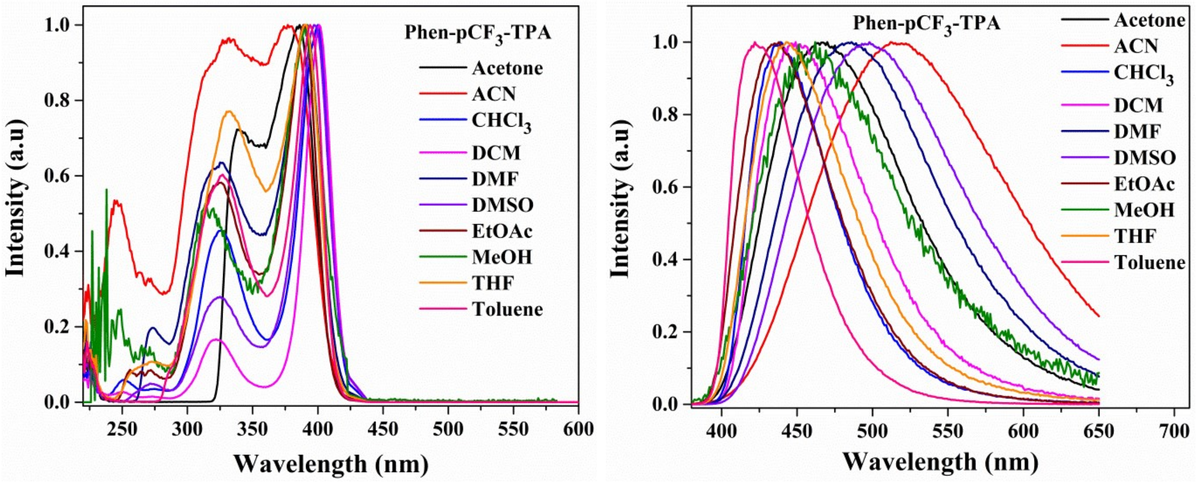


Figure S17. The PL excitation (left) and emission (right) spectra of the ligand (3L) in different solvents.

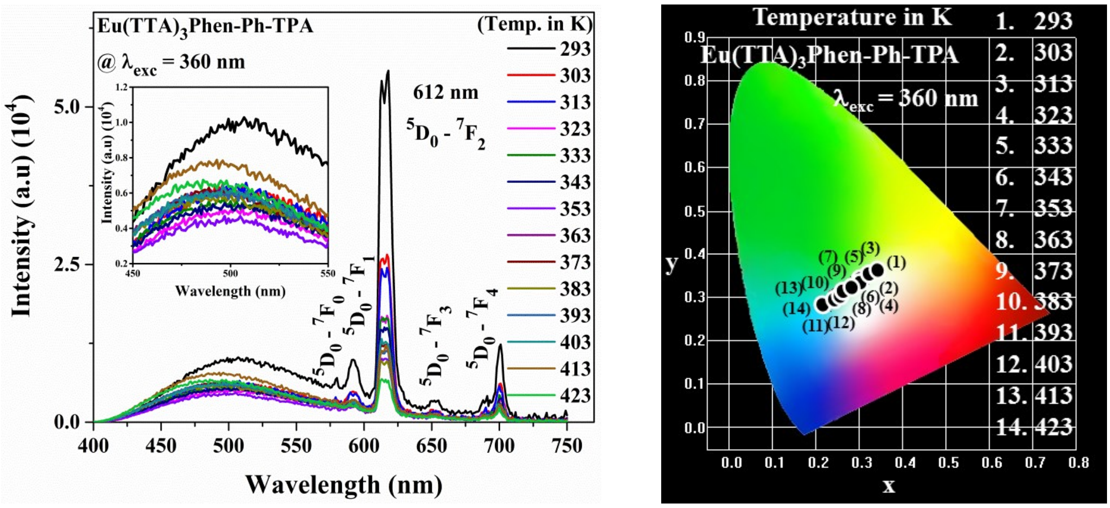


Figure S18. The PL emission spectra of Eu(TTA)$_3$Phen-Ph-TPA at 293-423 K under 360 nm excitation (left) and correspondiong CIE color coordinates (right).

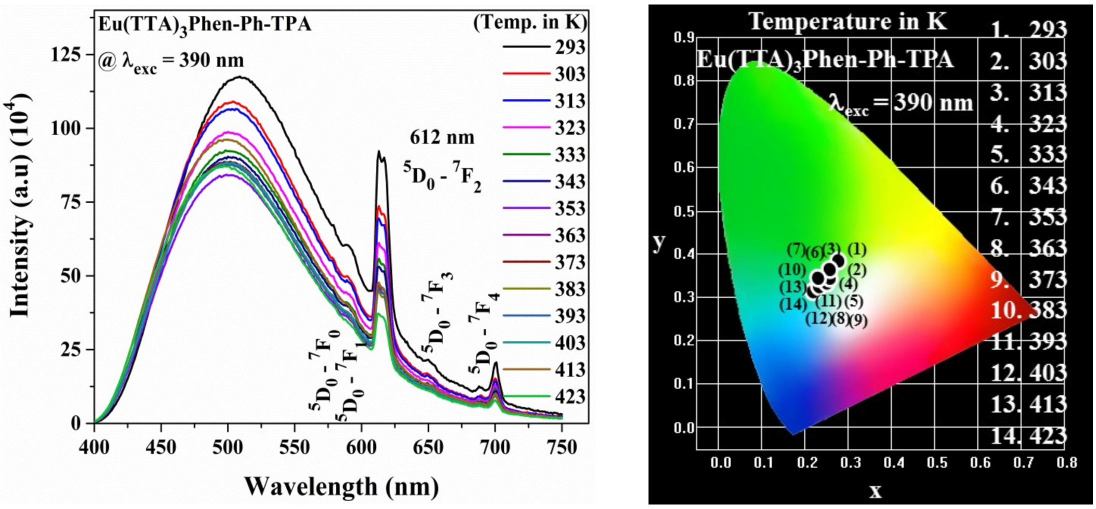


Figure S19. The PL emission spectra of Eu(TTA)$_3$Phen-Ph-TPA at 293-423 K under 390 nm excitation (left) and correspondiong CIE color coordinates (right).

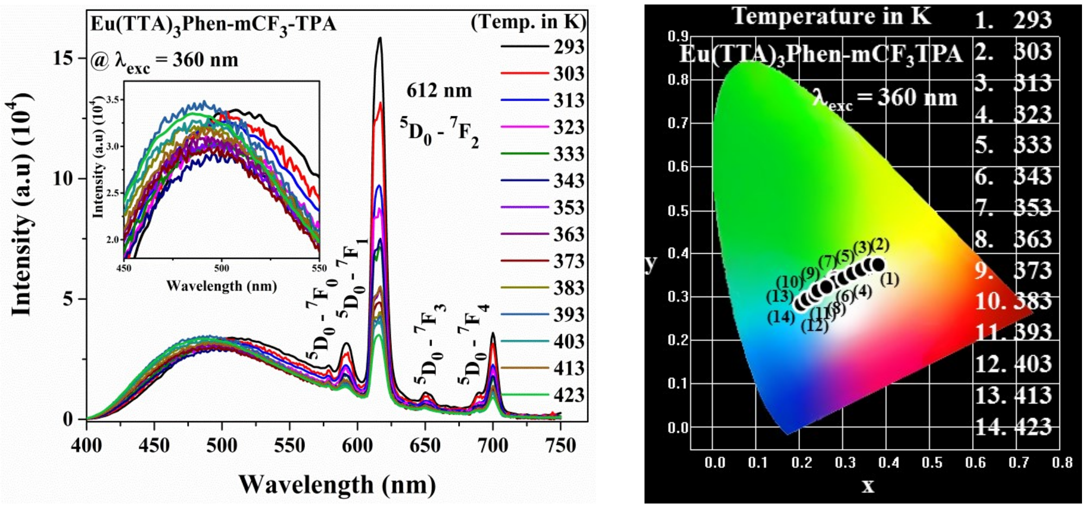


Figure S20. The PL emission spectra of Eu(TTA)$_3$Phen-mCF$_3$-TPA at 293-423 K under 360 nm excitation (left) and correspondiong CIE color coordinates (right).

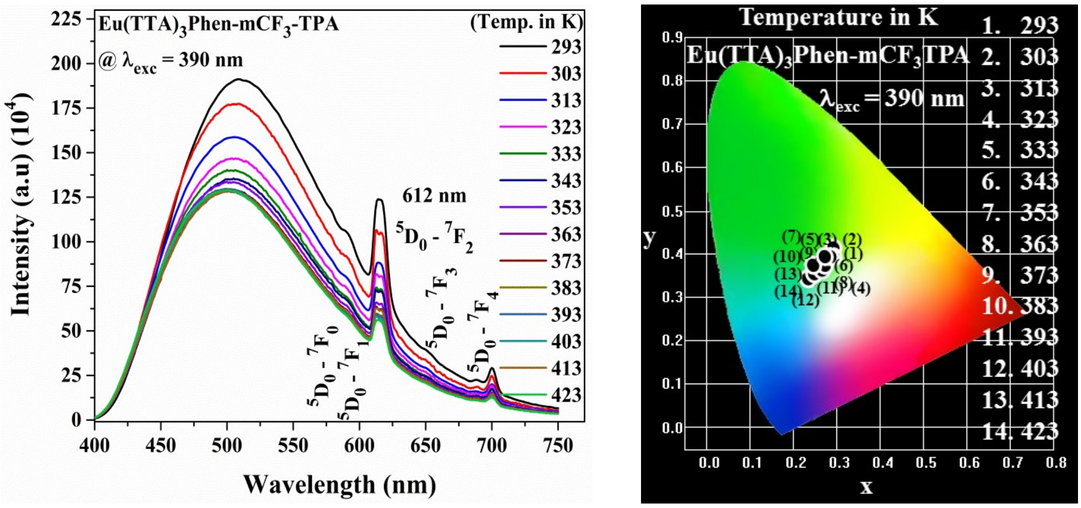


Figure S21. The PL emission spectra of Eu(TTA)$_3$Phen-mCF$_3$-TPA at 293-423 K under 390 nm excitation (left) and correspondiong CIE color coordinates (right).

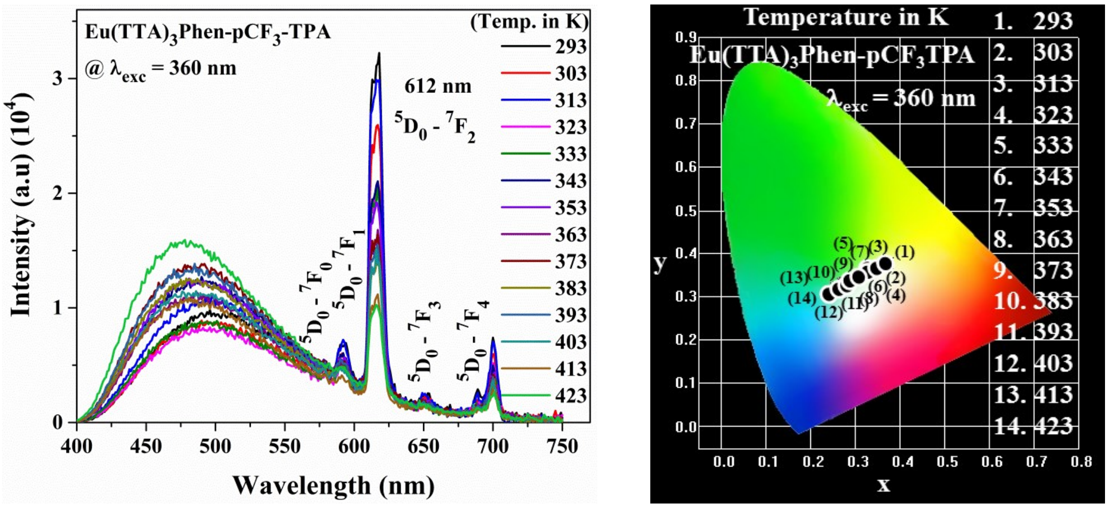


Figure S22. The PL emission spectra of Eu(TTA)$_3$Phen-pCF$_3$-TPA at 293-423 K under 360 nm excitation (left) and correspondiong CIE color coordinates (right).

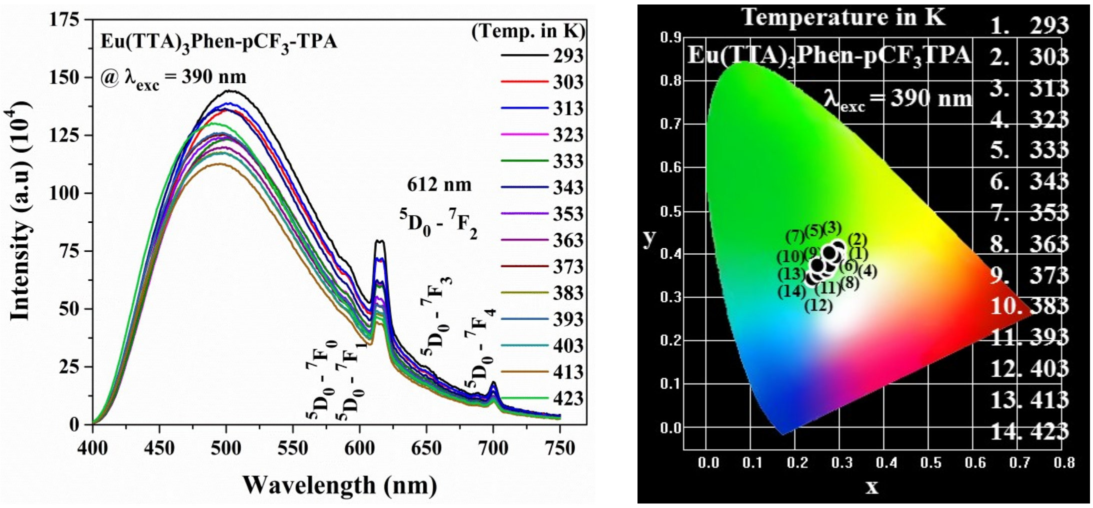


Figure S23. The PL emission spectra of Eu(TTA)$_3$Phen-pCF$_3$-TPA at 293-423 K under 390 nm excitation (left) and correspondiong CIE color coordinates (right).

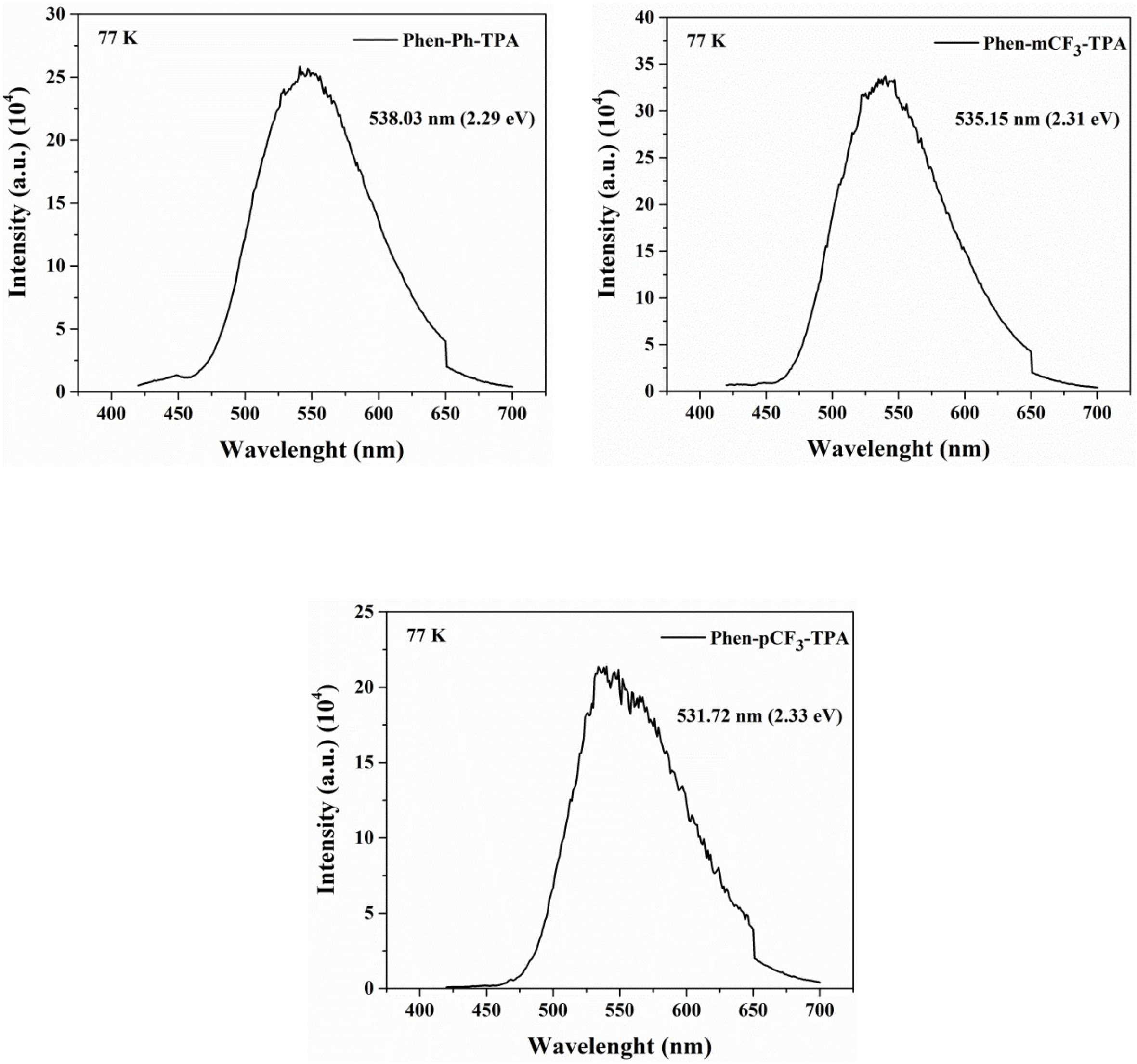


Figure S24. The phosphorescence emission spectra of the ligand measured at 77 K with respective Gd^{III}-complex and calculated triplet energy level.

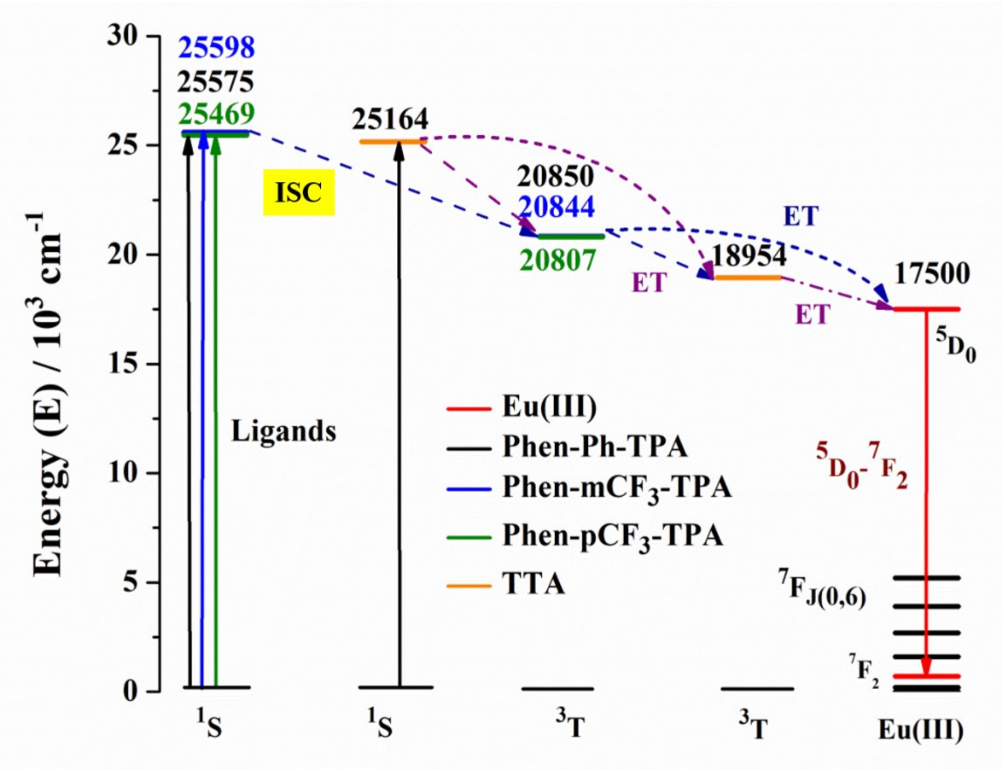


Figure S25. The emission pathway of the ligand and TTA towards Eu(III) metal ion.

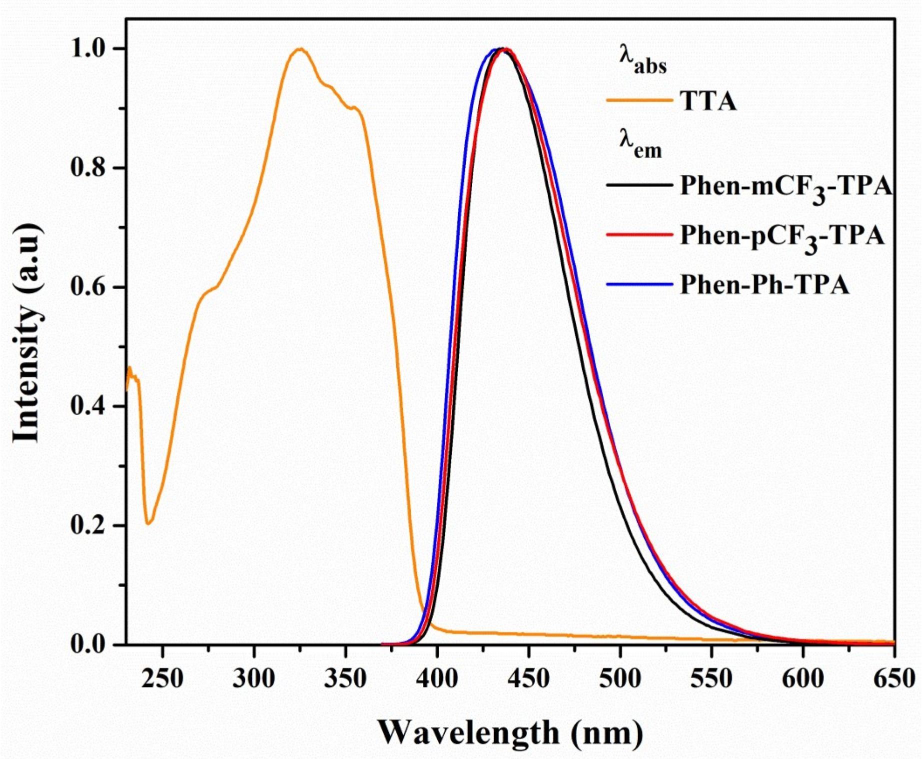


Figure S26. Overlap of the absorption spectrum of the TTA and the ligand emission spectrum at room-temperature.

Table ST1. The HOMO and LUMO energy levels of the ligands with their respective band gaps as well as singlet and triplet energy levels.

Molecule	**HOMO**	**HOMO-1**	**LUMO**	**LUMO+1**	$\mathbf{E_g}$	**S1**	**T1**
	in electron volts (eV)						
1L	-5.065	-5.799	-1.404	-1.375	3.661	3.17	2.58
2L	-5.066	-5.872	-1.528	-1.305	3.538	3.16	2.58
3L	-4.966	-5.689	-1.223	-1.129	3.743	3.17	2.58
Eu^{III} metal ion	**--.--**	--.--	--.--	--.--	--.--	$^5D_0$ level = 2.17	

Table ST2. Computed vertical transitions and their oscillator strengths and configurations[a]

Phen-Ph-TPA	**State**	**Energy (eV)**	λ_{max} **nm**	f	**Configuration**
Singlet	Gas	3.3200	373	0.8208	HOMO → LUMO (69.47%)
		3.6457	340.09	0.100	HOMO → LUMO+3 (68.37%)
	DCM	3.1709	391	0.5969	HOMO → LUMO (66.76%)
					HOMO→ LUMO+1 (17.60%)
		3.2908	376.75	0.3244	HOMO → LUMO+1 (65.99%)
					HOMO → LUMO+2 (11.80%)
		3.6167	342.81	0.2296	HOMO → LUMO+3 (67.64%)
Triplet	Gas	2.5835	479.9	-	HOMO-1 → LUMO (19.0%)
					HOMO → LUMO (58.80%)

	DCM	2.5851	479	-	HOMO-1 → LUMO (13.41%) HOMO-1 → LUMO+1 (19.04%) HOMO → LUMO (36.65%) HOMO → LUMO+1 (40.52%) HOMO → LUMO+3 (20.94%)

[a]Orbital contributions below 10% are omitted.

Table ST3. Computed vertical transitions and their oscillator strengths and configurations[a]

Phen-mCF$_3$-TPA	**State**	**Energy (eV)**	**λ_{max} nm**	***f***	**Configuration**
Singlet	Gas	3.1771	390.25	0.019	HOMO → LUMO (68.25%)
		3.2368	383.04	0.3283	HOMO → LUMO (11.62%) HOMO → LUMO+1 (67.62%) HOMO → LUMO+3 (18.16%)
		3.3716	367.73	0.4266	HOMO → LUMO+2 (67.29%)
	DCM	3.1737	390.66	0.6536	HOMO → LUMO (64.81%)
		3.2594	380.39	0.1905	HOMO → LUMO+1 (64.30%)
Triplet	Gas	2.5792	480.71	-	HOMO-1 → LUMO (10.83%) HOMO-1 → LUMO+1 (15.67%) HOMO-1 → LUMO+3 (10.46%) HOMO →LUMO (26.79%) HOMO →LUMO+1 (45.71%)

	DCM	2.5844	479.73	-	HOMO-1 → LUMO (13.98%) HOMO-1 → LUMO+1 (19.31%) HOMO → LUMO (36.66%) HOMO → LUMO+1 (44.53%) HOMO → LUMO+3 (15.67%) HOMO → LUMO+4 (14.17%)

[a]Orbital contributions below 10% are omitted.

Table ST4. Computed vertical transitions and their oscillator strengths and configurations[a]

Phen-pCF$_3$-TPA	**State**	**Energy (eV)**	**λ_{max} nm**	***f***	**Configuration**
Singlet	Gas	3.0513	405.67	0.0834	HOMO → LUMO (69.45%)
		3.373	371.51	0.5742	HOMO → LUMO+1 (68.84%)
		3.3759	367.26	0.1780	HOMO → LUMO+2 (67.65%)
	DCM	3.1578	392.63	0.6917	HOMO → LUMO (60.8%) HOMO → LUMO+1 (33.08%) HOMO → LUMO+3 (10.30%)
		3.4311	361.36	0.2351	HOMO → LUMO+2 (67.83%)
Triplet	Gas	2.5705	482.34	-	HOMO-1 → LUMO (13.49%) HOMO-1 → LUMO+1 (12.65%) HOMO → LUMO (36.66%) HOMO →LUMO+1 (38.99%)

				HOMO →LUMO+2 (27.21%)
				HOMO →LUMO+3 (10.63%)
				HOMO →LUMO+4 (13.15%)
DCM	2.5798	480.60	-	HOMO-1 → LUMO (15.74%)
				HOMO-1 → LUMO+1 (16.21%)
				HOMO → LUMO (41.13%)
				HOMO →LUMO+1 (37.12%)
				HOMO →LUMO+3 (19.10%)

[a]Orbital contributions below 10% are omitted.

Table ST5. The calculated CIE color coordinates of the thin film of the complexes in different ratios and their intensity ratios.

		Eu(TTA)$_3$Phen-Ph-TPA	**Eu(TTA)$_3$Phen-pCF$_3$-TPA**	**Eu(TTA)$_3$Phen-mCF$_3$-TPA**
I_2/I_1 (% of Eu^{3+})		24.42 (PURE)	23.06 (PURE)	20.12 (PURE)
		21.23 (0.1)	27.11 (0.1)	25.27 (0.1)
		19.58 (0.5)	18.56 (0.5)	27.11 (0.5)
		17.81 (1.0)	22.65 (1.0)	26.91 (1.0)
CIE	**x**	0.54 (PURE)	0.56 (PURE)	0.61 (PURE)
		0.58 (0.1)	0.65 (0.1)	0.66 (0.1)
		0.61 (0.5)	0.65 (0.5)	0.66 (0.5)
		0.66 (1.0)	0.55 (1.0)	0.64 (1.0)

y	0.27 (PURE)	0.28 (PURE)	0.31 (PURE)
	0.29 (0.1)	0.33 (0.1)	0.33 (0.1)
	0.31 (0.5)	0.33 (0.5)	0.33 (0.5)
	0.33 (1.0)	0.28 (1.0)	0.32 (1.0)

Reference:

1. (a) L. Ji, Q. Fang, M. Yuan, Z. Liu, Y. Shen and H. Chen, Organic letters, 2010, 12, 5192; (b) Z. Ning, Z. Chen, Q. Zhang, Y. Yan, S. Qian, Y. Cao and H. Tian, Adv. Funct. Mater., 2007, 17, 3799.

2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.

3. B. Rajamouli, P. Sood, S. Giri, V. Krishnan and V. Sivakumar, Eur. J. Inorg. Chem., 2016, 24, 3900–3911.