SUPPLEMENTARY INFORMATION

Manuscript ID: TC-ART-02-2025-000861

Efficient Narrow Band Pure Red Emitting Molecular Europium Complexes for White Light-Emitting Diodes and Anticounterfeiting Applications

Rachna Devi[a], Kasturi Singh[a,b], Sibani Mund[a,b], Samatha Devineni[b], and Sivakumar Vaidyanathan[b]*

[a]Department of Chemistry, National Institute of Technology Rourkela, Rourkela-769 008, Odisha, India.

[b]Department of Chemistry, Indian Institute of Technology, Hyderabad, Kandi, Sangareddy-502285, Telangana, India

General Information for synthesis:

All the reaction was done in an inert atmosphere. Solvent THF is dried and distilled by using Na metal. All the commercially available reagents (Sigma Aldrich and Alpha Ezar) were used without further refinement unless otherwise needed. The progress of all the reactions was checked by thin-layer chromatography (TLC) with silica gel 60 F254 Aluminium plates (Merck) at a regular interval of time. Further purification of the crude reaction mass was carried out by column chromatography using silica gel (Sigma-Aldrich).

Measurements:

For recording the ^{1}H and ^{13}C-NMR spectra theAV 400 Advance-III 400MHz Fourier transform nuclear magnetic resonance (FT-NMR) Spectrometer Bruker Biospin International, Switzerland was used. All the ^{1}H and ^{13}C-NMR spectra were recorded in deuterated chloroform/dimethyl sulfoxide solution and tetramethylsilane (TMS) was used as a standard reference for chemical shift measurement. The Fourier transform infrared spectroscopy (FTIR) was executed by PerkinElmer Spectrum Version 10.4.00, in the spectrum range of 400 – 4000 cm-1 making KBr pellets. The PL emission and excitation spectra in the solution and solid were recorded by using the Edinburg spectrofluorometric FS– 5 instruments associated with SC – 10 modules and SC – 5 modules respectively. The photoluminescence (excitation and emission) spectra, lifetime and quantum yield were monitored by using Edinburg Spectrofluorometer FS–5 instruments with attaching SC – 10 modules andSC – 30 integrating

sphere module. The CIE color coordinate for all emission spectra is calculated by MATLAB software. The absorption spectra of all the synthesized compounds in solution form were utilizing UV-Visible spectrometer (Shimadzu Corporation, Japan or UV-2450 Perkin Elmer, USA/Lamda 25 and Lamda Perkin Elmer). The electrochemical properties of the ligands and their respective complex were estimated by utilizing cyclic voltammetry (CV), AUTOLAB 302N Modular potentiostat at RT in Dimethylformamide (DMF). The CV analysis is the set-up of mainly three electrode, the working (glass-carbon rod), auxiliary (counter, Pt wire) and reference (Ag/Agcl wire) electrodes.

Dimethylformamide (DMF) containing 0.1 M Bu_4NClO_4 was used as an electrolyte and the sweep rate was kept as 100 mV s^{-1}.

The ligand sub-atomic structures were optimized within density functional theory (DFT) frame work utilizing B3LYP/6-31G (d, p) level of theory.

A UV-visible spectrum of the molecule is obtained by exciting molecule vertically after conformation of ground state geometry of the ligand. Further, to the depiction of PL emission and excitation mechanism of the Eu(III) complex, triplet energized condition of the ligand is additionally accessed by utilizing the same procedure specified previously. The optimization study of ligand is effectively accomplished by the G09W program. The Lifetime of the Eu(III) complex, as well as the ligand, were measured at 298 K with Edinburgh Instruments FLS 980 based on the time-correlated single photon counting technology upon the excitation at 380 nm. A pulsed xenon lamp was used as the excitation source, and the signals were detected with a photomultiplier. All the measurements were carried out at room temperature (RT).

Materials:

The synthesis of Eu(III) chloride($EuCl_3.6H_2O$) from europium(III) oxide is done by the well-known process.[1]The resultant product ($EuCl_3.6H_2O$) was then treated with an alcoholic solution of DBM (3 eq.) in the presence of 1 N sodium hydroxide solution (3.1 eq.) to get $Eu(DBM)_3(H_2O)_2$. 1,10-Phenanthroline-5,6-dione was synthesized from 1,10-phenanthroline by a previously reported procedure.[2-4] All the ligands were successfully synthesized by a well-reported procedure [5,6]

4 General synthesis of ligands and their respective Eu (III) complexes

Phen-pCH_3-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 obtaining the clear solution, we added 4-methylbenzylamine (0.618 g, 5.238 mmol) and 3-(trifluoromethyl) benzaldehyde (0.910 g, 5.238 mmol) followed by ammonium acetate. The whole reaction mixture is stirred overnight at 110oC 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 the reaction, the reaction mass was neutralized 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 the product is obtained by dissolving it in THF and excess amount of hexane. After getting the solid product in the bottom of the round bottom flask, the solution mixture is decanted slowly. 1H-NMR Data (400 MHz, CDCl3-d6): 1H(d) = 9.25(J = 6), 2H(dd) = 9.151(J = 13.2), 1H(m) = 8.057-8.031, 2H(dd) = 7.88(J = 6), 2H(m) = 7.839-7.808, 2H(m) = 7.729-7.679, 1H(d) = 7.53(J = 7.6), 2H(m) = 7.439-7.28. 13C-NMR (100 MHz, CDCl3, TMS, □ ppm):148.62, 134.17, 133.34, 132.06, 131.82, 130.68, 129.33, 123.89, 77.33, 77.01, 76.70, ESI-MS: m/z ratio = 456.61, found: m/z ratio = 466.71[M + H] +.

Phen-pCH_3-pCH_3: Same procedure is followed as above for synthesis of Phen-pCH3-pCH3; 1, 10-phenanthroline-5,6-dione (phen-dione) (1.0 g, 4.762 mmol), 4-methylbenzylamine (0.618 g, 5.238 mmol) and 4-methylbenzaldehyde (0.818 g, 5.238 mmol). 1H-NMR Data (400 MHz, CDCl3-d6): 1H(dd) = 9.265(J = 4), 2H(dd) = 9.17(J = 12), 3H(m) = 7.95-7.86, 1H(m) = 7.83-7.80, 2H(m) = 7.76-7.72, 1H(dd) = 7.66(J = 8), 3H(m) = 7.57-7.53, 4H(m) = 7.50-7.40.13C-NMR (100 MHz, CDCl3, TMS, δ ppm): 149.49, 148.52, 133.41, 132.71, 131.50130.97, 130.78, 129.49, 128.55, 127.67, 127.44, 126.69, 125.18, 124.61, 123.85, 122.38, 77.34, 77.02, 76.71, Calculated m/z = 447.49 found m/z ratio = 448.69

Eu(DBM)$_3$Phen-pCH_3-mCF_3 : The solution of Eu(DBM)3(H2O)2 (0.150 g, 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-pCH_3-mCF_3(0.0810g, 0.174) in dry THF was added slowly drop by drop. The reaction mixture was then stirred for 6 hours at 60^{o}C in inert condition. The completion of the reaction is monitored by TLC then the mixture was concentrated by Rota evaporator and then dissolved in the least amount of THF. To this solution, excess hexane was added by the wall of the round bottom flask; the precipitate was obtained. The upper solvent layer was then decanted slowly, and the residue was dried. The same procedure was repeated several times to achieve the final complex in pure powder form. ESI-MS: m/z = 1290.16, found: m/z = 1313.28 [M + Na] +.

Eu(DBM)$_3$Phen-pCH_3-pCH_3: The complex was synthesized by previously described procedure using phen-pCH_3-pCH_3 as the ligand instead of Phen-pCH_3-mCF_3. ESI-MS: m/z = 1272.31, found: m/z = 1273.32 [M + H] +.

Computational details:

The geometries of the molecules were optimized using density functional theory employing Becke three-parameter hybrid functional (B3LYP).[7] The 6-31G** basis set was used for the main group elements and hydrogen atoms[8]. For the Eu atom, the Stuttgart RSC 1997 + Quadruple Zeta Basis Set designed for an ECP was used[9]. The optimized geometries were confirmed to be at the minima on the potential energy surface through frequency calculations at the same level. All the calculations were carried out using Gaussian 16 program.[10]

1. **NMR Spectroscopy:**

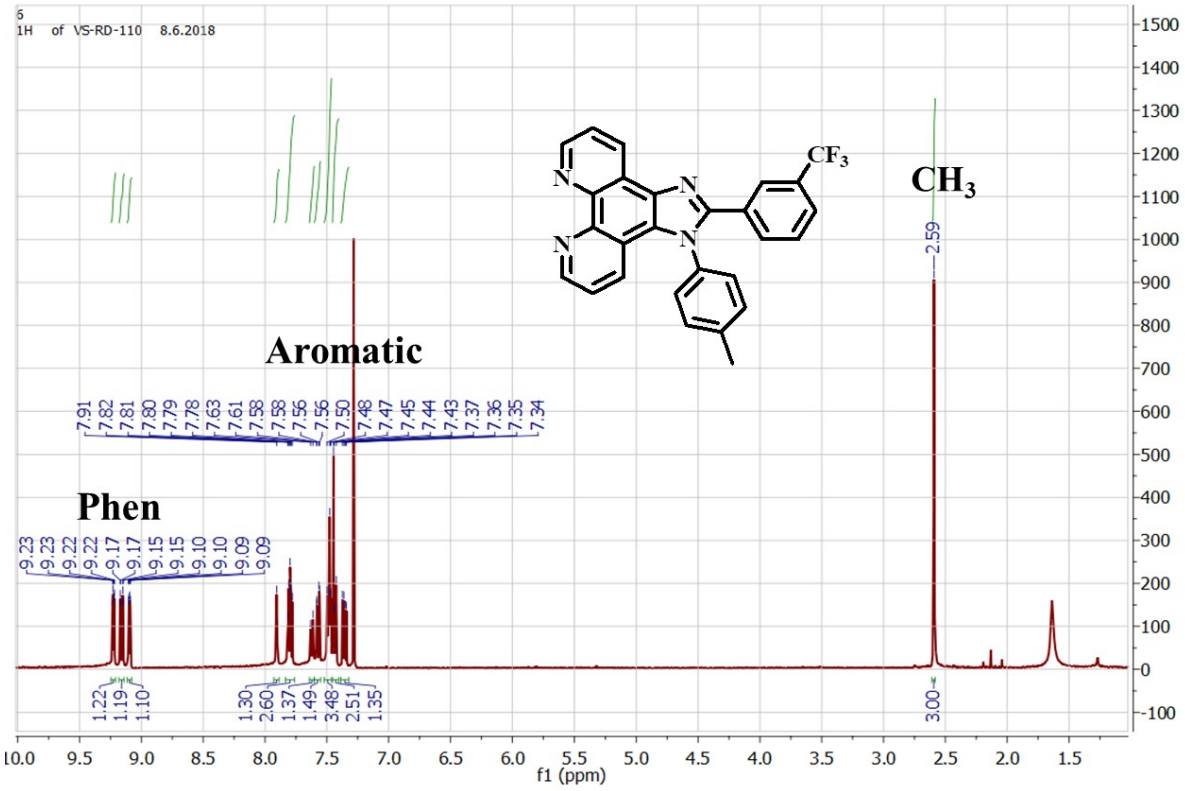


Figure. S1.[1]H NMR spectroscopy of Phen-pCH3-mCF3 in $CDCl_3$

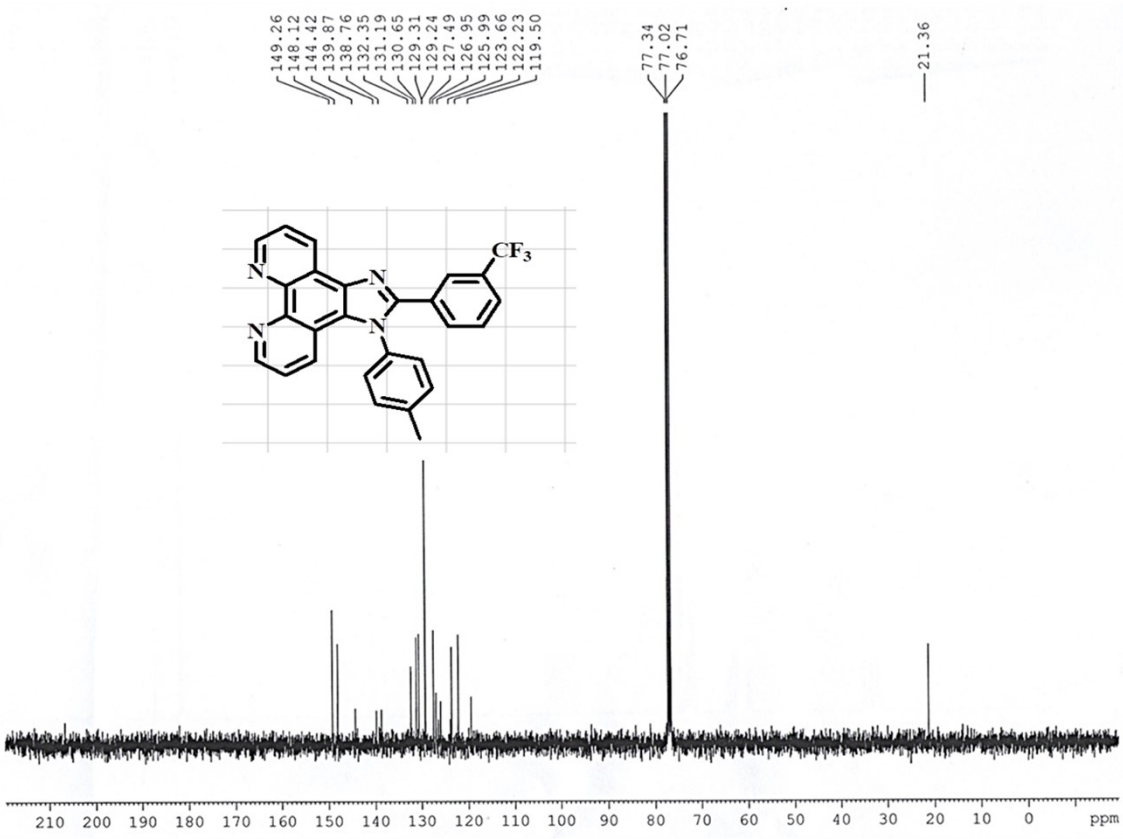


Figure. S2. ^{13}C-NMR spectroscopy of Phen-pCH_3-mCF_3 in $CDCl_3$

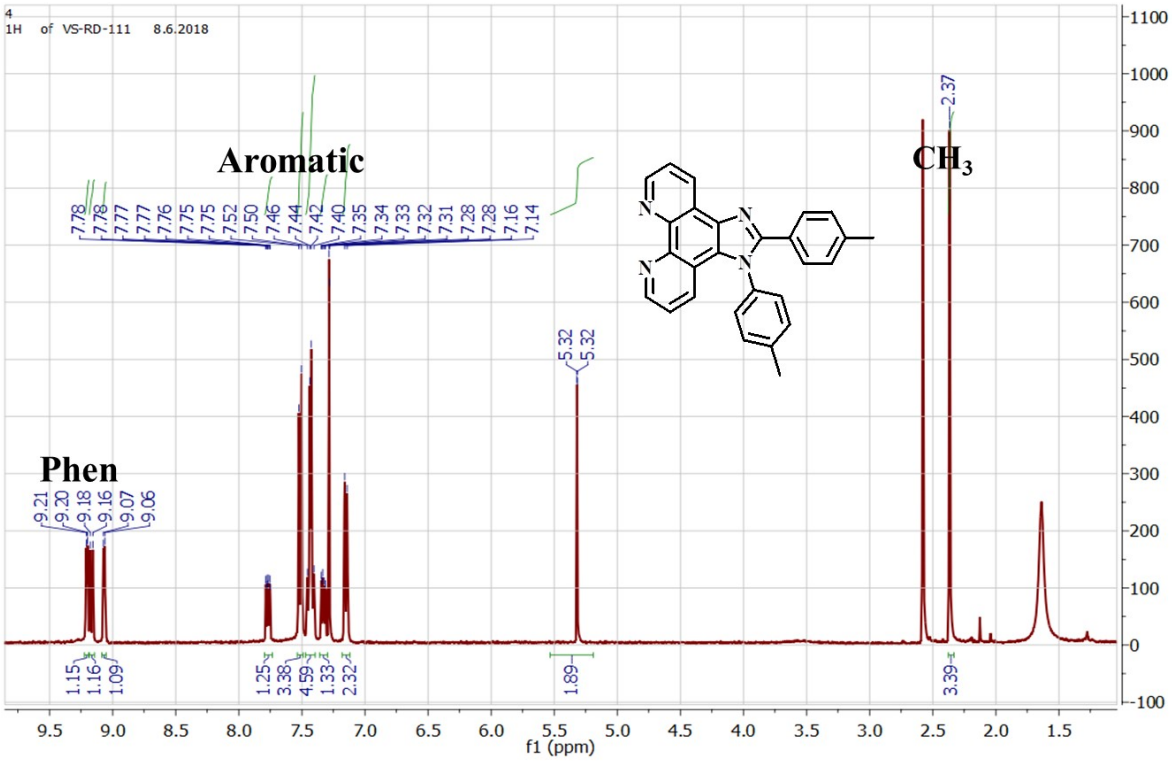


Figure.S3. ^{1}H NMR spectroscopy of Phen-pCH_3-pCH_3 in $CDCl_3$

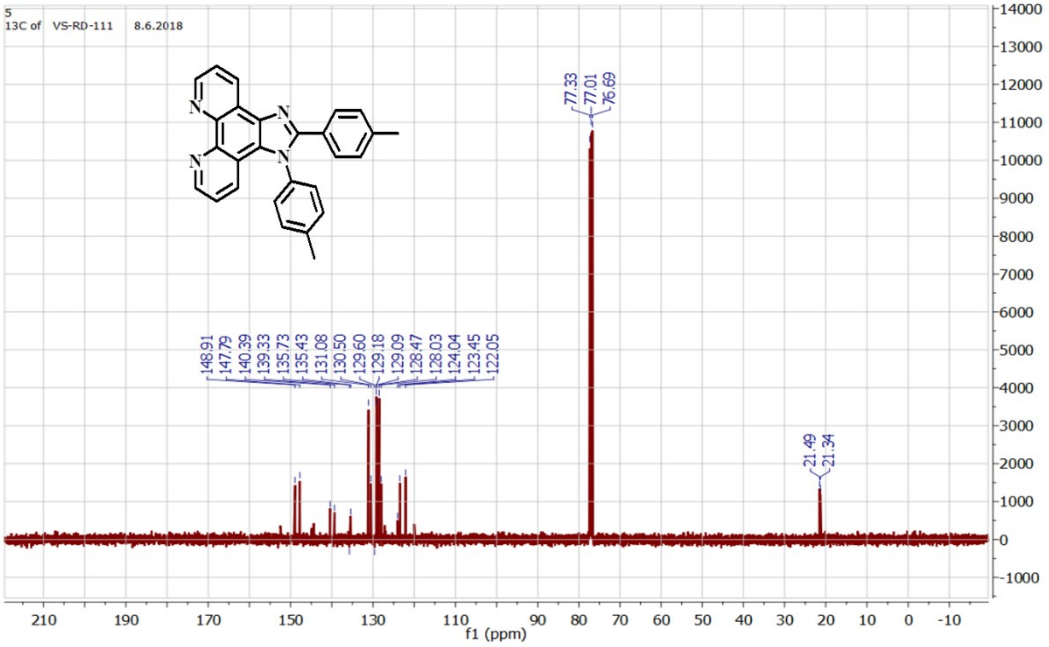


Figure S4. ^{13}C NMR spectroscopy of Phen-pCH_3-pCH_3 in $CDCl_3$

Mass spectral analysis:

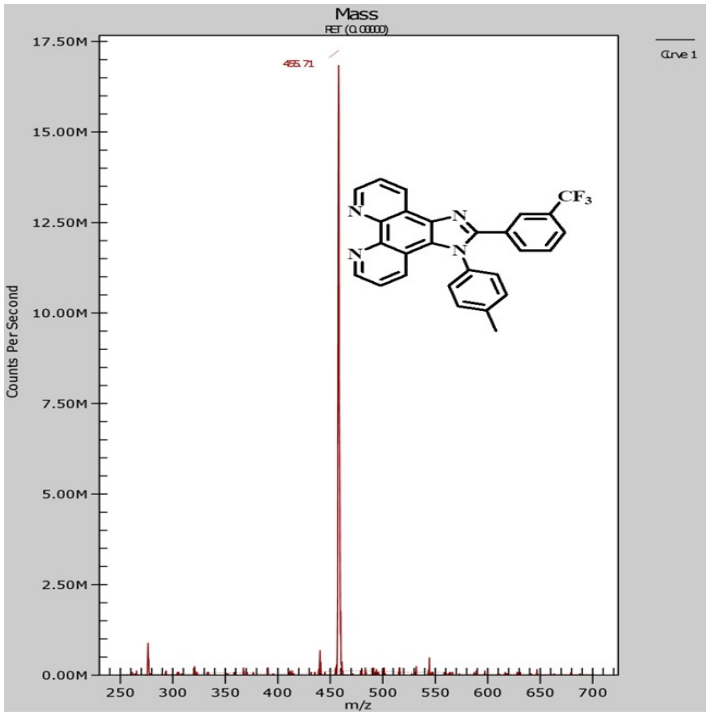


Figure S5. Mass spectral data of Phen-pCH_3-mCF_3

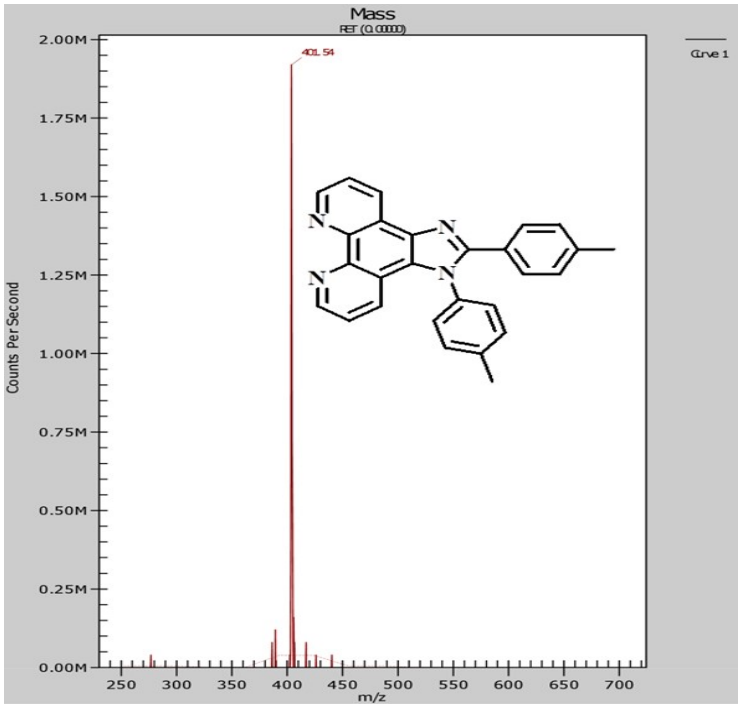


Figure S6. Mass spectral data of Phen-pCH_3-pCH_3

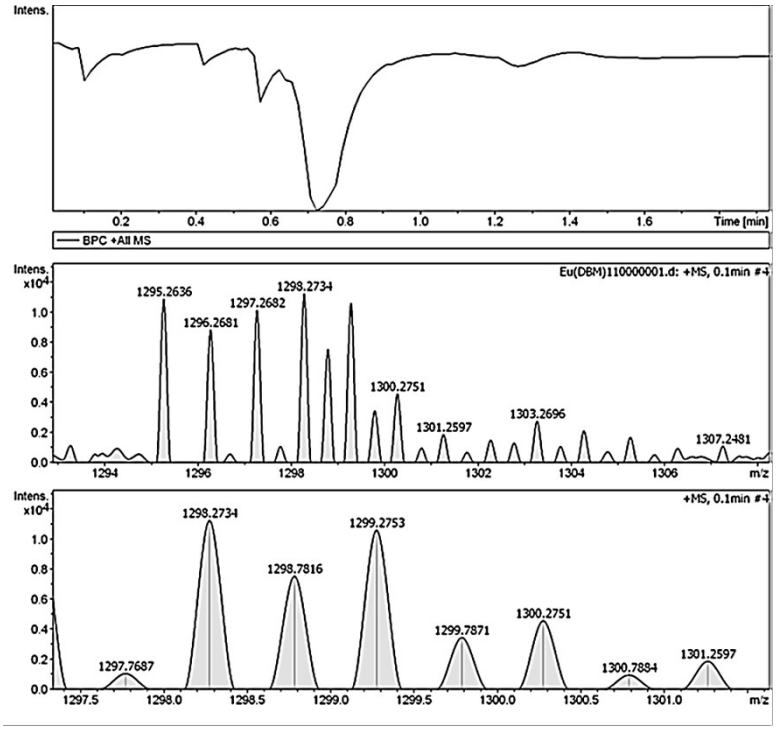


Figure S7. Mass spectral data of $Eu(DBM)_3$Phen-pCH_3-mCF_3

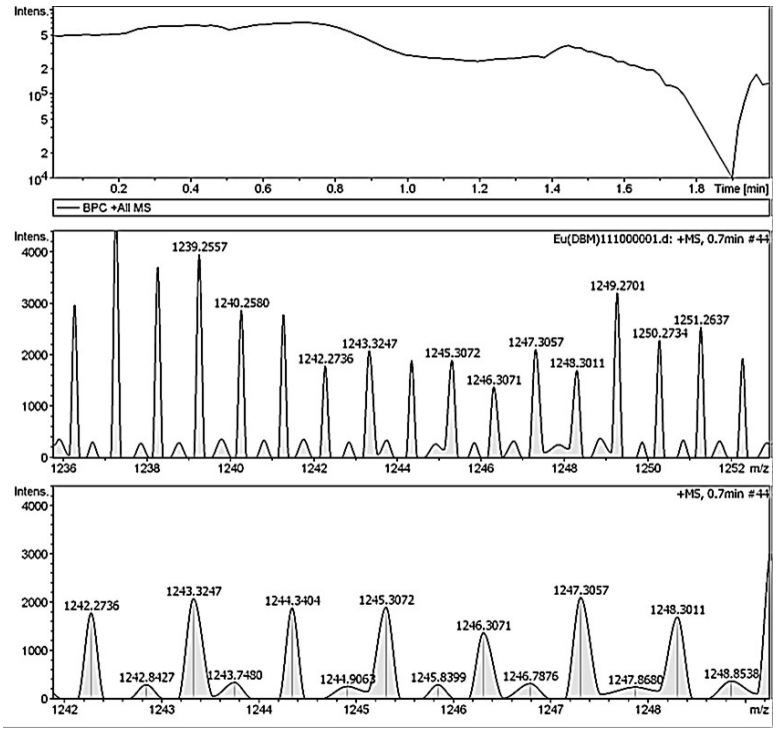
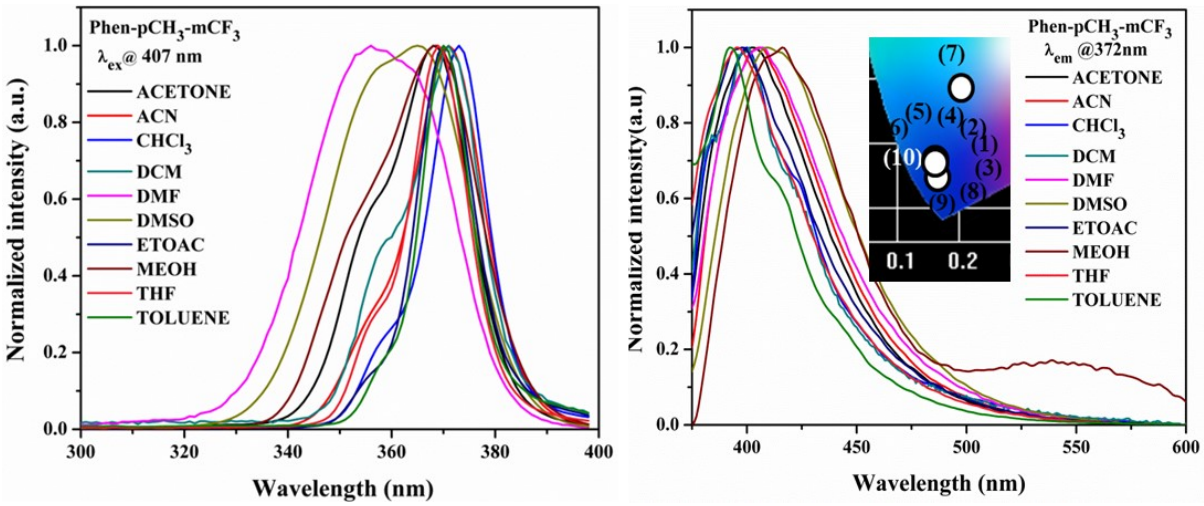


Figure S8. Mass spectral data of $Eu(DBM)_3Phen\text{-}pCH_3\text{-}pCH_3$

Solvatochromism study of ligands:



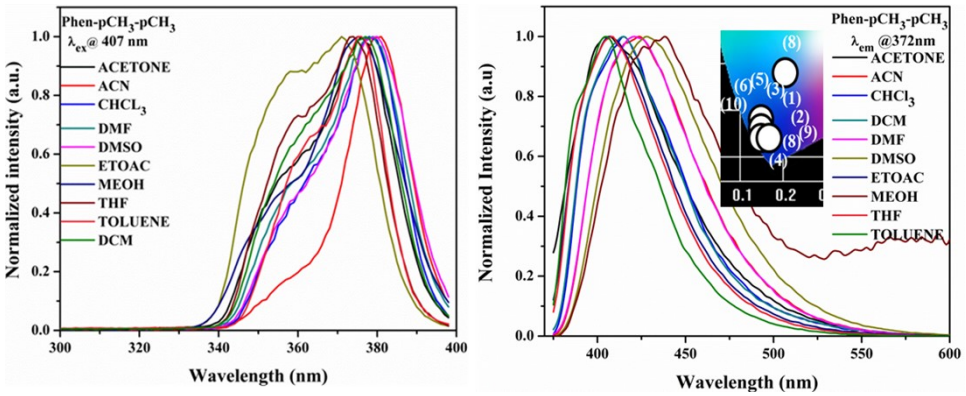


Figure S9. Solvatochromism PL excitation and emission spectra of the all ligands

Stoke's shift:

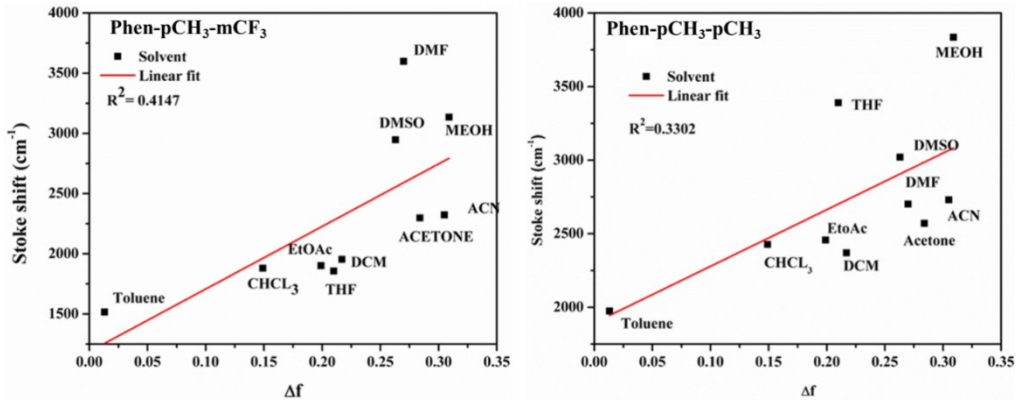


Figure S10. Stoke's shift of all ligands Δυ versus the Lippert solvent parameter Δf = f(ε) – f(n2) The straight line represents the linear fit to the 10 data points.

Δf = (ε - 1)/(2ε + 1) − (n² − 1)/(2n² + 1), where **ε** is the dielectric constant of the solvent. **n** is the refractive index.Represents the polarity of the solvent, relevant for dipolar interactions with excited states.

PMMA of ligands

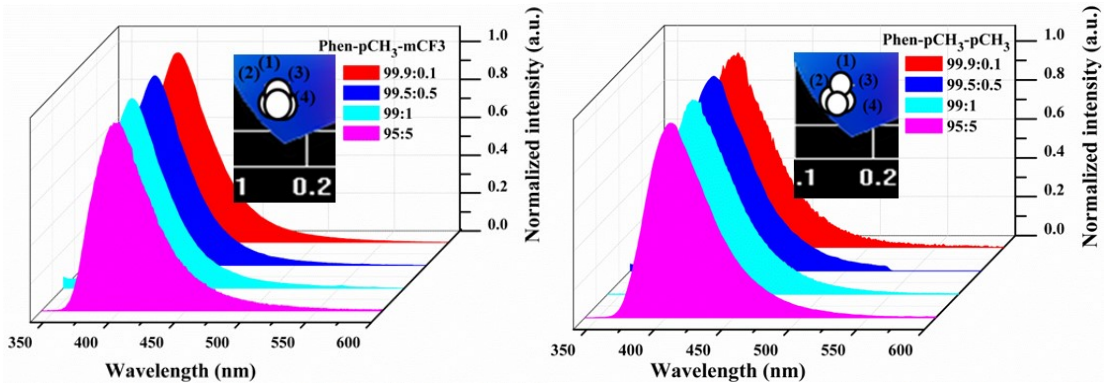


Figure S11. PL emission spectra of the all the Phen-pCH_3-mCF_3 and Phen-pCH_3-pCH_3 in thin films using a PMMA matrix.

PL lifetime

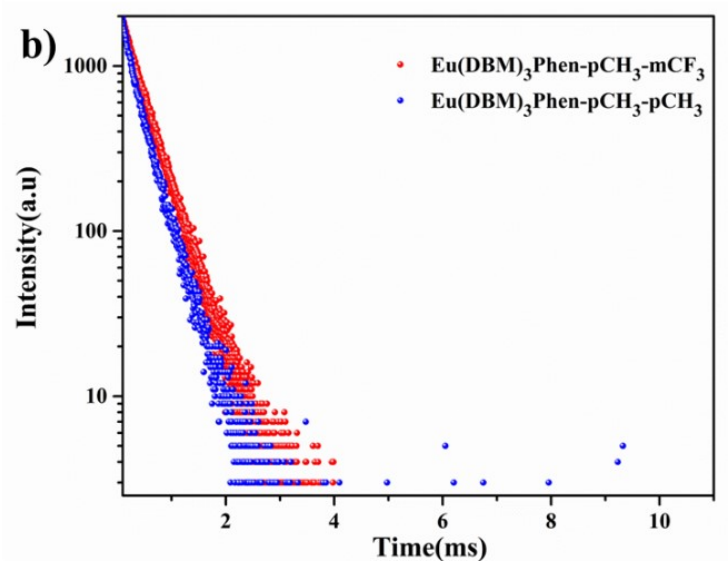


Figure S12. PL lifetime of complexes in solution $CHCl_3$(conc $1x10^{-5}$).

PL Quantum Efficiency

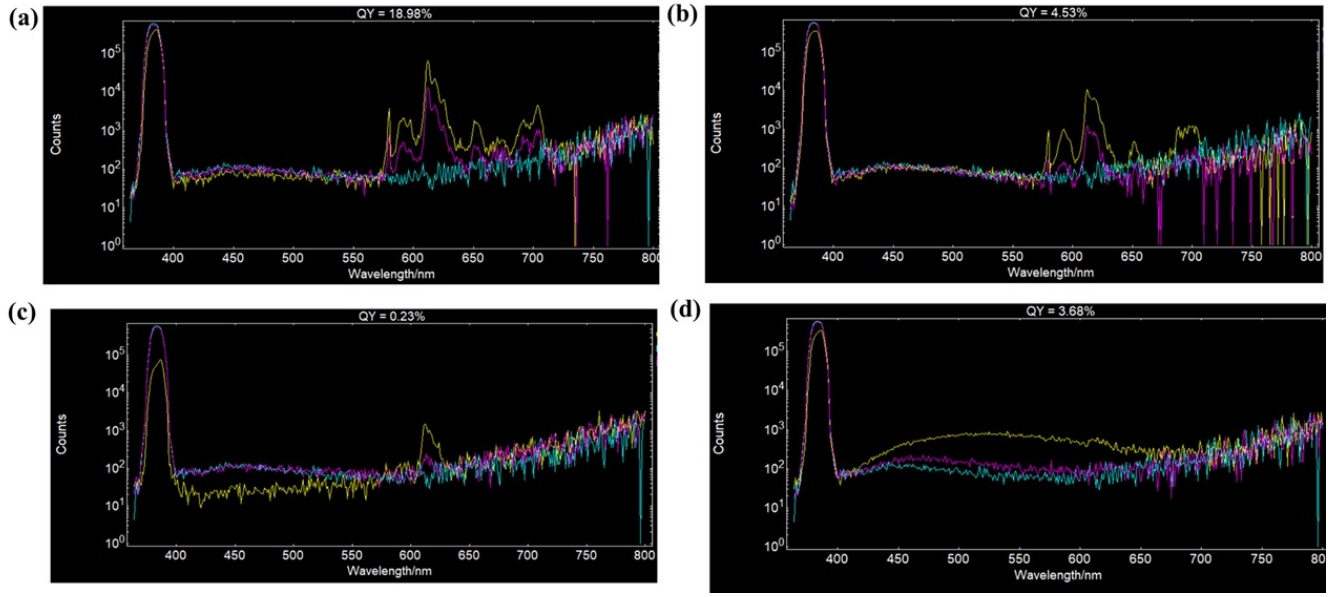


Figure S13. (a) Quantum efficiency of $Eu(DBM)_3Phen\text{-}pCH_3\text{-}mCF_3$ (b) Quantum efficiency of $Eu(DBM)_3Phen\text{-}pCH_3\text{-}mCF_3$ doped in PMMA (c) Quantum efficiency of $Eu(DBM)_3Phen\text{-}pCH_3\text{-}pCH_3$ (d) Quantum efficiency of $Eu(DBM)_3Phen\text{-}pCH_3\text{-}pCH_3$ doped in PMMA.

Phosphorescence at 77K spectra

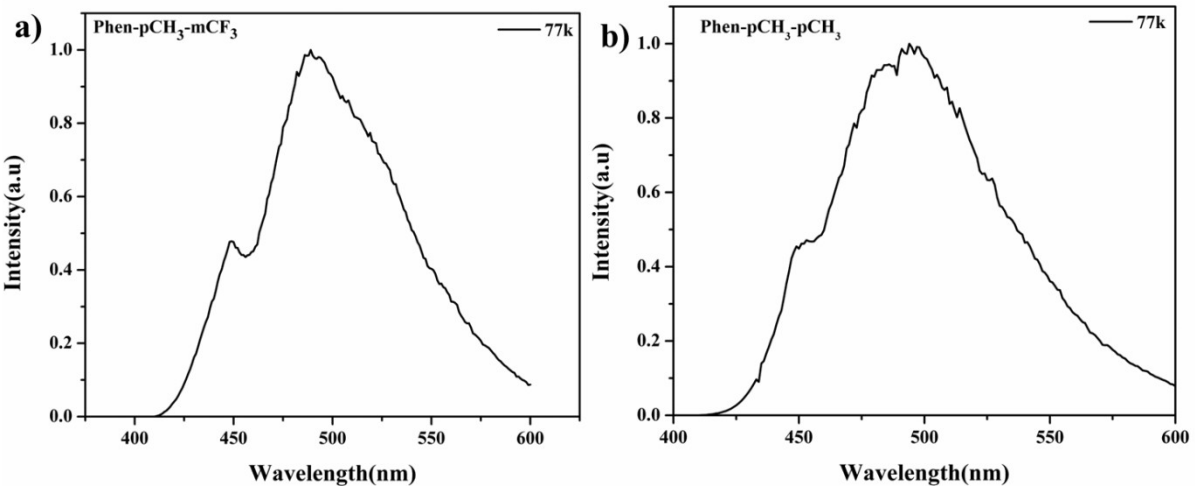


Figure S14. Phosphorescence emission spectrum of Phen-pCH_3-mCF_3 and Phen-pCH_3-pCH_3 at 77 K.

DFT Analysis:

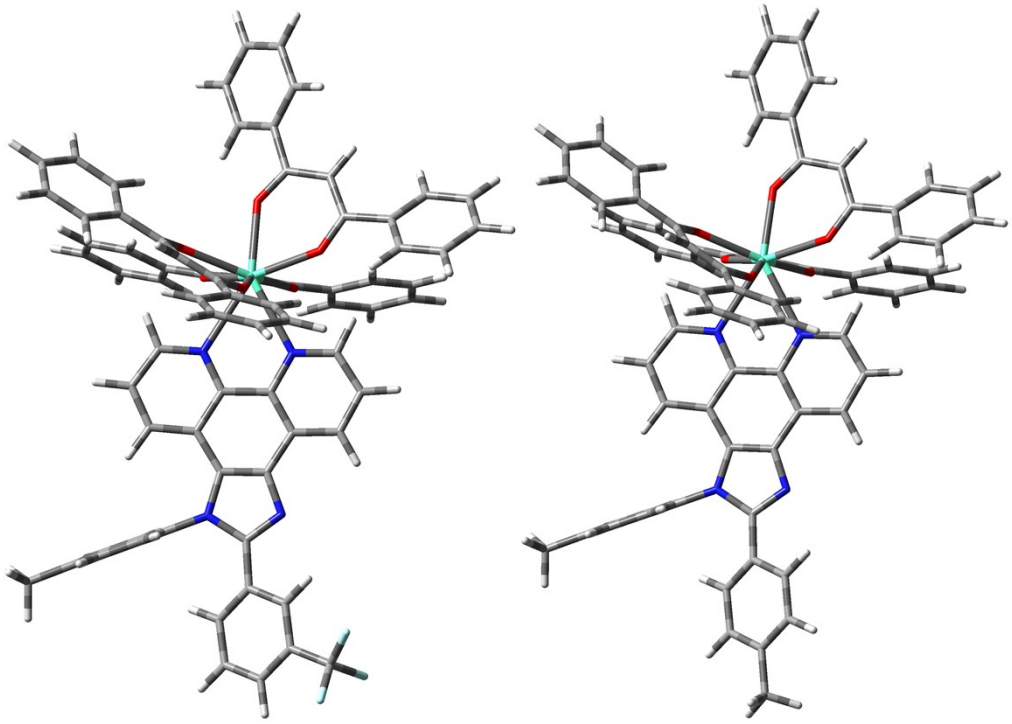


Figure S15. Optimized geometries of the Eu-complexes **Eu(DBM)$_3$Phen-pCH_3-mCF3 in left and Eu(DBM)$_3$Phen-pCH_3-pCH_3 in right** at DFT B3LYP functional along with the 6-31G** basis set for H, C, N, O atoms and Stuttgart/Dresden ECP – SDD basis set for Eu atom. The colour codes for the atoms are: H-white, C-grey, N-blue, O-red and Eu-cyan.

Sensing

The red emission of Eu(III) complex can be quenched or alter when exposed to acidic vapours and recovered the same by basic vapours. After exposing the complexes to the deadly vapours, an emission intensity study was done to turn the Eu(III) complexes on and off, as shown in the manuscript. When the Eu(III) complex was showing to HCl gas in a closed environment, the red emission of the complex vanished. The red luminescence of the non-luminescent Eu(III) complex (switched off) became apparent to the naked eye after repeated exposure to basic gas. This demonstrates that the presently studied Eu-complexes can be employed as potential vapoluminescent sensors for visual detection of gases. The protonation of ancillary ligands/DBM in the existence of HCl vapours generates Eu(III) complexes with an imperfect coordination, which shifts or diminishes the emission intensity (612 nm) in the presence of the HCl vapours, and the reappearance of the same (612 nm) in the presence of the basic vapours environment.1 However, in the presence of NH_3 vapours the deprotonation of DBM takes place through neutralization, which favours the complete coordination of Eu(III) ion, leading to enhancement in the emission intensity (612 nm) as shown in the **Figure S16**.

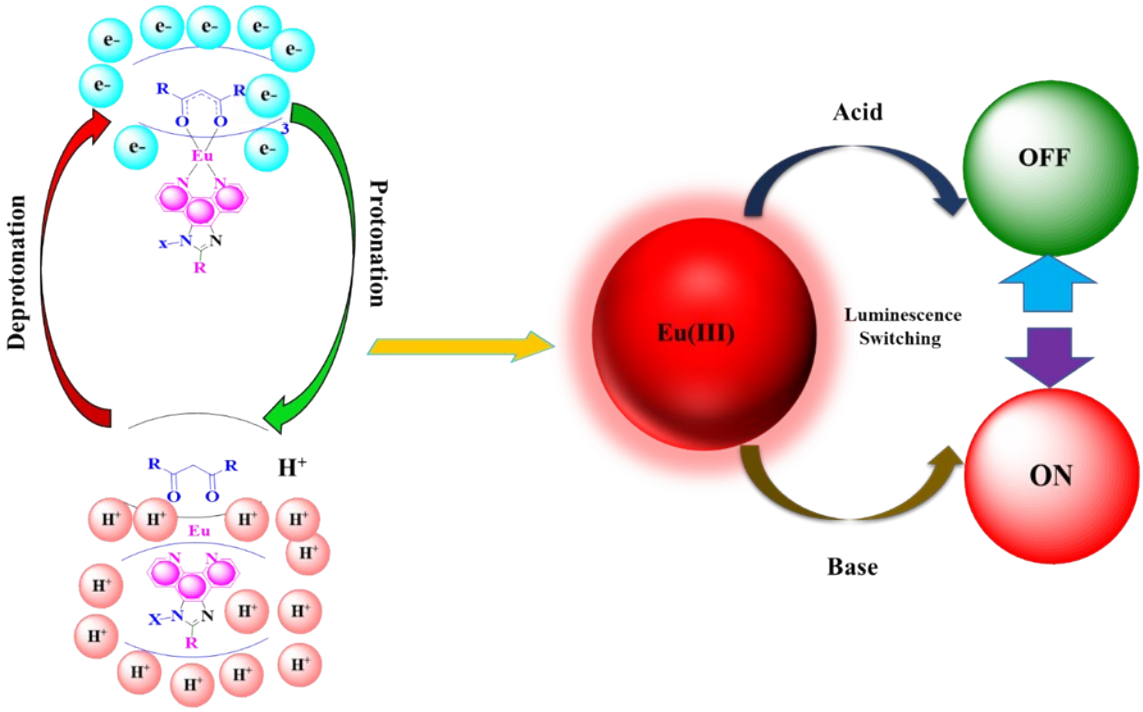


Figure S16. Schematic representation of protonation-deprotonation and on-off-on luminescence switching.

Table S2. The computed vertical transitions and there oscillator strengths (*f*) and configuration of the ligands.

Luminophores	State	Energy (eV)	λ_{max} nm	*f*	Configuration
Phen-pCH_3-mCF_3 Singlet	Gas	3.693	335.6	0.131	HOMO-1→LUMO (12.42%) HOMO→LUMO (36.09%) HOMO→LUMO+1 (57.27%)
		3.751	330.5	0.354	HOMO→LUMO (58.47%)
		3.941	314.6	0.0001	HOMO-2→LUMO (26.00%) HOMO-2→LUMO+1 (61.90%)
Triplet	Gas	2.738	452.6	0	HOMO→LUMO (61.67%) HOMO→LUMO+4 (12.30%)
		3.178	390.1	0	HOMO-7→LUMO+1 (10.07%) HOMO-1→LUMO+1 (28.69%) HOMO→LUMO (22.27%) HOMO→LUMO+1 (17.61%) HOMO→LUMO+3 (34.09%)
		3.276	378.4	0	HOMO→LUMO (13.91%) HOMO→LUMO+2 (49.53%)
Phen-pCH_3-pCH_3 Singlet	Gas	3.602	344.1	0.026	HOMO→LUMO+1 (49.94%)
		3.784	327.6	0.349	HOMO→LUMO (47.83%) HOMO→LUMO+1 (46.24%)
		3.953	313.6	0.000	HOMO-2→LUMO (52.69%)
Triplet	Gas	2.765	448.3	0	HOMO-4→LUMO+4 (11.20%) HOMO-1→LUMO (14.33%) HOMO→LUMO (48.29%) HOMO→LUMO+2 (39.99%)
		3.169	391.1	0	HOMO-4→LUMO+1 (10.42%) HOMO-1→LUMO+1 (11.84%) HOMO→LUMO (44.17%) HOMO→LUMO+2 (21.31%) HOMO→LUMO+4 (17.75%)
		3.222	384.7	0	HOMO-5→LUMO+5 (11.67%) HOMO-4→LUMO (22.63%) HOMO-1→LUMO+1 (16.94%) HOMO→LUMO+1 (34.24%) HOMO→LUMO+2 (16.86%) HOMO→LUMO+3 (14.47%) HOMO→LUMO+4 (37.62%)

Table ST2 Cartesian coordinates for optimized geometry of Phen-pCH_3-mCF_3

6	-4.848218000	1.712184000	0.377373000
6	-3.489396000	1.529453000	0.232149000
6	-2.973320000	0.226369000	0.075130000
6	-3.910954000	-0.856899000	0.095478000
6	-5.681473000	0.585186000	0.364826000
6	-1.587794000	-0.119086000	-0.085508000
6	-3.456327000	-2.250678000	-0.023425000
6	-2.073537000	-2.534848000	-0.147601000
6	-1.154556000	-1.435665000	-0.171052000
6	-1.667311000	-3.876757000	-0.245782000
1	-0.612323000	-4.102648000	-0.342380000
6	-2.628623000	-4.863547000	-0.219101000
6	-3.976393000	-4.481763000	-0.096083000
1	-5.267286000	2.703901000	0.500962000
1	-2.827177000	2.382449000	0.244252000
1	-6.757888000	0.696627000	0.471036000
1	-2.363581000	-5.911790000	-0.292180000
1	-4.755622000	-5.240060000	-0.075044000
6	0.632839000	-0.253713000	-0.274904000
7	0.205220000	-1.500306000	-0.280052000
7	-0.424652000	0.647401000	-0.162280000
6	-0.337368000	2.075872000	-0.058201000
6	0.017166000	2.664942000	1.152931000
6	-0.615896000	2.874589000	-1.166735000
6	0.099456000	4.050898000	1.248297000
1	0.223382000	2.038256000	2.012240000
6	-0.534866000	4.259263000	-1.057630000
1	-0.899043000	2.408772000	-2.103483000
6	-0.171572000	4.871467000	0.147989000

6	2.065460000	0.078216000	-0.359256000
6	2.578337000	1.284684000	-0.854886000
6	2.970142000	-0.916178000	0.049054000
6	3.953807000	1.494236000	-0.924029000
1	1.914083000	2.062601000	-1.201251000
6	4.338737000	-0.698205000	-0.023534000
1	2.580532000	-1.853767000	0.419180000
6	4.842154000	0.511626000	-0.507844000
1	4.331347000	2.433300000	-1.311302000
1	5.911232000	0.677043000	-0.552037000
6	5.299455000	-1.784603000	0.378008000
9	4.736700000	-2.694283000	1.198854000
9	6.382932000	-1.284100000	1.015839000
9	5.765896000	-2.460990000	-0.698109000
7	-5.233252000	-0.650721000	0.233604000
7	-4.384479000	-3.228196000	-0.001130000
1	0.375031000	4.501298000	2.195914000
1	-0.757723000	4.873530000	-1.923578000
6	-0.051171000	6.371891000	0.251712000
1	-0.299494000	6.722954000	1.255551000
1	0.972674000	6.695704000	0.035915000
1	-0.710438000	6.875327000	-0.458302000

Table ST3 Cartesian coordinates for optimized geometry of Phen-pCH_3-pCH_3

6	3.004335000	3.319933000	-0.155360000
6	1.916404000	2.474455000	-0.107701000
6	2.117947000	1.080753000	-0.023988000
6	3.473283000	0.614898000	-0.016089000
6	4.289785000	2.761969000	-0.120068000
6	1.087897000	0.081118000	0.032505000

6	3.774627000	-0.823484000	0.025437000
6	2.716470000	-1.766728000	0.043623000
6	1.369875000	-1.277978000	0.040400000
6	3.034920000	-3.135641000	0.069691000
1	2.231482000	-3.862076000	0.085790000
6	4.361480000	-3.507842000	0.078021000
6	5.340011000	-2.497925000	0.061249000
1	2.873156000	4.393734000	-0.220961000
1	0.916568000	2.881104000	-0.139744000
1	5.167864000	3.402830000	-0.149304000
1	4.655294000	-4.550869000	0.099018000
1	6.394616000	-2.763767000	0.069720000
6	-0.773377000	-1.156699000	0.062577000
7	0.222744000	-2.020524000	0.052082000
7	-0.305596000	0.157558000	0.055810000
6	-1.091729000	1.356361000	0.016764000
6	-1.668731000	1.773970000	-1.179778000
6	-1.267044000	2.112722000	1.175071000
6	-2.421100000	2.944369000	-1.212470000
1	-1.523120000	1.184222000	-2.076692000
6	-2.016939000	3.283510000	1.129045000
1	-0.809820000	1.784483000	2.101212000
6	-2.609537000	3.718243000	-0.062464000
6	-2.182782000	-1.581379000	0.053599000
6	-3.241947000	-0.843409000	0.596888000
6	-2.471904000	-2.843451000	-0.494517000
6	-4.540499000	-1.346282000	0.577014000
1	-3.064493000	0.118277000	1.056443000
6	-3.768196000	-3.333316000	-0.509901000
1	-1.656667000	-3.429750000	-0.897805000

6	-4.832391000	-2.592805000	0.021609000
1	-5.340118000	-0.755779000	1.012414000
6	-6.241829000	-3.129560000	-0.013644000
7	4.517928000	1.462212000	-0.057891000
7	5.068055000	-1.204841000	0.035621000
1	-2.865071000	3.262784000	-2.149704000
1	-3.960300000	-4.310366000	-0.942346000
1	-6.290404000	-4.143967000	0.392714000
1	-6.621110000	-3.174466000	-1.040001000
1	-6.922467000	-2.501845000	0.564786000
1	-2.143057000	3.868787000	2.033755000
6	-3.448982000	4.971813000	-0.099718000
1	-3.392814000	5.459996000	-1.075034000
1	-4.502711000	4.741117000	0.090567000
1	-3.129029000	5.689037000	0.659027000

Table ST4 Cartesian coordinates for optimized geometry of $Eu(DBM)_3Phen\text{-}pCH_3\text{-}mCF_3$

C	-3.68614000	5.22091200	2.69626800
C	-3.35855300	3.93541800	2.27031100
C	-3.03232600	2.93475300	3.20031200
C	-3.02238600	3.25984600	4.56560900
C	-3.34088300	4.54937000	4.99085100
C	-3.67901700	5.53253800	4.05837800
H	-3.94765900	5.98111500	1.96513800
H	-3.35270900	3.67783400	1.21630700
H	-2.74044000	2.51127100	5.29889100
H	-3.32040800	4.78801600	6.05068800
H	-3.93110300	6.53572400	4.39125700
C	-2.69418800	1.56669300	2.67695300
C	-2.81037800	0.44414200	3.52338100

C	-2.48392200	-0.86571300	3.12064100
H	-3.20583400	0.58898900	4.51849500
C	-2.57817300	-1.99075900	4.11053000
C	-2.74889100	-3.29697600	3.62552700
C	-2.48344600	-1.79396900	5.49718200
C	-2.84457000	-4.37440300	4.50338600
H	-2.81206300	-3.44373600	2.55299000
C	-2.56868800	-2.87357000	6.37563300
H	-2.31505400	-0.79690900	5.89099100
C	-2.75504400	-4.16656300	5.88211000
H	-2.98887900	-5.37803700	4.11278400
H	-2.48369300	-2.70601700	7.44578300
H	-2.82506400	-5.00689000	6.56732500
O	-2.32692800	1.51493500	1.46140900
O	-2.11629200	-1.18418400	1.94267000
C	-9.03661900	-0.85745100	-0.45568900
C	-7.74316900	-1.34256000	-0.64600300
C	-6.64210300	-0.67871600	-0.08274300
C	-6.86607600	0.48757400	0.66613000
C	-8.15931500	0.96475900	0.86606800
C	-9.24928900	0.29357600	0.30588200
H	-9.87829500	-1.37506800	-0.90738500
H	-7.58970300	-2.22371700	-1.26051800
H	-6.00881000	1.00075100	1.08782700
H	-8.31842800	1.86151500	1.45856100
H	-10.25801300	0.66796900	0.45725900
C	-5.22797000	-1.14740600	-0.26215500
C	-4.97382200	-2.50719300	-0.55321300
C	-3.69167300	-3.02555000	-0.79807400
H	-5.81348800	-3.18472500	-0.60985500

C	-3.53841800	-4.49237300	-1.08211900
C	-4.41366000	-5.45816600	-0.56056200
C	-2.46483300	-4.91713800	-1.88085400
C	-4.22374700	-6.81175100	-0.83786500
H	-5.22894100	-5.15285000	0.08755900
C	-2.28298100	-6.26835900	-2.16881700
H	-1.78834700	-4.16695800	-2.27619000
C	-3.16180900	-7.22102700	-1.64722000
H	-4.90271600	-7.54814200	-0.41701600
H	-1.45635600	-6.58000300	-2.80156100
H	-3.01810700	-8.27531200	-1.86673800
O	-4.32210100	-0.26987100	-0.11545100
O	-2.61641400	-2.33461900	-0.82837500
C	0.69220400	-2.15058400	-5.59453200
C	-0.00769300	-1.55489800	-4.54781000
C	-0.34473300	-0.19303200	-4.59259400
C	0.05795600	0.56274500	-5.70514000
C	0.76538000	-0.03109600	-6.74972700
C	1.08023200	-1.39079400	-6.70086100
H	0.93638800	-3.20844100	-5.54920000
H	-0.30901500	-2.12610500	-3.67668700
H	-0.15952300	1.62486500	-5.74648000
H	1.07542600	0.56938800	-7.60050300
H	1.62840900	-1.85341500	-7.51695800
C	-1.10190400	0.39301400	-3.43446000
C	-1.80353200	1.60424600	-3.59867600
C	-2.50836600	2.23848000	-2.55493300
H	-1.86882200	2.03120300	-4.58912700
C	-3.26598500	3.50418700	-2.83915400
C	-4.37042400	3.81230300	-2.02854300

C	-2.90806300	4.39520700	-3.86239300
C	-5.10925600	4.97285800	-2.24894100
H	-4.63853100	3.11733900	-1.23978300
C	-3.63973600	5.56388300	-4.07342600
H	-2.03908100	4.18880300	-4.47926400
C	-4.74534800	5.85360800	-3.27105800
H	-5.97156600	5.19059900	-1.62474600
H	-3.34443500	6.25031100	-4.86226500
H	-5.31834600	6.76120800	-3.44006300
O	-1.07498800	-0.27528300	-2.35122600
O	-2.56972500	1.81314300	-1.35742200
C	1.36427700	3.39080800	0.06339800
C	2.60694700	2.80466200	0.20610300
C	2.71309800	1.39829400	0.28571500
C	1.50025800	0.64623500	0.18676400
C	0.22654200	2.57379300	-0.00534100
C	3.92346100	0.63924800	0.44576300
C	1.50618100	-0.81393100	0.23539000
C	2.72626100	-1.51818100	0.37588400
C	3.93474900	-0.75251500	0.46970800
C	2.69288600	-2.92466300	0.42091800
H	3.62444400	-3.47021900	0.53032700
C	1.47314100	-3.56416400	0.32746900
C	0.30712100	-2.79046900	0.18777300
H	1.26018700	4.46897700	0.00445200
H	3.49322800	3.42291600	0.25698000
H	-0.77098600	2.98869700	-0.10351900
H	1.39790400	-4.64589000	0.35910900
H	-0.66953100	-3.25367400	0.09365200
C	5.99198900	-0.17474200	0.66000600

N	0.29780300	1.24801100	0.04676300
N	0.31849500	-1.46136800	0.14212300
C	5.77977200	2.34851000	0.54407000
C	5.71092700	3.15341100	1.68548100
C	6.34296900	2.84806600	-0.63151500
C	6.20625700	4.45550800	1.64238100
H	5.26533900	2.75854100	2.59337100
C	6.83951900	4.15094000	-0.65895100
H	6.38525600	2.21928500	-1.51504600
C	6.78219400	4.97547400	0.47316500
H	6.14424000	5.07774200	2.53113800
H	7.27413300	4.53406600	-1.57820500
N	5.26098200	1.01075900	0.57876300
N	5.20685000	-1.23578100	0.59609600
C	7.45608700	-0.29303000	0.78009100
C	8.28687600	0.66830300	1.37861200
C	8.03788900	-1.47759800	0.29376800
C	9.66278700	0.45526800	1.46972700
H	7.86726700	1.57758300	1.78890900
C	9.41065300	-1.68201200	0.39042700
H	7.39972000	-2.22667600	-0.15816900
C	10.23415300	-0.71386500	0.97511200
H	11.30477300	-0.87655300	1.03581400
C	7.34580300	6.37588100	0.44375200
H	8.39534800	6.38298400	0.76283300
H	7.30889000	6.80095600	-0.56316000
H	6.79752700	7.04241900	1.11569000
Eu	-1.97622500	-0.17031200	-0.17402000
H	10.29052600	1.20858900	1.93564800
C	10.01419300	-2.97535300	-0.09087600

F	9.26163800	-3.56371800	-1.04442600
F	10.14534300	-3.86738700	0.91781000
F	11.25035100	-2.78541100	-0.60643600

Table ST5 Cartesian coordinates for optimized geometry of $Eu(DBM)_3Phen\text{-}pCH_3\text{-}mCF_3$

C	-2.73071200	5.31885600	2.97051400
C	-2.54921600	4.02552400	2.48499900
C	-2.28849400	2.96114400	3.36357300
C	-2.19295200	3.22933000	4.73805900
C	-2.36517900	4.52561400	5.22246800
C	-2.63999900	5.57368800	4.34127500
H	-2.94307300	6.12977400	2.27906900
H	-2.60998900	3.81250000	1.42285000
H	-1.95775100	2.42828700	5.43123900
H	-2.27959000	4.71846200	6.28833100
H	-2.77778400	6.58266000	4.72030400
C	-2.10905500	1.58830300	2.78064400
C	-2.30782100	0.45210000	3.58643000
C	-2.14979700	-0.87264800	3.12205300
H	-2.64681200	0.59812000	4.60196600
C	-2.33918100	-2.01572000	4.07841400
C	-2.67812700	-3.27381500	3.55615800
C	-2.17218300	-1.88463900	5.46589700
C	-2.86691200	-4.36616600	4.39968200
H	-2.79545000	-3.36996300	2.48242000
C	-2.35017300	-2.98065300	6.30960500
H	-1.87484300	-0.92966900	5.88685500
C	-2.70374800	-4.22341000	5.77999800
H	-3.14112800	-5.33072600	3.98122800
H	-2.20730500	-2.86561500	7.38052900

H	-2.84629800	-5.07597900	6.43833900
O	-1.79248500	1.54953700	1.54647500
O	-1.86906100	-1.18601500	1.92240600
C	-8.75640200	0.07924500	-0.34667900
C	-7.53390100	-0.54915000	-0.58116300
C	-6.35240300	-0.04654800	-0.01368500
C	-6.42336200	1.10653100	0.78424800
C	-7.64653800	1.72692700	1.02778700
C	-8.81769800	1.21513200	0.46336000
H	-9.66081600	-0.31466600	-0.80195600
H	-7.49710200	-1.41609500	-1.23276900
H	-5.50464000	1.49618300	1.20865200
H	-7.68730700	2.61131000	1.65768400
H	-9.77153700	1.70135800	0.64881300
C	-5.00867200	-0.67506000	-0.23829200
C	-4.92283000	-2.03725800	-0.59244500
C	-3.71028400	-2.69291600	-0.87755400
H	-5.83822400	-2.60546800	-0.67263600
C	-3.74003300	-4.14912800	-1.24760300
C	-4.72185800	-5.03131200	-0.77004700
C	-2.73261300	-4.65128800	-2.08649700
C	-4.69972800	-6.37910300	-1.12844000
H	-5.48903100	-4.66900200	-0.09312400
C	-2.71887200	-5.99477100	-2.45604300
H	-1.97368800	-3.96528600	-2.44735200
C	-3.70228300	-6.86404600	-1.97703200
H	-5.45938000	-7.05220300	-0.74073500
H	-1.94179600	-6.36535200	-3.11910100
H	-3.68955000	-7.91291000	-2.26017100
O	-4.00066500	0.08318400	-0.07046600

O	-2.56255200	-2.13790400	-0.87719300
C	0.99562900	-2.27599400	-5.52318600
C	0.32872000	-1.62251300	-4.48960400
C	0.08367400	-0.24169500	-4.55197700
C	0.54518500	0.47191500	-5.66952700
C	1.21923600	-0.18023000	-6.70146700
C	1.44198600	-1.55716100	-6.63488200
H	1.16901000	-3.34703700	-5.46310600
H	-0.01478600	-2.16092100	-3.61326100
H	0.40033400	1.54547800	-5.72699300
H	1.57488200	0.38827500	-7.55638000
H	1.96413900	-2.06491500	-7.44120100
C	-0.64304100	0.40376500	-3.40352800
C	-1.22306700	1.68155700	-3.57401300
C	-1.89277200	2.36889800	-2.54651400
H	-1.21696100	2.12405600	-4.55957100
C	-2.50907400	3.70860900	-2.82634400
C	-3.59440500	4.11912400	-2.03548800
C	-2.03772500	4.57076500	-3.82840200
C	-4.20515900	5.35192000	-2.25572200
H	-3.95043000	3.44704000	-1.26190400
C	-2.64134100	5.81021500	-4.03941300
H	-1.17942600	4.28420800	-4.42789800
C	-3.72999600	6.20236000	-3.25748900
H	-5.05422600	5.65001300	-1.64676600
H	-2.25896000	6.47202400	-4.81170400
H	-4.20304600	7.16590300	-3.42612200
O	-0.70339600	-0.27071300	-2.32979300
O	-2.03813400	1.92990000	-1.35728100
C	2.09348600	3.00485100	0.16526700

C	3.25380500	2.26004000	0.24901700
C	3.18171200	0.84926400	0.27079400
C	1.88018400	0.26131400	0.17682900
C	0.85966100	2.34216900	0.09991800
C	4.28901600	-0.06153300	0.36598800
C	1.70167000	-1.18802400	0.16359600
C	2.82676100	-2.04463400	0.24230300
C	4.12458900	-1.44300600	0.33367200
C	2.61621000	-3.43644400	0.23097200
H	3.47380500	-4.09831200	0.29338700
C	1.32347700	-3.91222000	0.14443700
C	0.26187900	-2.99230400	0.06640400
H	2.12675000	4.08905200	0.15047900
H	4.21292000	2.75802900	0.29793900
H	-0.07722700	2.88686300	0.04882700
H	1.11205200	-4.97633700	0.13470500
H	-0.76715900	-3.32403000	-0.02193600
C	6.24428600	-1.13941100	0.48885000
N	0.76137300	1.01692400	0.09898600
N	0.43998600	-1.67517400	0.07380500
C	6.34928500	1.39322800	0.47999600
C	6.40379400	2.15382500	1.65209400
C	6.94877500	1.86673500	-0.68836800
C	7.05703700	3.38502200	1.64696100
H	5.93027000	1.78020900	2.55479400
C	7.60389500	3.09771300	-0.67828900
H	6.89632800	1.27302800	-1.59522600
C	7.67154000	3.87633200	0.48521600
H	7.09059100	3.97325000	2.56015100
H	8.06622900	3.46070600	-1.59226300

N	5.66647900	0.13165400	0.47548200
N	5.32735500	-2.08860100	0.40537800
C	7.68408100	-1.44017700	0.55874400
C	8.64029500	-0.62390000	1.18325100
C	8.11476800	-2.65938800	0.00146800
C	9.97911200	-1.01084200	1.23009700
H	8.34774200	0.30507800	1.65588900
C	9.45125700	-3.03402700	0.05429200
H	7.37822200	-3.30462500	-0.46404600
C	10.41358700	-2.21440500	0.66393000
C	8.40635000	5.19541700	0.49595100
H	9.45453900	5.05835200	0.78923300
H	8.40359800	5.66316600	-0.49264600
H	7.95955400	5.89713200	1.20624200
Eu	-1.67986100	-0.04538100	-0.15408600
H	10.69822300	-0.36467200	1.72736300
H	9.75607100	-3.98043200	-0.38590400
C	11.86863100	-2.61528200	0.69218200
H	12.34892200	-2.43127000	-0.27710100
H	12.42521300	-2.05149200	1.44616300
H	11.98536200	-3.68169800	0.91090000

References

1. M. L. ChaolongYang, JianxinLuo, JianyingMa, LiyanLiang, 2011, 14, 61–63.

2. J. Tomasi, B. Mennucci and R. Cammi, Chem. Rev., 2005, 105, 2999–3093.

3. N. Sabbatini, M. Guardigli and J.-M. Lehn, Coord. Chem. Rev., 1993, 123, 201–228.

4. L. Jun and S. Qiang, 1994, 38, 98–101.

5. G. Zhang, J. Lu, M. Sabat and C. L. Fraser, J. Am. Chem. Soc., 2010, 132, 2160–2162.

6. K. Ueno and A. E. Martell, J. Phys. Chem., 1956, 60, 1270–1275.

7. (a) Becke AD (1993), 98:5648-5652. (b) Lee C, Yang W, Parr RG (1988) Physical Review B 37:785-789.

8. (a) Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) The Journal of Physical Chemistry 98:11623-11627. (b) Vosko SH, Wilk L, Nusair M (1980) Canadian Journal of Physics 58:1200-1211. (c) Hariharan PC, Pople JA (1973) Theoretica chimica acta 28:213-222.

9. a) M. Dolg, H. Stoll, A. Savin, H. Preuss, Theor. Chim. Acta 1989, 75, 173; b) D. Feller, J. Comp. Chem. 1996, 17, 1571; c) K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, J. Chem. Inf. Model. 2007, 47, 1045.

10. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H *et al* Gaussian 16 rev. A.03. In. Wallingford, CT; 2016.