Cooperation in energy transfer between ligands and Eu^{III} ion in molecular europium complexes for vapoluminescence sensor (reversible on/off emission switching) and hybrid white LEDs/Plant-growth applications.

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EXPERIMENTAL STUDIES:

All the reagents were used as purchased without any further purification. All the operations involving air-sensitive reagents were performed under dry nitrogen atmosphere. The procedure for the synthesis of Phen-fl-mCF_3 were adopted from the literature and modified accordingly.

General information for Measurements:

^{1}H and ^{13}C-NMR spectra were measured on a BRUKER AV 400 Avance- III (400 MHz) instrument with tetramethyl silane as the internal standard. The absorption spectra of the synthesized luminophores were measured using a SHIMADZU UV-2450 spectrophotometer. The photoluminescence (excitation and emission) spectra, lifetime and quantum yield, were recorded by using Edinburg Spectrofluorometer FS–5 instruments with attaching SC – 10 modules and SC – 30 integrating sphere module. A pulsed xenon lamp was used as the excitation source, and the signals were detected with a photomultiplier. Cyclic voltammetry experiments were performed in dimethyl formamide solution containing 0.1 M tert-butyl ammonium perchlorate using Ag/AgCl as the reference electrode at a scan rate of 100 mV s^{-1} using an AUTOLAB 302NModular potentiostat. The CIE colour chromaticity coordinates of the phosphor were calculated from the emission spectral values by using MATLAB software.

Computational details

The molecules under study were optimized in the gas phase using density functional theory and the Becke three parameter Lee–Yang–Parr (B3LYP) form for the exchange– correlation potential and the 6-31G (d, p) basis set. All the structures were found to be in the minima of the potential energy surface as the normal mode of frequencies were all positive. Theory (TD-DFT) with gas phase optimized geometries. It is expected that the geometry of the molecule will change in the solvent phase in comparison to that of the gas phase, has been carried out. We found that there is no prominent change in the geometries of the molecules. As the UV-Vis experiment was done in the solution phase. Singlet and triplet energy calculations were performed by using the TD-SCF and B3LYP/6-31G (P) approach. All the calculations were carried out using the Gaussian09 Wand Gaussian View suite of programs. The optoelectronic properties including FMOs, absorption and emission spectra were calculated using TD-DFT analysis. [18-20]

General synthesis procedure of fluorophores:

Phen-fl-mCF$_3$: 1,10-phenanthroline-5,6-dione (phen-dione) (1.0 g, 4.762 mmol) solution in acetic acid is poured in two neck round bottom flask and vigorously stirrer for 15 min. after obtained the clear solution we added Fluerene-NH_2 (0.619 g, 5.238 mmol) and 3-(trifluoromethyl)benzaldehyde (0.910 g, 5.238 mmol) followed by ammonium acetate. The whole reaction mixture is stirrer overnight at 110^{o}C under inert condition. The progress of the reaction is monitored by TLC (MeOH:DCM=1 : 9) at a regular interval of time. After completion of reaction the reaction mass is neutralize with ammonium hydroxide solution and extracted with DCM followed by drying with sodium sulphate. It was concentrated by Rota evaporator and purification is done by column chromatography using silica bed (100–

200 mesh) with 5% MeOH in DCM as the eluent. The powder form of product is obtained by dissolving it in THF and excess amount of hexane. After getting the solid product in the bottom of round bottom flask the solution mixture is decant slowly. Then ligand is confirmed by ^{1}H and ^{13}C NMR as shown below in Fig.S1-S4. **^{1}H NMR Data (400MHz, $CDCl_3$, δppm):**δ 9.23 (dd,1H), 9.19 (dd,1H), 9.103 (dd,1H) ,8.05(s,1H) ,7.96(dd,1H), 7.88-7.79(m,4H), 7.59(m, 2H), 7.61-7.41(m,7H), 7.39-7.24(m,1H), 2.12-2.00 (m,4H) , 0.460 (t,3H) ,0.294 (t,3H). **^{13}C NMR Data (400MHz, $CDCl_3$, δppm):**152.88, 150.41, 150.26,149.25, 148.28,145.15, 144.54, 144.06, 139.70, 136.22, 135.96, 132.17, 131.17, 130.84, 130.56, 128.86, 128.61, 128.20, 127.46, 127.34, 127.27, 126.22, 126.19, 125.89, 125.85, 123.97, 123.68, 123.16, 123.11, 122.06, 121.53, 120.56, 119.84, 32.86, 32.58, 8.47, 8.16. Elemental Analysis: Anal. Calc. for. $C_{37}H_{27}F_3N_4$; C, 76.01; H, 4.65; N, 9.58 %, Found: C, 75.89; H, 4.57; N, 9.66%.

Phen-fl-pCH_3: Same procedure is followed as above for synthesis of Phen-fl-mCF_3; 1,10-phenanthroline-5,6-dione (phen-dione) (1.0 g, 4.762 mmol), Fluerene-NH_2 (0.619 g, 5.238 mmol) and 4-methylbenzaldehyde (0.629 g, 5.238 mmol).**^{1}H NMR Data: (400MHz, $CDCl_3$, δppm):** δ 9.21 (d,1H), 9.19 (d, J=,1H), 9.05 (d,1H) ,7.93 (d,1H), 7.85(s,1H), 7.85-7.77(m,1H), 7.65 (d, 1H) 7.56-7.43(m, 7H) 7.28-7.22(m,1H) 7.09(d, 2H). **^{13}C NMR Data (400MHz, $CDCl_3$, δppm):**152.48, 152.37, 150.19, 148.93, 147.90, 144.83, 143.59, 139.95, 139.43, 136.55, 130.59, 129.20, 129.05, 128.43, 128.13, 127.37, 127.02, 126.88, 128.05, 123.53, 123.42, 123.11, 121.96, 121.34, 120.43, 119.95, 32.98, 32.70, 30.97, 21.30, 8.48, 8.16. Elemental Analysis: Anal. Calc. for. $C_{37}H_{30}N_4$; C, 83.74; H, 5.70; N, 10.56 %, Found: C, 83.72; H, 5.61; 10.71%.

$Eu(DBM)_3$-phen-fl-mCF_3; The solution of $Eu(DBM)_3(H_2O)_2$ (403 mg, 0.175mmol) in dry THF (15 mL) was taken in round bottom flask and stirrer constantly unless a clear solution obtain, after 20 minutes a mixture of phen-fl-mCF_3 (0.90 mg, 0.174) in dry THF was added slowly drop by drop. The reaction mixture was then stirred for 6 hours at 60°C in inert condition.The completion of the reaction is monitored by TLC then the mixture was concentrated and then dissolved in the minimum amount of THF. To this solution, excess hexane was added by the wall of the round bottom flask; the precipitate was obtained. The reaction mixture was filter and washed several time to achieve the final complex in powder (pale yellow color solid with 112 mg (~73.8%)) form. Elemental Analysis: Anal. Calc. for. $C_{83}H_{64}EuF_3N_4O_6$; C, 70.09; H, 4.54; N, 3.94 %, Found: C, 70.02; H, 4.47; N, 3.99%.

$Eu(DBM)_3$-phen-fl-pCH_3: The complex was synthesized by previously described procedure using phen-fl-pCH_3 as the ligand instead of phen-fl-mCF_3**.** Elemental Analysis: Anal. Calc. for. $C_{82}H_{63}EuN_4O_6$; C, 72.83; H, 4.70; N, 4.14 %, Found: C, 72.75; H, 4.63; N, 4.20%.

$Eu(TTA)_3$-phen-fl-mCF_3: Taken a 25 mL two neck round bottom flask with nitrogen balloon with adaptor and poured $Eu(TTA)_3.2H_2O$ (0.152 g, 0.178 mmol, 2 eq) dissolved in dry tetrahydrofuran (THF) (10 mL). The mixture of phen-fl-mCF_3 (0.100 g, 0.089 mmol, 1eq) in THF (5 mL) was added to the reaction mixture (RM) then stirred for 6 h at 60 °C. The resulting product was concentrated and dissolved in a minimum amount of THF. Then added the excess of hexane to get the solid product which is pale yellow, yield 0.112 g (70.2%). Elemental Analysis: Anal. Calc. for. $C_{63}H_{45}EuF_{12}N_4O_6S_3$; C, 52.87; H, 3.24; N, 3.91; S, 6.72 %, Found: C, 52.81; H, 3.19; N, 3.99; S, 6.76%.

Eu(TTA)$_3$-phen-fl-pCH3: The complex was synthesized by previously described procedure using phen-fl-pCH3 as the ligand instead of phen-fl-mCF_3. Elemental Analysis: Anal. Calc. for. $C_{63}H_{49}EuN_4O_6S_3$; C, 54.94; H, 3.59; N, 4.07; S, 6.98 %, Found: C, 54.87; H, 3.51; N, 4.13; S, 6.95%.

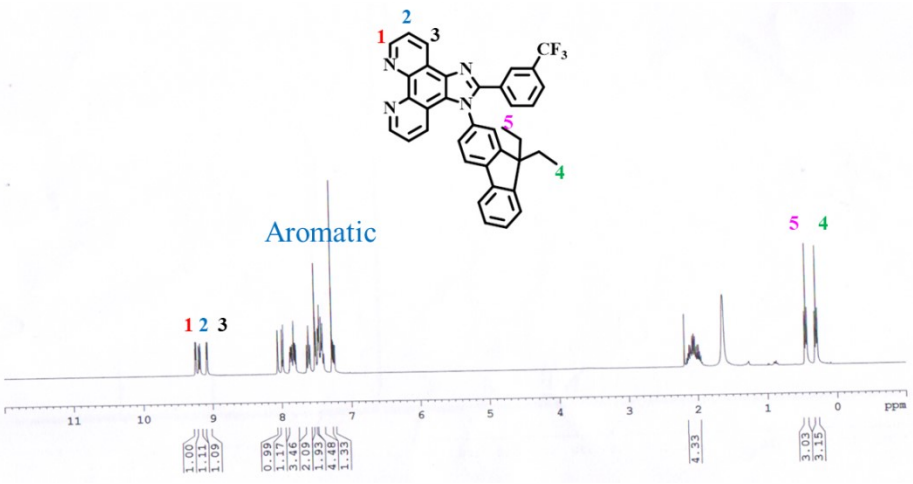


Fig. S1. ^{1}H NMR spectroscopy of Phen-fl-m-CF_3 in $CDCl_3$

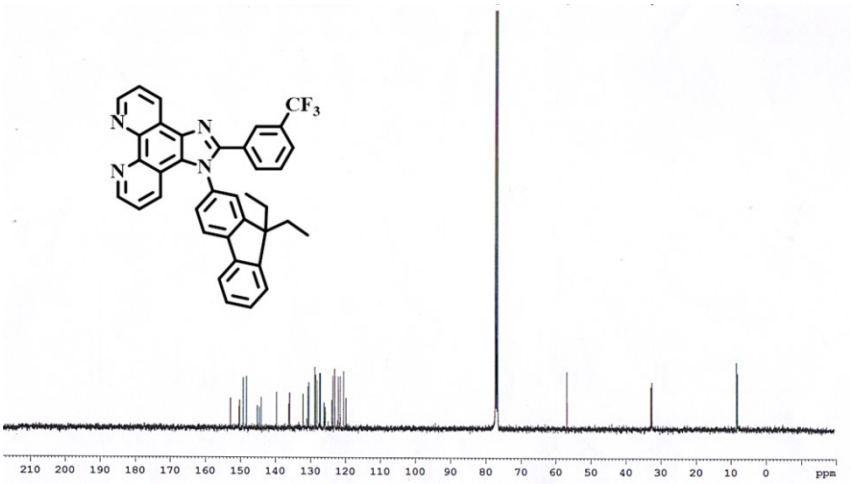


Fig. S2. ^{13}**C** NMR spectroscopy of Phen-fl-m-CF_3 in $CDCl_3$

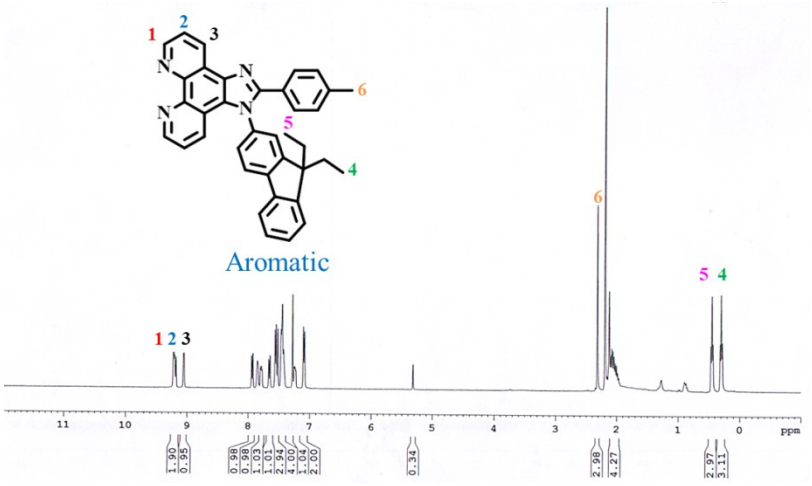


Fig. S3. ^{1}H NMR spectroscopy of Phen-fl-p-CH_3 in $CDCl_3$

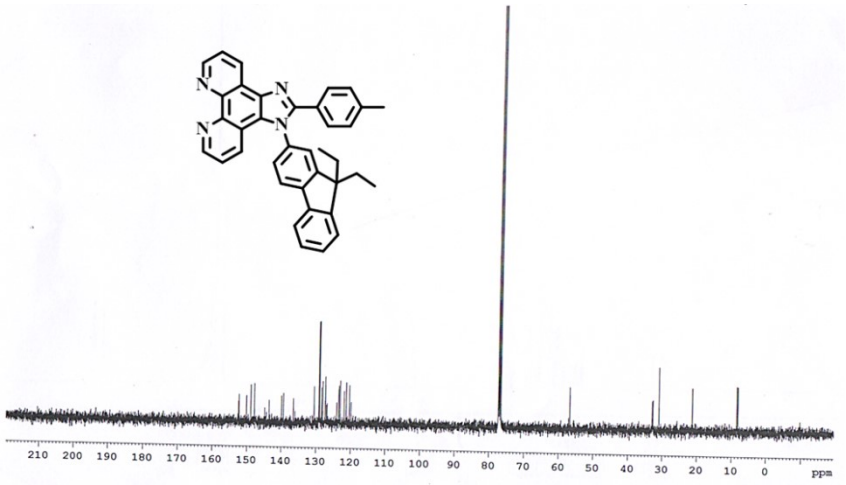
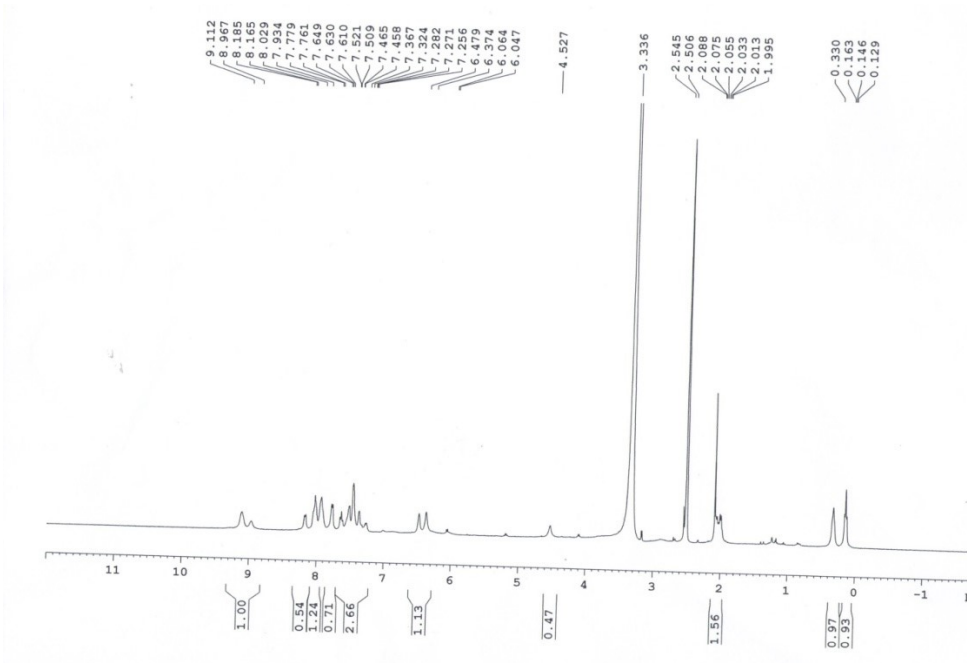


Fig. S4. ^{13}C NMR spectroscopy of Phen-fl-p-CH_3 in $CDCl_3$



1H NMR of the Complex:

Fig. S4.(a) ^{1}H NMR spectroscopy of $Eu(TTA)_3Phen\text{-}fl\text{-}m\text{-}CF_3$ in DMSO-d_6

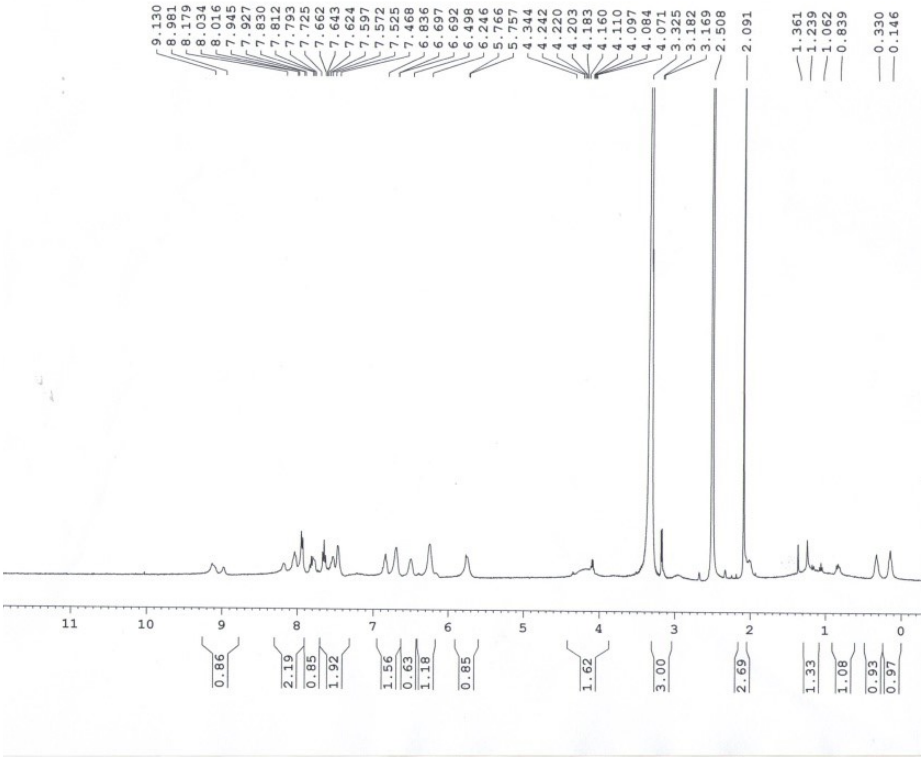


Fig. S4.(b) ^{1}H NMR spectroscopy of $Eu(DBM)_3Phen\text{-}fl\text{-}m\text{-}CF_3$ in DMSO-d_6

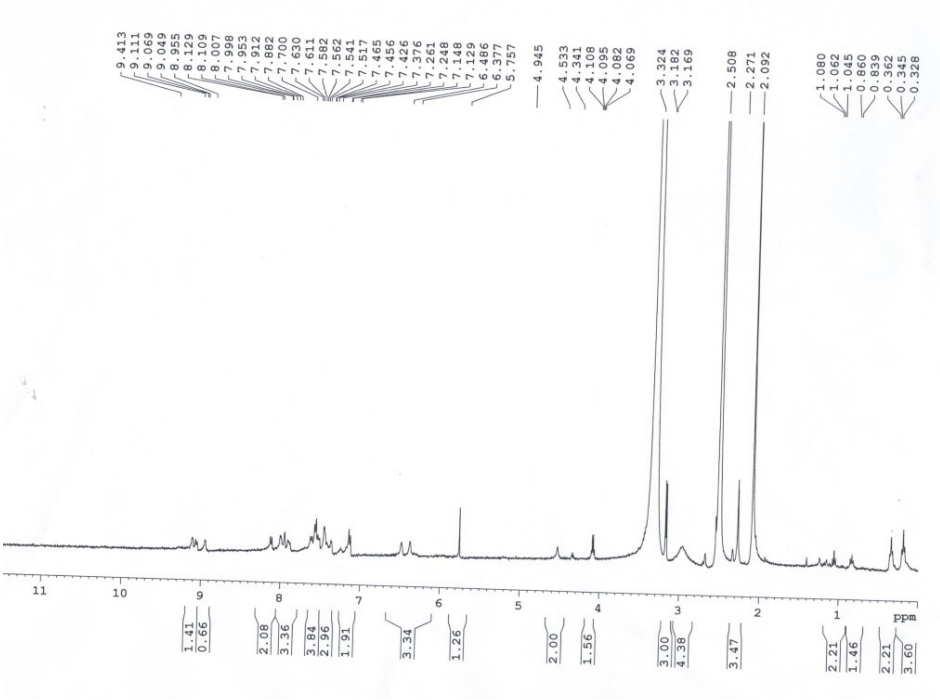


Fig. S4. (c) ^{1}H NMR spectroscopy of Eu(TTA)$_3$Phen-fl-p-CH$_3$ in DMSO-d$_6$

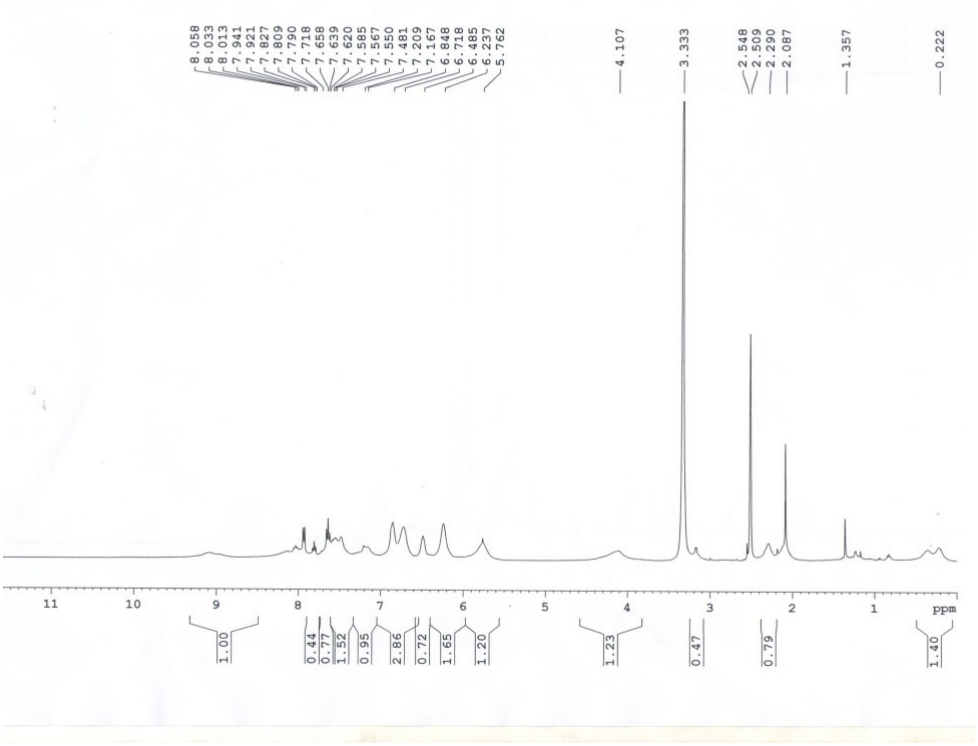


Fig. S4. (d) ^{1}H NMR spectroscopy of Eu(DBM)$_3$Phen-fl-p-CH$_3$ in DMSO-d$_6$

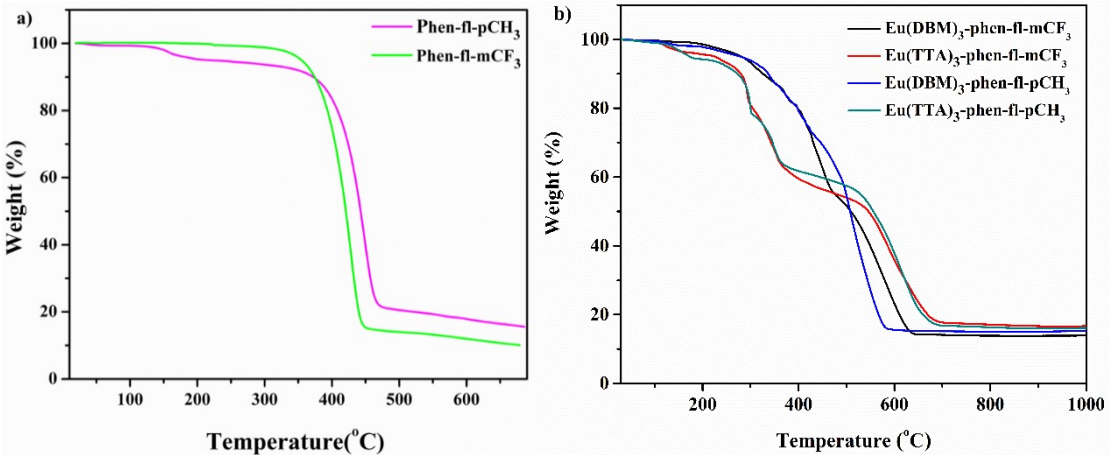


Fig. S5. TGA of ligand (a) and Eu(III) complexes (b).

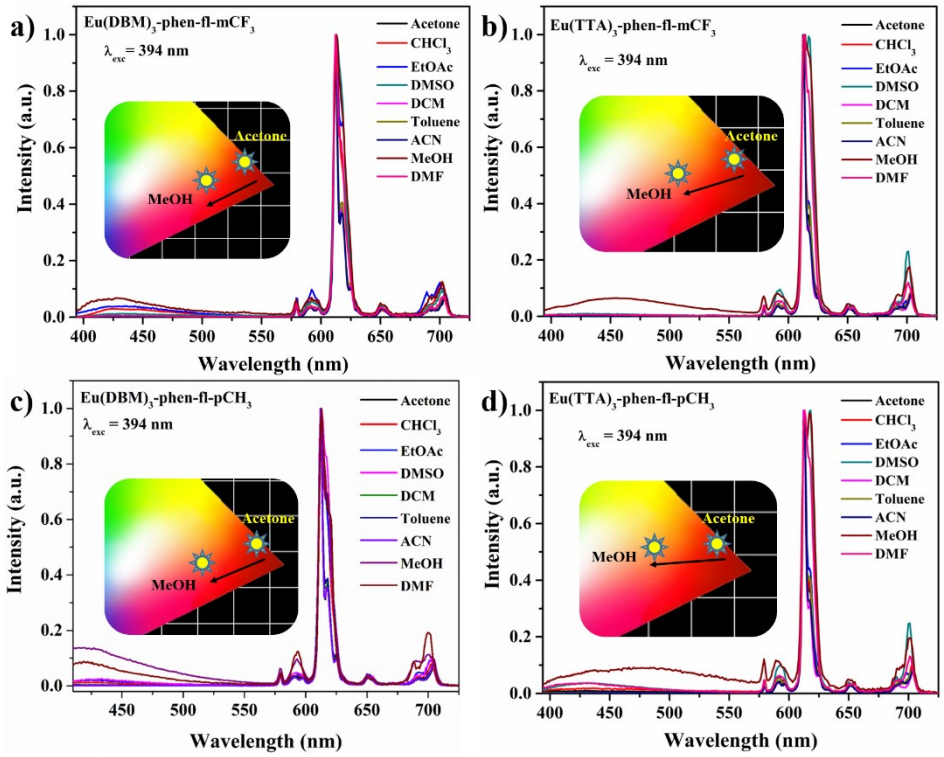


Fig. S6. PL of Eu(III) complexes at different solvents (non-polar to polar).

Table ST1: CIE Values of $Eu(DBM)_3$-phen-fl-mCF_3 and $Eu(DBM)_3$-phen-fl-pCH_3 complexes at different solvents (non-polar to polar).

Solvents	**$Eu(DBM)_3$-phen-fl-mCF_3**		**$Eu(DBM)_3$-phen-fl-pCH_3**	
	x	**y**	**x**	**y**
Acetone	0.6508	0.3266	0.6480	0.3241
$CHCl_3$	0.5737	0.2893	0.6338	0.3103
EtOAc	0.5543	0.2840	0.6061	0.3081
DMSO	0.6256	0.3190	0.6046	0.2981
DCM	0.6569	0.3260	0.6555	0.3291
Toluene	0.6553	0.3258	0.6501	0.3246
ACN	0.6570	0.3270	0.6574	0.3288

MeOH	0.5187	0.2778	0.4324	0.2338
DMF	0.6470	0.3223	0.5036	0.2597

Table ST2: CIE Values of $Eu(DBM)_3$-phen-fl-mCF_3 and $Eu(DBM)_3$-phen-fl-pCH_3 complexes at different solvents (non-polar to polar).

Solvents	**$Eu(TTA)_3$-phen-fl-mCF_3**		**$Eu(TTA)_3$-phen-fl-pCH_3**	
	x	**y**	**x**	**y**
Acetone	0.6224	0.3209	0.6312	0.3172
$CHCl_3$	0.6567	0.3252	0.5923	0.3096
EtOAc	0.6457	0.3232	0.6508	0.3255
DMSO	0.6366	0.3192	0.5714	0.2889
DCM	0.6590	0.3288	0.6616	0.3296
Toluene	0.6644	0.3288	0.6618	0.3282
ACN	0.6606	0.3285	0.6541	0.3295
MeOH	0.5002	0.2867	0.4482	0.3095
DMF	0.6437	0.3208	0.5728	0.2853

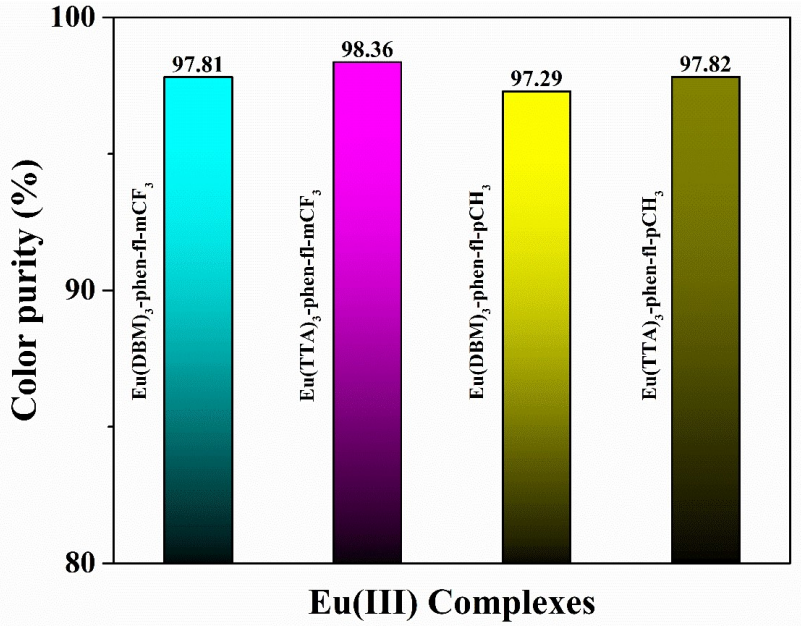


Fig. S7. Color purity of the Eu(III) complexes.

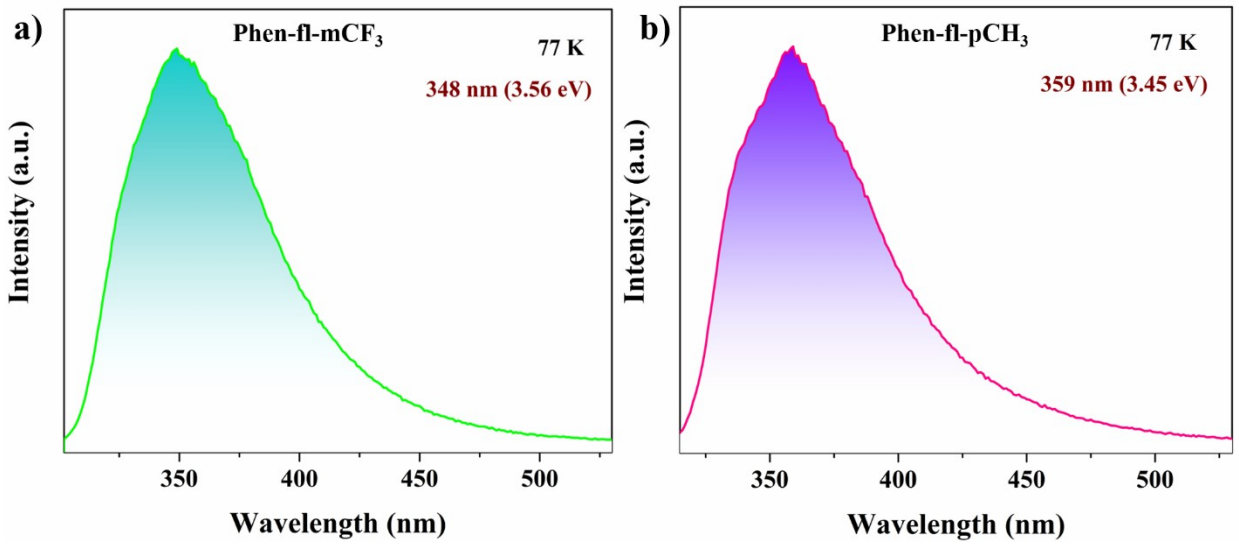


Fig. S8. Phosphorescence emission of the ancillary ligands.

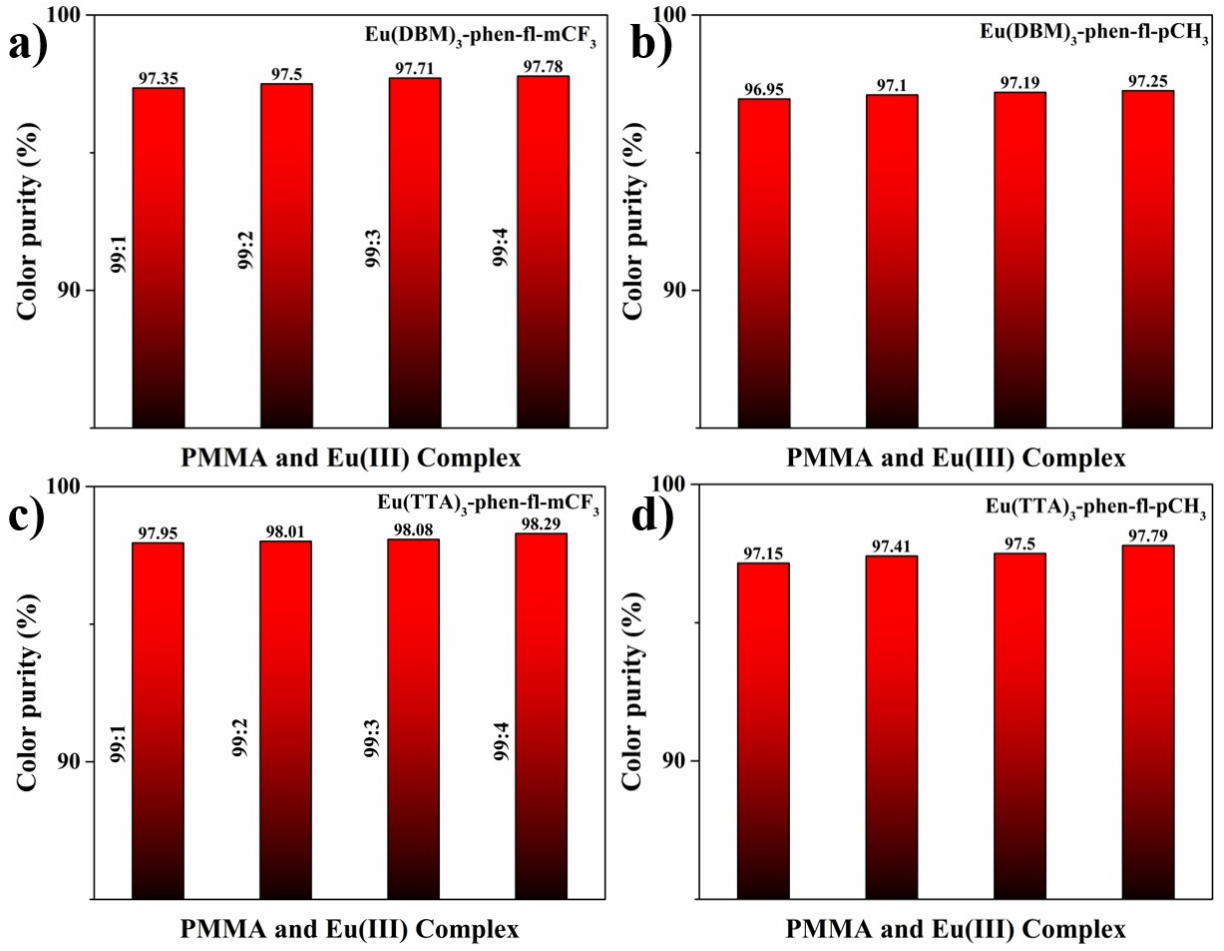


Fig. S9. Color purity of the Eu(III) complexes with PMMA matrix.

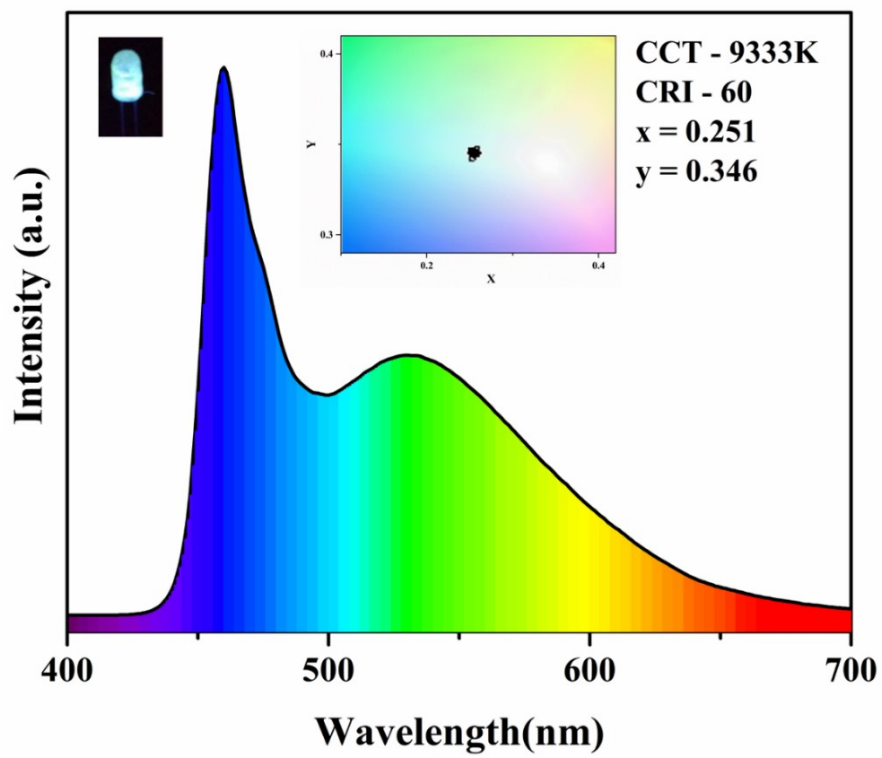


Fig. S10. EL spectrum of white LED by using blue LED with yellow organic dye.

Table ST3. LER values for the red LEDs.

Complexes	**LER (lm W^{-1})**	
	1:10	**1:50**
$Eu(DBM)_3$-phen-fl-mCF_3	286	289
$Eu(DBM)_3$-phen-fl-pCH_3	281	298
$Eu(TTA)_3$-phen-fl-mCF_3	278	289
$Eu(TTA)_3$-phen-fl-pCH_3	280	327

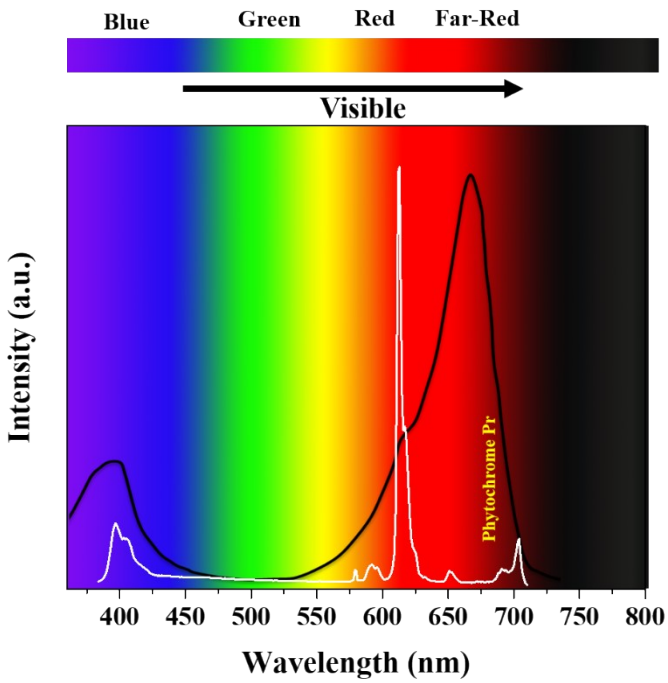


Fig. S11. EL spectrum of $Eu(TTA)_3$-phen-fl-mCF_3 red LED merging with Pr absorption lines.

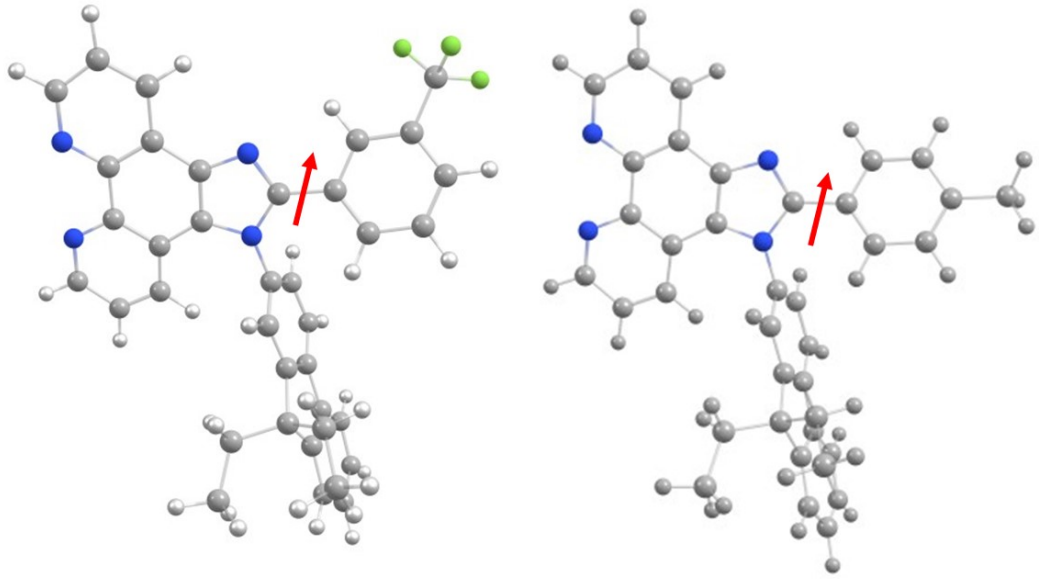


Fig. S12. Optimised geometry of the ligands with torsional angle

Table ST4. The HOMO-LUMO and HOMO-1, LUMO+1 energy levels of the ancillary ligands.

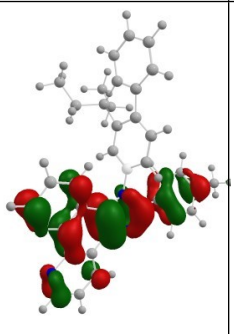
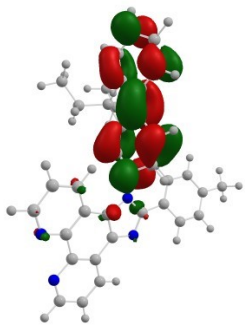
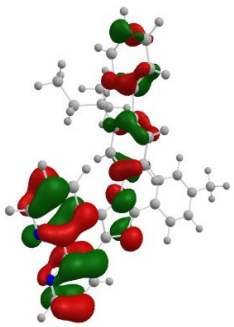
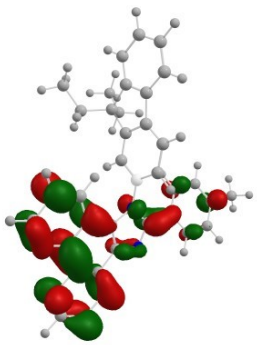
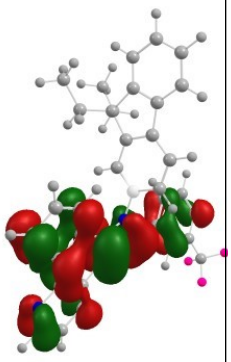
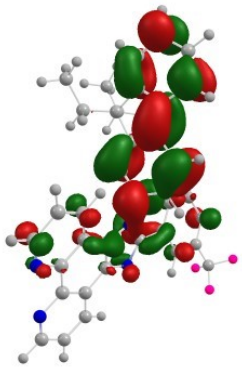
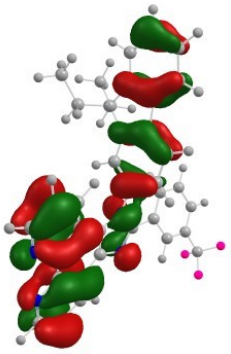
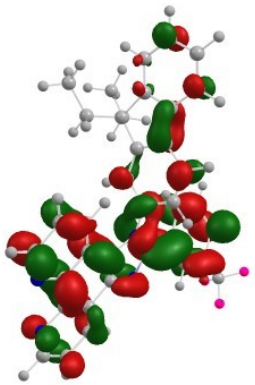
Ligands	HOMO	LUMO	HOMO-1	LUMO+1
Phen-fl-pCH_3				
Phen-fl-mCF_3				

Table ST5. The computed vertical transitions and their oscillator strengths (*f*) and configuration of the ligands.

Ligands	State	Energy (eV)	λ_{max} (nm)	*f*	Configuration
Phen-fl-pCH_3 Singlet	Gas	3.4619 (s_1)	358.14	0.0176	HOMO→LUMO(34.61%)
		3.6492 (s_2)	339.75	0.0702	HOMO→LUMO+1(58.03%)
		3.8688 (s_3)	320.13	0.3265	HOMO+1→LUMO+1(15.23%) HOMO→LUMO+1(34.14) HOMO→LUMO+2(57.05)%
Triplet	Gas	2.7549 (T_1)	450.12	0	HOMO→LUMO (22.49%) HOMO-5→LUMO+3(11.57%) HOMO-1→LUMO (13.64%) HOMO→LUMO+1 (42.62%) HOMO→LUMO+2 (41.24%)
		2.9911 (T_2)	414.51	0	HOMO-9→LUMO +3(11.12%) HOMO-7→LUMO(14.53%) HOMO-2→LUMO (35.32%) HOMO-1→LUMO (35.81%)
		3.1722 (T_3)	390.8	0	HOMO-7→LUMO+2 (10.25%) HOMO-1→LUMO+2 (10.07%) HOMO→LUMO+1(43.72%) HOMO→LUMO+3 (20.95%) HOMO→LUMO+4 (23.63%)
		3.5540 (s_1)	348.26	0.069	HOMO→LUMO (16.21%)
					HOMO-2→LUMO (12.58%)

Singlet	DCM	3.7442 (s_2)	315.01	0.296	HOMO→LUMO (13.68%) HOMO→LUMO+1 (66.98%)
		3.8929 (s_3)	299.22	0.1471	HOMO→LUMO+2(67.40%)
Triplet	DCM	(T_1)	445.80	0	HOMO-6→LUMO +3(11.43%) HOMO-2→LUMO (28.61%) HOMO→LUMO (28.61%) HOMO→LUMO+1(49.35%)
		(T_2)	412.70	0	HOMO-4→LUMO +6(10.74%) HOMO-1→LUMO+1(39.63%) HOMO-1→LUMO+1(48.81%)

		(T_3)	396.78	0	H OMO→LUMO(58.71%) HOMO→LUMO+2(14.58%) HOMO→LUMO+4(16.98%)
phen-fl-mCF_3 Singlet	Gas	3.5661 (s_1)	347.68	0.0046	HOMO→LUMO (66.66%)
		3.7230 (s_2)	333.02	0.1325	HOMO→HOMO-1 (18.05%) HOMO→LUMO+1 (44.50%) HOMO→LUMO+2 (44.59%)
		3.8539 (s_3)	321.17	0.3582	HOMO→LUMO+3(50.62%)
Triplet	Gas	2.7417 (T_1)	452.25	0	HOMO→LUMO (35.54%) HOMO-1→LUMO+1 (10.40%) HOMO→LUMO+1 (48.42%) HOMO→LUMO+4 (11.50%)
		2.9926 (T_2)	414.31	0	HOMO-3→LUMO+1 (16.08%) HOMO-2→LUMO (25.41%) HOMO-1→LUMO+1 (36.12%)
		3.1721 (T_3)	390.45	0	HOMO-9→LUMO+2 (13.10%) HOMO-2→LUMO+2 (15.62%) HOMO→LUMO+1 (25.53%) HOMO→LUMO+2 (15.80%) HOMO→LUMO+3 (31.83%)
Singlet	DCM	3.6612 (s_1)	339.57	0.1584	HOMO→LUMO (53.69%) HOMO-2→LUMO+1 (42.25%)

		3.7917 (s_2)	326.99	0.04321	HOMO-2→LUMO+1 (54.18%)
		3.9811 (s_3)	311.51	0.0740	HOMO-2→LUMO+2 (69.11%)
Triplet	DCM	2.7832 (T_1)	448.48	0	HOMO-2→LUMO (13.97%) HOMO-2→LUMO+1(10.48%) HOMO→LUMO (55.12%) HOMO→LUMO+3 (13.41%)
		3.0060 (T_2)	412.31	0	HOMO-4→LUMO+7 (14.38%) HOMO-1→LUMO (10.84%) HOMO-1→LUMO +2(55.30%) HOMO-1→LUMO+4 (11.31%)
		3.1690 (T_3)	391.24	0	HOMO-7→LUMO (10.91%) HOMO-2→LUMO (15.80%) HOMO-2→LUMO +1(20.81%) HOMO→LUMO+3 (40.69%)

xyz coordinates

Phen-fl-mCF$_3$:

6 -0.825954 4.562481 -1.073686

6 -0.437852 3.255351 -0.853155

6 0.887416 2.979264 -0.450585

6 1.778929 4.095186 -0.311508

6 0.119417 5.583877 -0.888722

6 1.435560 1.676628 -0.184731

6	3.188320	3.894593	0.061880
6	3.684494	2.581826	0.276326
6	2.774289	1.482063	0.139459
6	5.040206	2.418555	0.616820
1	5.425780	1.417890	0.782188
6	5.835029	3.541371	0.732116
6	5.250063	4.802063	0.504197
1	-1.838192	4.798762	-1.386456
1	-1.145221	2.449317	-0.995215
1	-0.159739	6.624476	-1.048833
1	6.885860	3.465378	0.993299
1	5.855395	5.703510	0.591797
7	3.978357	4.984241	0.180783
7	1.373833	5.363317	-0.526754
7	3.056327	0.154047	0.302770
7	0.881003	0.395937	-0.203750
6	-0.476430	0.061020	-0.527209
6	-1.474332	0.215170	0.446876
6	-0.784830	-0.410865	-1.807054
6	-2.785569	-0.109915	0.122320
1	-1.201141	0.587060	1.429877
6	-2.101306	-0.740750	-2.130986
1	0.009531	-0.515469	-2.538485

6	-4.036821	-0.028130	1.006111
6	-3.098492	-0.588456	-1.165365
1	-2.337977	-1.107810	-3.125077
6	-5.110308	-0.521300	0.026325
6	-4.539502	-0.847594	-1.223595
6	-6.481929	-0.693921	0.211499
6	-5.319506	-1.336013	-2.272935
6	-7.265041	-1.184004	-0.840304
1	-6.954754	-0.450176	1.155636
6	-6.690080	-1.502690	-2.073392
1	-4.869990	-1.584062	-3.230334
1	-8.332864	-1.316803	-0.693770
1	-7.312224	-1.881387	-2.878735
6	-4.216553	1.461914	1.452243
6	-5.589824	1.933360	1.946818
1	-3.940210	2.093409	0.599937
1	-3.464128	1.660875	2.226546
1	-5.522898	2.984067	2.247671
1	-6.342347	1.867817	1.156957
1	-5.954957	1.370768	2.808890
6	-3.815905	-1.014784	2.199699
6	-4.922073	-1.184000	3.246433
1	-2.900102	-0.697262	2.714516

1	-3.593539	-1.997405	1.766154
1	-4.624745	-1.956196	3.963583
1	-5.100818	-0.268584	3.815768
1	-5.867483	-1.504236	2.800897
6	1.919008	-0.486514	0.096476
6	1.830213	-1.955855	0.170286
6	0.660833	-2.674683	0.467692
6	3.023495	-2.671641	-0.035532
6	0.684661	-4.067742	0.538376
1	-0.268715	-2.155603	0.659851
6	3.038326	-4.060371	0.039985
1	3.930378	-2.122021	-0.253741
6	1.866433	-4.770071	0.322485
1	-0.229626	-4.606076	0.767942
1	1.884345	-5.853431	0.367234
6	4.334813	-4.806779	-0.130708
9	4.929245	-5.051729	1.060670
9	5.222878	-4.120370	-0.880949
9	4.144383	-6.008063	-0.724075

Phen-fl-p-CH_3:

6	-1.325533	-4.000149	-0.984558
6	-1.169156	-2.639718	-0.804477

6	-2.279779	-1.852578	-0.427400
6	-3.538626	-2.524507	-0.271421
6	-2.596758	-4.562279	-0.786018
6	-2.271603	-0.432404	-0.204918
6	-4.755439	-1.775012	0.077625
6	-4.694394	-0.366783	0.250662
6	-3.425811	0.282941	0.094527
6	-5.876877	0.326308	0.570814
1	-5.836181	1.402333	0.704655
6	-7.049716	-0.388812	0.706827
6	-7.008637	-1.784087	0.518822
1	-0.486693	-4.624180	-1.276737
1	-0.201703	-2.180998	-0.958596
1	-2.748662	-5.633237	-0.914650
1	-7.985860	0.102181	0.953836
1	-7.920383	-2.371337	0.622745
7	-5.911463	-2.461488	0.215542
7	-3.664264	-3.855811	-0.447825
7	-3.164691	1.620443	0.214522
7	-1.258753	0.527649	-0.254507
6	0.121383	0.290705	-0.564946
6	0.973327	-0.215526	0.427988
6	0.597156	0.563012	-1.851406

6	2.306959	-0.447483	0.115244
1	0.571457	-0.415275	1.416748
6	1.937142	0.332131	-2.164400
1	-0.087673	0.954086	-2.596279
6	3.420924	-0.986192	1.022377
6	2.788303	-0.174702	-1.180146
1	2.303828	0.545005	-3.164090
6	4.604970	-0.993915	0.045698
6	4.213837	-0.511234	-1.222787
6	5.931686	-1.373990	0.247391
6	5.126379	-0.410750	-2.274001
6	6.847899	-1.272661	-0.806301
1	6.266181	-1.753395	1.205901
6	6.449806	-0.795528	-2.057765
1	4.814471	-0.038788	-3.245885
1	7.880022	-1.570496	-0.646823
1	7.172970	-0.724212	-2.864697
6	2.996044	-2.408916	1.517584
6	4.068581	-3.361830	2.060526
1	2.503286	-2.912932	0.678086
1	2.217524	-2.268200	2.278735
1	3.591779	-4.290219	2.391831
1	4.795243	-3.626036	1.288182

1	4.615503	-2.954090	2.913463
6	3.604131	0.050996	2.178653
6	4.686360	-0.186541	3.237302
1	2.636279	0.138538	2.688611
1	3.786036	1.024868	1.708215
1	4.715265	0.668628	3.920671
1	4.490447	-1.074814	3.843056
1	5.682428	-0.281360	2.797011
6	-1.866632	1.757839	0.004318
6	-1.203400	3.072794	0.026068
6	0.147026	3.283882	0.345415
6	-2.001968	4.199767	-0.247216
6	0.675816	4.573666	0.372316
1	0.790764	2.450746	0.595813
6	-1.464200	5.479637	-0.216513
1	-3.050748	4.046607	-0.474587
6	-0.111281	5.694078	0.087133
1	1.723218	4.708959	0.629945
1	-2.105113	6.330742	-0.433493
6	0.472749	7.085802	0.089120
1	1.423199	7.120843	0.628903
1	0.662026	7.437853	-0.932683
1	-0.208716	7.804849	0.555159