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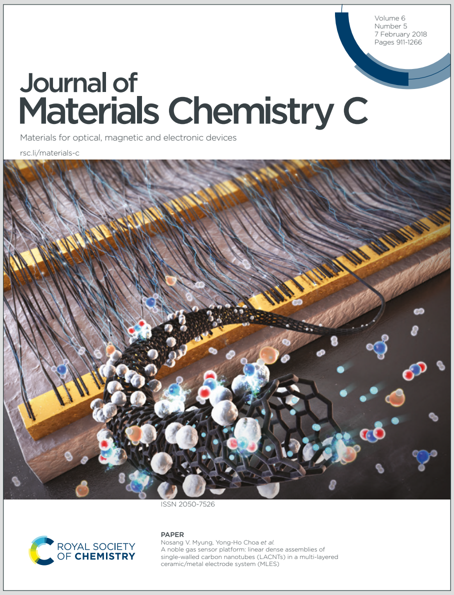

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Synergy in energy transfer between ligand and Eu^{III} ion in molecular Europium complex: a single-component white light emissive luminogens

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Abstract

Promoting from the structural flexibility and easy solution process capability, single component white light emitting pure organo-lanthanide complexes have considered as a promising candidate for solid state lighting. Here in we report a series of ancillary ligand by using imidazo-bipyridyl derivatives and dibenzoylmethane (DBM), as anionic ligand are employed to synthesized ternary Eu(III) complex Eu(DBM)$_3$L-mCF$_3$, Eu(DBM)$_3$L-pCF$_3$, Eu(DBM)$_3$L-pCH$_3$, Eu(DBM)$_3$L-Naph-OCH$_3$. The photophysical and electrochemical properties of the ligand and their Eu(III) complexes were carefully investigated and the energy transfer mechanism were understood by combined experimental and theoretical calculation. Multiple-emission from both ligand and Eu(III)-ion leads to single component white light emission. White light emitting diodes (LED) was fabricated by conjugating the Eu-complex with near UV LED, the results showed superior performance (Commission Internationale de l'Éclairage CIE (x = 0.33, y = 0.33, close to National Television System Committee (NTSC) standard for pure white emission), correlated color temperature CCT (5386K) and color rendering index CRI (63%)). The selected Eu-complex was further coated on blue LED chip and the corresponding white LED showed CIE (x = 0.36, y = 0.35), CCT (4234K) and CRI (75%). In addition, taking benefit of dual characteristic emission of the Eu-complexes, the ratiometric sensing behavior was explored. The Eu(DBM)$_3$L-mCF$_3$ have the relative sensitivity value of 4.9% K^{-1} at 323 K.

Key words: Europium complex, Energy transfer, Temperature sensor, hybrid White LEDs,

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Introduction

In the modern world, a white light-emitting diode (LEDs) has drawn extensive attention due to their diverse advantages over conventional sources. White LEDs are considered as the next-generation lighting foundation that has been utilized broadly in illuminating system and display lighting.[1] White LEDs exhibit, high brightness, low power consumption, long operating time, mechanically robust and thermal stability, has a long lifetime and environmentally-friendly nature.[2] The low color rendering index (CRI) was observed in the white LED generated by combing the blue-chip with YAG: Ce^{3+} yellow phosphors due to lack of red spectral component.[3,4] The alternative approach to produce efficient white-light-emission with good CRI ~~color rendering index~~ is mixing three primary colors (RGB: red, green, and blue) in the appropriate ratio (cover the entire visible spectral range). This can be accomplished by either comprised of multiple luminogens or just a single emitter; comparatively the single component emitters are superior to that of using the multiple emitters.[5-7] This depends on the molecular engineering of the luminogens and precise control of energy transfer. The unique optical characteristics such as sharp emission bands, large Stoke's shift, long lifetime, and tunable emission make lanthanides fascinating luminescent materials, and considered as a potential phosphors for solid state lightings.[8] The organo-lanthanide complexes can give emission in the entire visible spectrum with high color purity by choosing appropriate trivalent lanthanides in the core (for example, generation of primary colors, the following lanthanides could be desired choice, for red- (Eu^{III}, Pr^{III}, Sm^{III}), green- (Tb^{III}, Er^{III}), and blue (Tm^{III}, Ce^{III}, Dy^{III})). Specifically, synergy in energy transfer between ligand and Ln^{III} ion in molecular lanthanide complex plays

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vital role in generation of white light in single component system. Recently, other single component white light emissive luminogens were also been reviewed [which includes perovskite quantum dots, pure organic molecule and organometallic complexes and metal-organic frameworks].[9] The use of single emitters can overcome several complications allied with usage of multiple emitters.[10] Trivalent europium complexes can produce white light by having suitable coordinated ligands (location of excited state levels), which facilitate inefficient energy transfer from triplet excited state to Eu(III) ion excited levels. Controlled energy transfer from a ligand to Eu(III) ion plays a significant role to generate white light emission.[11,12] White light was realized for the single-component europium complexes in organic solvents[13]. Best of our knowledge, obtaining white light emission in solid-state based on europium single component system is very rarely reported.[11,12] Single component white light emissive system is still bottle neck for the solid state lighting applications. In this context, we designed new series of imidazo-bipyridyl derivatives by introducing the electron donating as well as withdrawing group (EDG and EWG) as substitute in the core structure (Fig. 1) and executed excited state calculation to elucidate the location of the singlet and triplet levels. It is well accepted that the location of the higher energy levels (S_1 and T_1) plays vital role in energy transfer from ligand to Eu(III) ion in the molecular complex. According to Latva *et al.,* for efficient energy transfer, the energy difference ΔE ($E(T_1)$ of ancillary ligand to Eu excited level $E(^5D_0)$) should be in the range 2500−4000 cm^{-1}.[14] All the ancillary ligands were further used to coordinate the Eu(III) ion and synthesized series of Eu-molecular complexes. It is further confirms that the Eu-complexes are exhibited white light emission with good Commission International del'Eclairage (CIE) value (close to National Television System Committee (NTSC) standard). Among all, the $Eu(DBM)_3L\text{-}pCH_3$ in 1:50 is showed CIE (x = 0.33, 0.33), which is exactly matching with the NTSC standard value for

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natural light and superior than that of the reported Eu(III) complexes.[11,12] In addition, dual emission behavior motivate to study the ratiometric temperature sensing applications and the selected Eu-complexes showed good sensitivity.

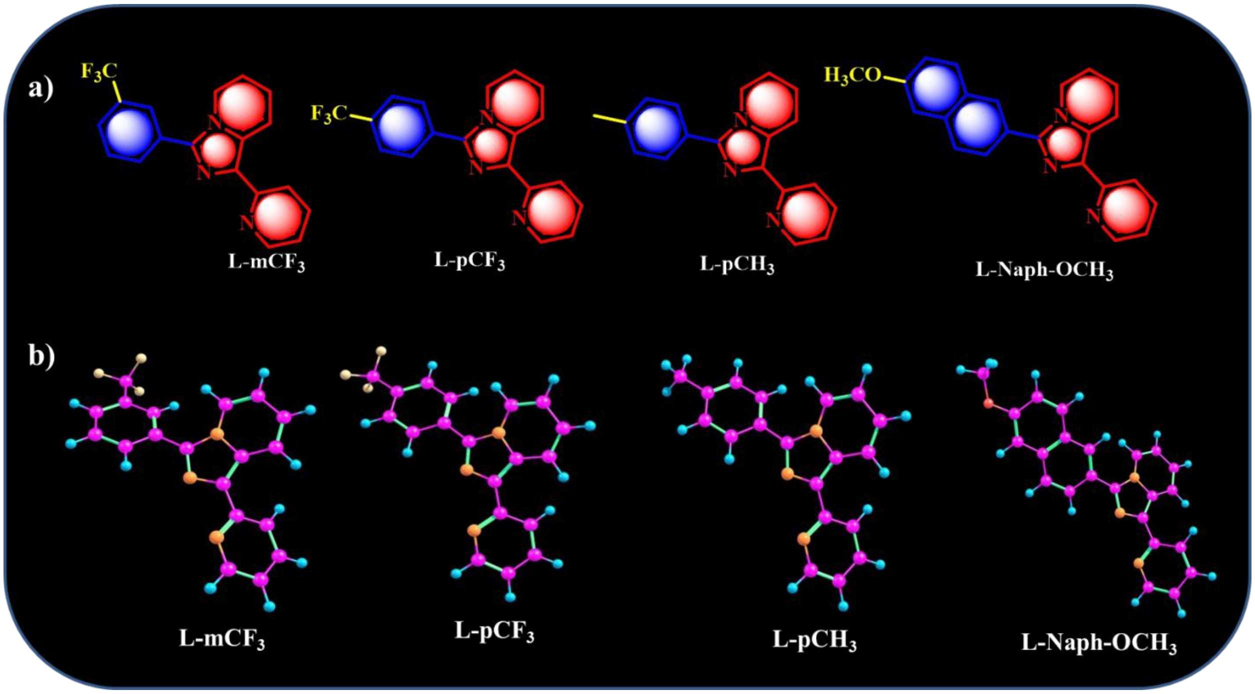

Fig. 1 a) Designed structure and b) optimized geometry of the ligands

Results and Discussion

Density functional theory (DFT) calculations:

A series of imidazo-bipyridyl derivatives were design and synthesized by introducing the electron donating as well as withdrawing group ~~(EDG and EWG)~~ in the core structure. As per the introduction, location of the singlet and triplet level of ancillary as well as anionic ligands are the key component to harvest the energy from ligand to Eu(III) ion in the molecular complexes. DFT and time-dependent density functional theory (TD-DFT) calculation predicts exact location of ground and excited state calculation. In the present investigation, initially theoretical calculation were made to predict the excited state location before proceeding for the synthesis of

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the ligand as well as their respective Eu(III) molecular complexes. The DFT and TD-DFT calculation were executed at the B3LYP/6-31G (d,p) basis set to optimize~~d~~ the geometry of ancillary ligand as well as UV-Vis characteristics and excited state location. The obtained optimized structures of all the ancillary ligands are shown in the Fig. 1. The S_1 and T_1 energy state calculation were also completed with the aid of TD-DFT calculation. The triplet and singlet energy level located at 18841, 18784, 18470, 18171 cm^{-1} and 26834, 26737, 26213, 25551 cm^{-1} for L-mCF_3, L-pCF_3, L-pCH_3, L-Naph-OCH_3, respectively. The excited state (18800 ($^5D_1$) and 17500($^5D_0$) cm^{-1}) of Eu(III) ion and the singlet (28328 cm^{-1}) and triplet(20408 cm^{-1}) energy level of dibenzoylmethane (DBM) is well reported.[15] It is reported by Latva *et al.,* the energy difference ΔE is [E(T1) of ancillary ligand to Eu excited level E($^5D_0$)] should be in the range 2500−4000 cm^{-1} for an efficient energy ransfer.[14] The currently designed ancillary ligands are violating the rule (energy difference between T_1 state of ligand and ($^5D_0$) excited state of Eu(III) ion are <2500 cm^{-1}) as predicted by the DFT calculations as shown in the Fig. 2. Hence, there is a probability of back energy transfer Eu(III) to ligand triplet level, which is responsible for multiple or white emission.[12] The calculated UV-Vis spectra of all the ligands by the ~~time-dependent density functional theory (~~TD-DFT~~)~~ in gas as well as in solution phase are represented in the Fig.S19. Also the electronic distribution on HOMO-LOMO orbitals of ancillary ligands was also identified with the help of DFT calculation as shown in the Table ST8. The energy difference between HOMO and LUMO (band gap) based on theoretical calculation is shown in Fig. 2. The electrochemical analysis of the ancillary ligands as well as their respective Eu-complexes also been executed (details are given in SI). The computed energies of the vertical excitations, their oscillator strengths, orbital contributions as well as Cartesian coordinates (xyz) are tabulated in Table ST9- ST12. The theoretical states that the designed ligands are capable of

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emitting multiple emissions due to insufficient energy transfer. The DFT study is further encouraged to synthesis the ligands and their corresponding Eu-complexes, also to investigate their optical properties in detailed. In addition, the synthesized Eu-complexes can be used as a single component white light emitter and temperature sensors.

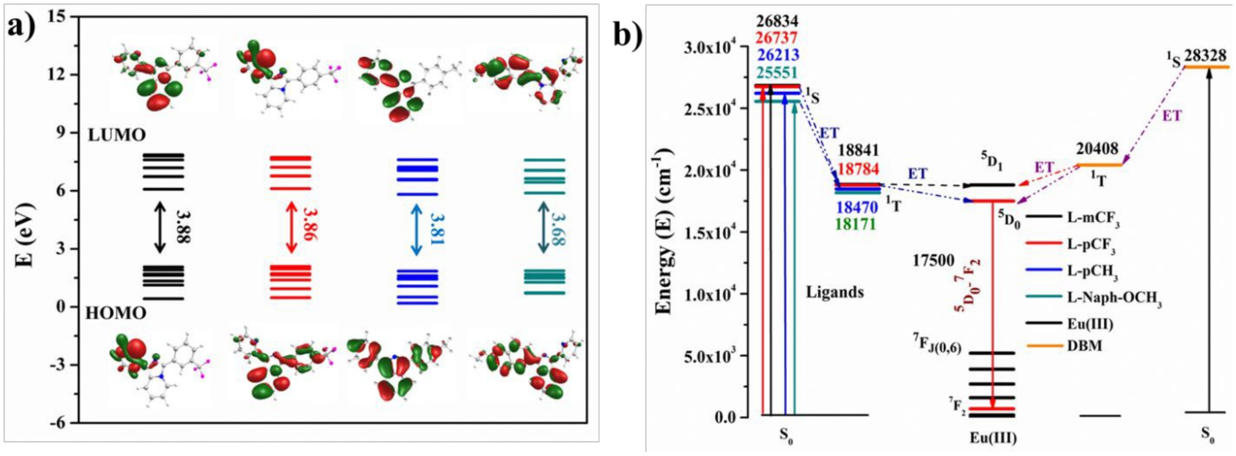

Fig. 2 a) HOMO–LUMO energy gap diagram and b) The energy transfer process from the ligand as well as from DBM to Eu(III) metal ion.

3.1. Synthesis

The synthesis procedures of all the ligands; L-mCF$_3$, L-pCF$_3$, L-pCH$_3$ and L-Naph-OCH$_3$ and their respective Eu(III) complexes; Eu(DBM)$_3$L-mCF$_3$, Eu(DBM)$_3$L-pCF$_3$, Eu(DBM)$_3$L-pCH$_3$, Eu(DBM)$_3$L-Naph-OCH$_3$ are presented in Scheme S1. The NMR (^{1}H and ^{13}C) and mass spectra of the synthesized ligands and their respective complexes are presented in Fig. S1-S8 and Fig.10-17. Fourier transform-Infrared spectroscopy (FT-IR), Electrochemical Properties (CV), TGA (Thermal Study), Judd-Ofelt (J –O) analysis of the ligand and their respective Eu(III) complexes also been executed (details are presented in the SI).

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Photophysical properties

UV-Visible absorption study:

Fig.3 represents the normalized UV-visible absorption spectra of ligand and their corresponding Eu(III)-complex in chloroform (1×10^{-5} mol/L) solution. Ligands exhibit strong UV absorption in the range of 250–350 nm. The broadband appears at 270 nm due to the π→π* transition of the ligand. The theoretical calculation is well agreed with the experimental result as exhibited in Fig. S19. All the Eu(III) complexes exhibit two absorption peak at ~282 nm (intense and high energy) and 352 nm (strong and low energy), the former band is associated to π→π* transition of the aromatic ring of ancillary ligand and the latter absorption is assigned to π→π* transition of the DBM anionic ligand. The observed UV-visible absorption values of all the ancillary ligands and their respective Eu(III) are listed in Table 2.

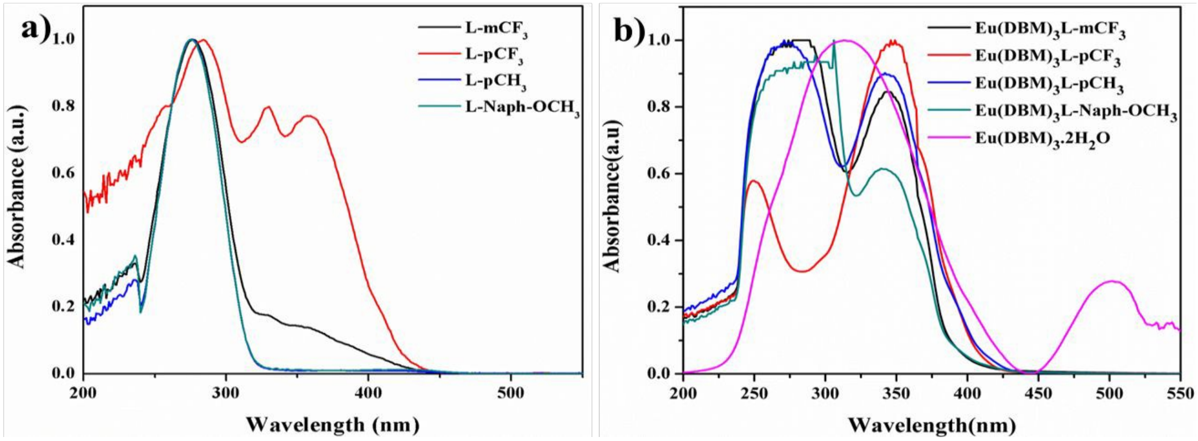

Fig. 3 UV-Vis absorption spectra of a) ligands and b) their respective complexes in chloroform

Photoluminescence (PL) studies:

It is worth to note that the triplet energy state of ligand plays a vital role in energy harvesting process, in addition it also act as a mediator between S1 and excited state Eu levels ($^5D_{0/1}$) in the luminescence process of the Eu(III) complex. The PL spectra of all the ligands and their respective Eu(III) complex were recorded in solid as well as

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solution. The PL spectra of all the ligands L-mCF_3, L-pCF_3, L-pCH_3, L-Naph-OCH_3 displayed in the Fig. 4 shown emission strong band at 466, 480, 509 and 468 nm upon excitation at 428, 429, 438, 445 nm respectively (in solid phase). Similar observation in the solution, the emission band is observed 457, 458, 467 and 473nm upon excitation at 418, 420, 425, 430 nm respectively. There is red shift observed in solid PL spectra compare to the solution state PL spectra, it is due to the aggregation of the molecule in the solid state.

Table 2. The UV-absorption and PL emission data of synthesized ligands and corresponding Eu(III) complexes

S.No.	Compound	λ_{max} (abs) (nm) Solution$^{a\ b}$	$\lambda_{ex}{}^{a}$ (nm)	$\lambda_{em}{}^{a\ c}$ (nm)	I_2/I_1 ratio^{a}	FWHM
1	Eu(DBM)$_3$L-mCF_3	277, 344	382	613	6.65	10.3
2	Eu(DBM)$_3$L-pCF_3	249, 348	382	613	36.5	11.96
3	Eu(DBM)$_3$L-pCH_3	271, 342	390	613	30.0	5.95
4	Eu(DBM)$_3$L-Naph-OCH_3	280, 341	401	613	4.6	9.1
6	Phen-mCF_3-mCF_3	276	418	457	NA	NA
7	Phen-mCF_3-pCF_3	284	420	458	NA	NA
8	Phen-mCF_3-pCH_3	276	425	467	NA	NA
9	Phen-mCF_3-1Naph	277	430	473	NA	NA

[a] measured in chloroform solution at 298 K, [b]absorption peaks from the UV-Vis absorption spectra. [c] emission peaks from photoluminescence emission spectra.

Solvatochromism study for all the synthesized ligand were also been successfully executed (Fig. S20). The PL spectra of all the synthesized Eu(III) complexes in the solid and solution phase are

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exhibited in Fig. 5. All the Eu(III) complexes are excited at ~384 nm, showed strong emission at ~612 nm (due to electric dipole ($^5D_0 \rightarrow ^7F_2$) transition) in solid as well as in solution. Five distinct emission band (Fig. 5) are observed, which can be allotted to the following 4f-4f transitions of Eu^{III} ion: $^5D_0 \rightarrow ^7F_0$ (577 nm), $^5D_0 \rightarrow ^7F_1$ (586 nm), $^5D_0 \rightarrow ^7F_2$ (612 nm), $^5D_0 \rightarrow ^7F_3$ (648 nm) and $^5D_0 \rightarrow ^7F_4$ (710 nm). The two $^5D_0 \rightarrow ^7F_{0,\ 3}$ (~580 nm and 653 nm) transitions are very weak, both are not allowed in electric and magnetic dipole (ED and MD) scheme. The $^5D_0 \rightarrow ^7F_1$ (586 nm) is MD transition and independent of the coordination environment.

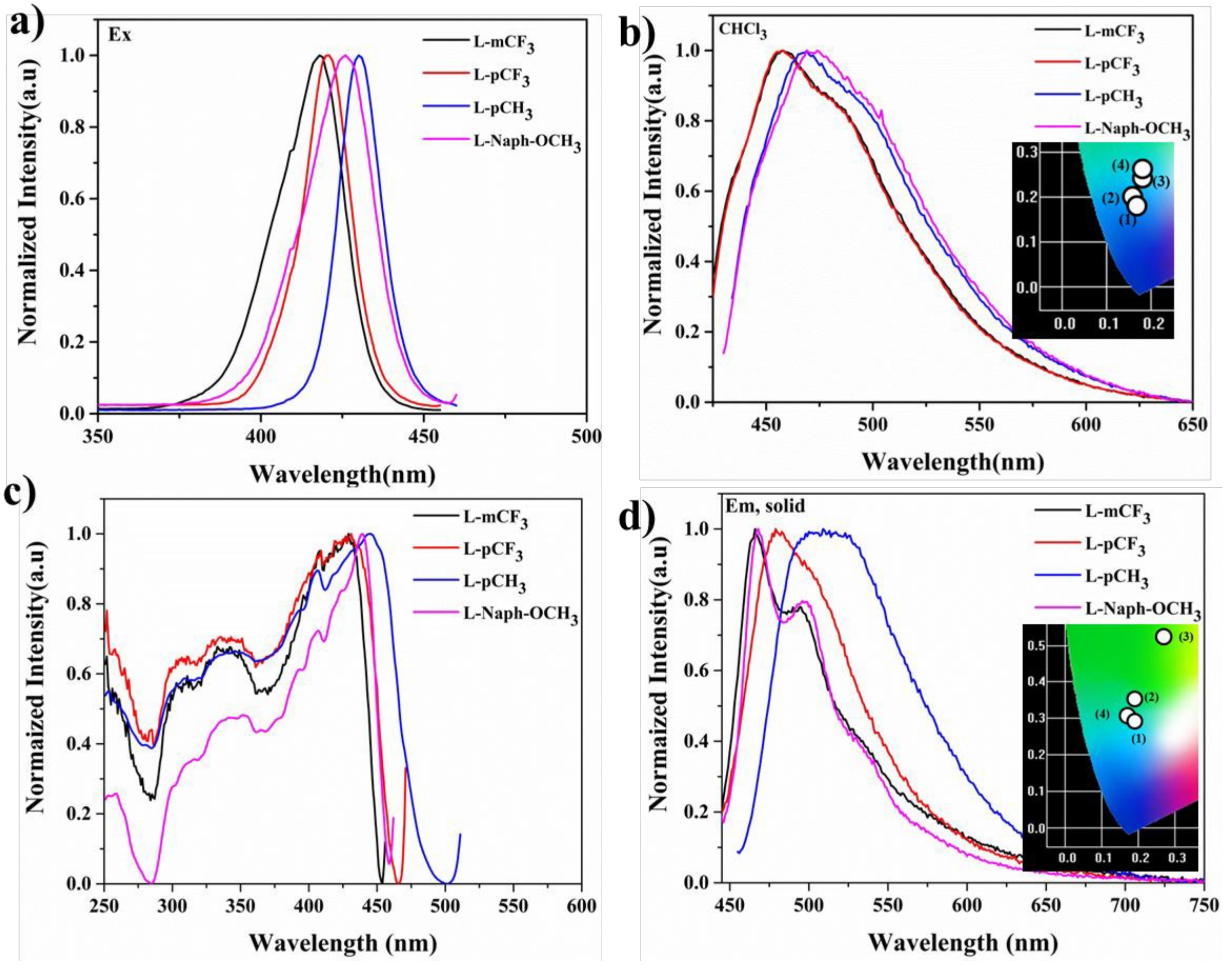

Fig. 4 PL spectra (Excitation and emission) of the ligands in solution (a,b) and in solid (c,d)

Among all, the $^5D_0 \rightarrow ^7F_2$ (612 nm) peak is hypersensitive due to ED transition and ~~is~~ accountable for the red emission of Eu(III) complex. The Eu(III) ion in the complex does

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not possess the inversion centre due to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ (612 nm), electric dipole transition.[16] Unsymmetrical coordination environment around Eu(III) ion in respective complexes is responsible to increase intensity of ED ($^5D_0 \rightarrow {}^7F_2$) transition. The nature of coordination environment around Eu(III) ion can be identified by using luminescent intensity ratio ($I_{02}/I_{01} = {}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$) of electric to magnetic dipole transition. In addition, the Judd–Ofelt (J-O) intensity parameters (Ω_2, Ω_4, and Ω_6) were calculated to identify the nature ligand field and rigidity in a chemical and structural environment given in supporting information and all the calculated value are tabulated in the Table ST3. There is a broad emission band also been observed (ancillary ligand) in the blue region, which arises due to back energy transfer from excited state of Eu(III) metal ion to triplet state of the same (insufficient energy transfer). The complete process of energy transfer (ET) has well explained in the ET mechanism with the support of experimental (Fig. 6) and theoretical calculation (Fig. 2). PL quantum yield of all Eu(III) complexes were recorded by using integrating sphere in solid form at room temperature. The absolute quantum yield of all Eu(III) complexes can be calculated by well reported method.[17,18] The obtained PLQYs of the complexes are 2.83, 4.09, 4.32, 3.37 for Eu(DBM)$_3$L-mCF$_3$ Eu(DBM)$_3$L-pCF$_3$ Eu(DBM)$_3$L-pCH$_3$ Eu(DBM)$_3$L-Naph-OCH$_3$, respectively. The comparatively less quantum yield is attributed to the energy from ligand to Eu(III) ion is not sufficient and there may be back energy transfer from excited state of EuIII ion to ligand triplet level.

The PL spectra of all the ligand and their respective Eu(III) complexes in different polar and non-polar solvent are given in the Fig. S20 & S22 respectively. There is a notable solvent dependent shift (redshift) was obtained in the emission maxima, with increasing

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non-polarity of solvent. The stoke's shift calculation were also performed using existing formula (Fig.S21).[19] This might be interpreted as the dipole of the excited state is more in polar solvents and leads to peak shift. The CIE color coordinate of ligands are given in the Fig. S20 inset. In addition, solvatochromism study for all the synthesized Eu(III) complexes were executed in both polar and non-polar solvent shown in the Fig. S22 and their respective CIE color coordinates and asymmetric ratio values are tabulated in the Table ST2. The ligand and Eu(III) ion peak combining together was observed in solvent effect studies due to the inefficient energy transfer. All Eu(III) complexes are nearly white emitting as shown in the CIE color coordinates with different solvent (Fig. S22 inset). The energy transfer mechanism can be better comprehended with the help of the DFT calculation.

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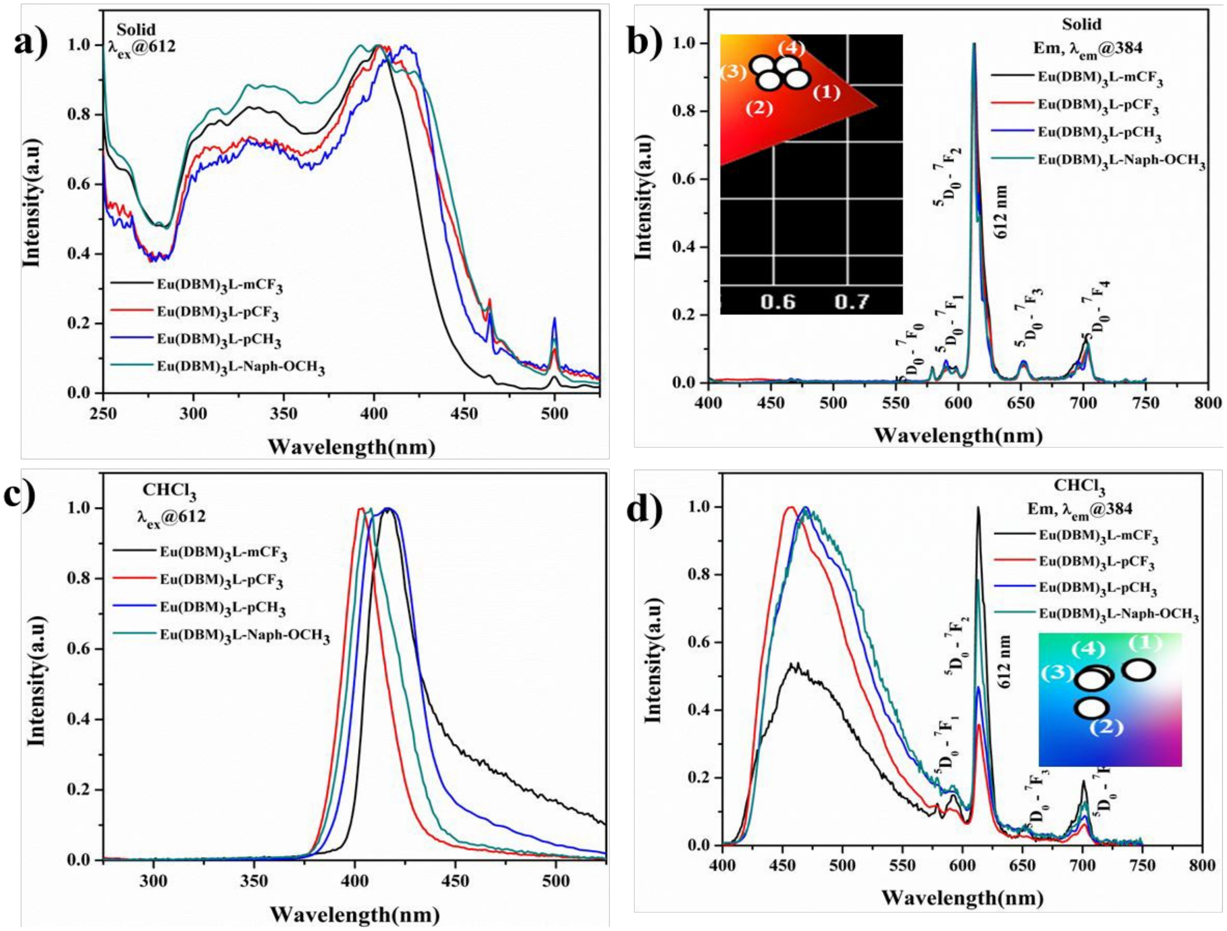

Fig. 5 The PL excitation (a,c) and emission (b,d) spectra of the Eu(III) complexes in solid and solution phase

Energy transfer (ET) mechanism (Experimentally):

The energy transfer mechanism from ligand to Eu(III) metal ion and vice-versa was understood by DFT and experimental calculation. The singlet and triplet energy levels of the ligands were estimated theoretically (DFT and TD-DFT calculation) as explained above in DFT. The experimental value of triplet and singlet energy of ligands are 20790, 20576, 20317, 19301 and 21053, 21413, 20661, 21368 cm^{-1} for L-mCF$_3$, L-pCF$_3$, L-pCH$_3$, L-Naph-OCH$_3$ respectively. The Triplet energy of the ligands were confirmed experimentally with 77K (phosphorescence studies) shown in Fig. S25. The excited state

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values (18800 ($^5D_1$) and 17500($^5D_0$) cm^{-1}) for Eu(III) ion and the singlet (28328 cm^{-1}) & triplet(20408 cm^{-1}) energy level of DBM are well known.[15] In the present investigation energy difference between triplet level (ligand) and the $^5D_0$ level of Eu ion is less, which is responsible for back energy transfer.

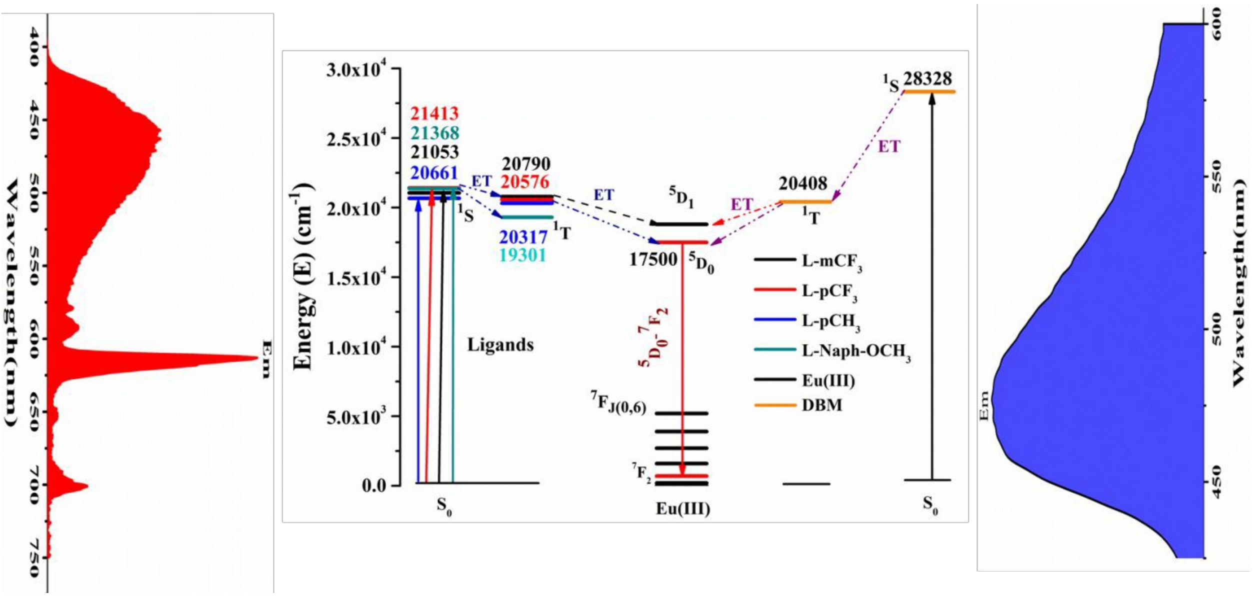

Fig. 6 The energy transfer mechanism from the ligand as well as from DBM to Eu(III) metal ion through its singlet(with florescence) and triplet excited states (with phosphorescence) experimentally.

Lifetime studies:

The fluorescence decay curve of the ligands and their corresponding Eu(III) complexes were given in Fig. 7. The fluorescence lifetime curves of the Eu(III) complexes were obtained by observing the $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm (Fig. 7). Decay curve of Eu(III) complexes was determined to be mono-exponential, the corresponding lifetime values verify the presence of single luminescent centre. The lifetime (τ_{obs}) values were found in the range of 0.15-0.41ms (Table ST3). The luminescence lifetime (τ) decay of the Eu(III) complexes follow the order: Eu(DBM)$_3$L-pCF$_3$ > Eu(DBM)$_3$L-mCF$_3$ > Eu(DBM)$_3$L-

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pCH$_3$> Eu(DBM)$_3$L-Naph-OCH$_3$. However, the ligands are showing bi-exponential decay. The PL lifetime values of ancillary ligands and their corresponding Eu(III) complex are tabulated in Table ST3. The observed higher life time value of Eu-complexes indicates that the photoluminescence stability of coordinated system in presence of second ancillary ligands. Higher the PL decay time values of the trivalent europium complexes are the significance of extended π-conjugated system of second ancillary ligands which effectively coordinated to the europium ion.

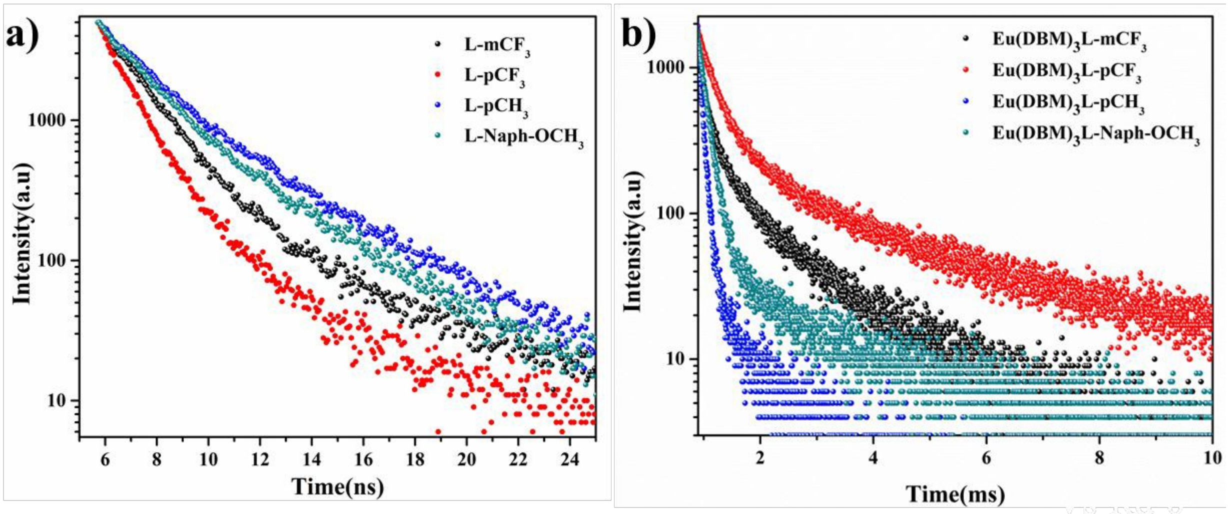

Fig. 7 Decay curves a) of ligands and b) of their respective Eu(III) complexes

Poly methyl methacrylate (PMMA) film of Eu(III) complexes:

The ligand and their respective Eu(III) complexes doped into a PMMA matrix, their optical properties were studied in detail. PMMA film study of ligands is represented in the Fig. S24. Fig. 8 shows Eu(III) complexes were doped in PMMA matrix with different concentration (Eu(III): PMMA; 1:99, 2:98, 3:97, 4:96). However, there is no noticeable change observed in the peak position of Eu(III) ion with and without PMMA, only the variation in the intensity was observed which depends on the coordinative environment. As revealed in the Fig. 8 that Eu(III) complexes concentration ratio is increasing from 1 to 4% at the interval of 1%, similarly the

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intensity, FWHM and CIE is also varying with concentration of Eu(III) in PMMA matrix. With increasing the Eu(III) ion concentration in PMMA the CIE coordinate is shifting from blue to red through white region as shown in the Fig. 8 inset. Intensity ratios and CIE color coordinates for the Eu(III) Complexes in different concentration ratio doped with PMMA matrix were tabulated in the Table ST5. The thermal study of the ligands and their respective europium complexes were exeucted and the results are presented and discussed in SI.

Fabrication of LED with Eu complexes:

To study the potential application of the presently synthesize Eu(III) complex in the photonic field light-emitting diodes (LEDs) were designed by conjugating the Eu(III) complex in different ratio of 1:10 and 1:50 with PMMA (Eu(III) complex: PMMA) on 395 nm emitting InGaN. Emission of Eu(III) complexes under 20mA forward-bias current illustrated in Fig. 9. One can perceive that Eu(III) complexes emit white light upon excitation. The CIE chromaticity coordinates of the Eu(III) complexes are tabulated in Table ST6. The CCT and CRI of coordinated LED in 1:10 and 1:50 is (NA, 40%) and (2247K, 34%), (6561K, 76%) and (3674K, 49%), (8513K, 69%) and (5386K, 63%), (4978K, 51%) and (3465K, 71%) for $Eu(DBM)_3L$-mCF_3, $Eu(DBM)_3L$-pCF_3, $Eu(DBM)_3L$-pCH_3 and $Eu(DBM)_3L$-Naph-OCH_3 respectively. The obtained results state that synthesized Eu(III) complexes are potent candidates for white light emission. Among all, the $Eu(DBM)_3L$-pCH_3 in 1:50 with the CIE value (x=0.33, 0.33), is exactly matching the NTSC standard value for natural white light. In case study, further the blue LED based white LED (Fig. 10) was also been fabricated with $Eu(DBM)_3L$-pCH_3. The white LED showed CIE (x = 0.36, y = 0.35), CCT (4234K) and CRI (75%).

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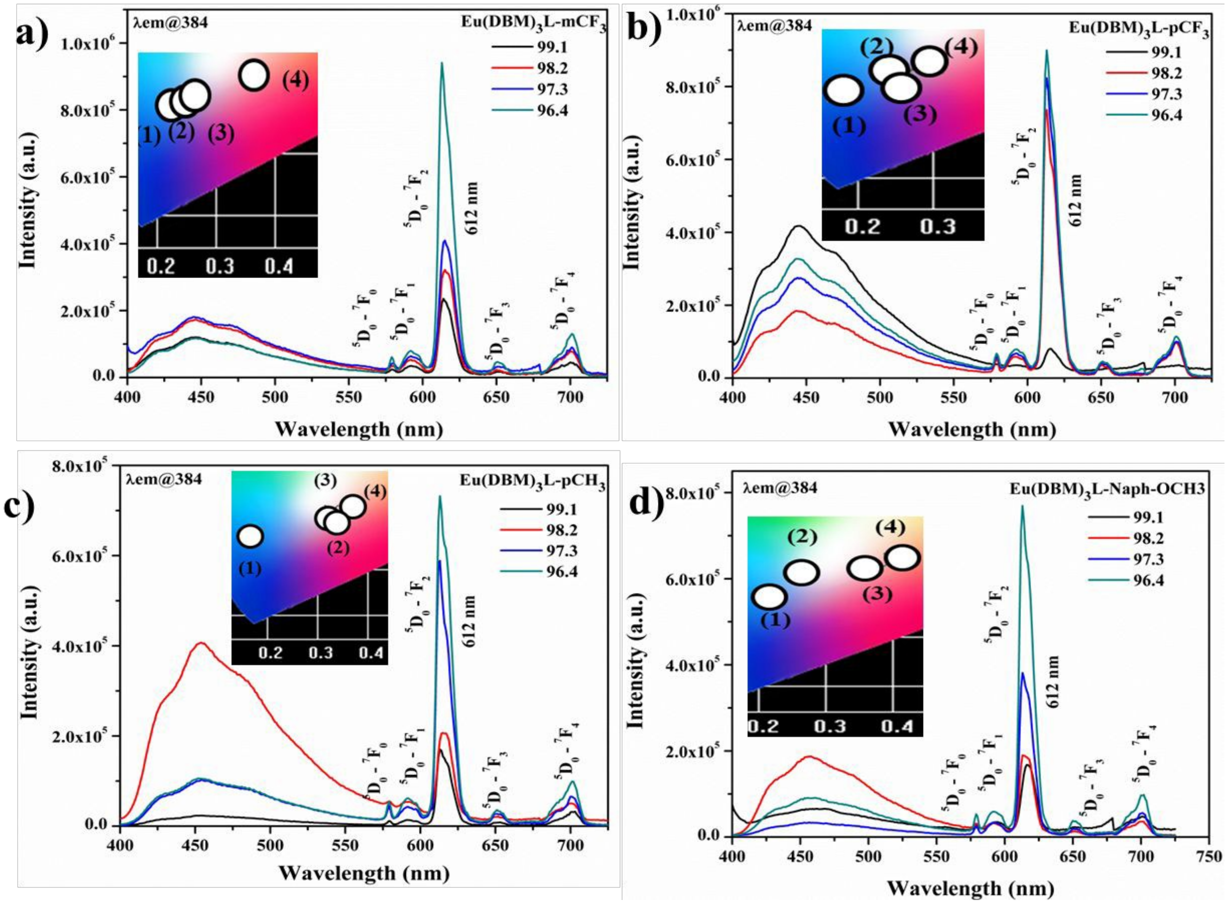

Fig. 8 PL emission spectra of the complexes Eu(DBM)$_3$L-mCF$_3$, Eu(DBM)$_3$L-pCF$_3$, Eu(DBM)$_3$L-pCH$_3$ and Eu(DBM)$_3$L-Naph-OCH$_3$ in thin films using a PMMA matrix.

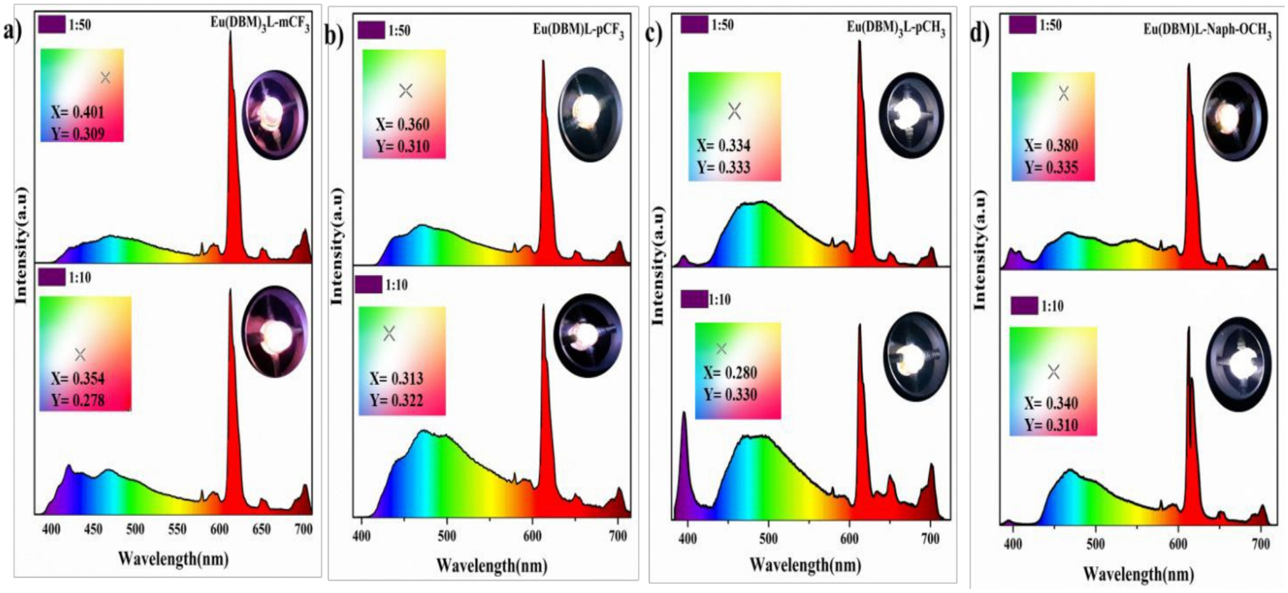

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Fig. 9 The emission spectra of the Eu(III) (Eu(DBM)$_3$L-mCF$_3$, Eu(DBM)$_3$L-pCF$_3$, Eu(DBM)$_3$L-pCH$_3$ and Eu(DBM)$_3$L-1Naph) complexes with n-UV under a 20 mA forward bias current. The insets are the fabricated LED devices and CIE color coordinate.

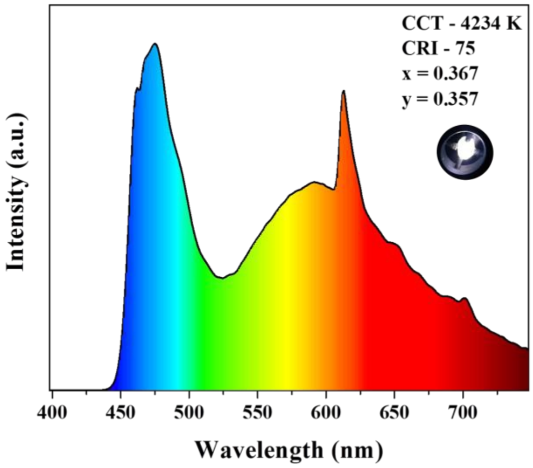

Fig. 10 White LED emission spectra of the Eu(DBM)$_3$L-pCH$_3$ complexes with Blue LED. The insets are the fabricated LED devices and CIE color coordinate.

Ratiometric temperature sensor of Eu(III)-complex (Eu(DBM)$_3$L-mCF$_3$):

The Eu(III) complex with ancillary ligand and β-diketones as anionic ligand can behave as temperature sensors.[20, 21] In the present study, temperature-dependent emission spectra of Eu(III) complexes (Eu(DBM)$_3$L-mCF$_3$, Eu(DBM)$_3$L-pCF$_3$, Eu(DBM)$_3$L-pCH$_3$ and Eu(DBM)$_3$L-Naph-OCH$_3$) were assembled in terms of intensity from 30 to 180 ^{o}C shown in the Fig 11. With escalating the temperature at the interim of 10^{o}C (from 30-180 ^{o}C), the intensity of the $^5D_0 \rightarrow {}^7F_2$ of Eu(III) complex at ~612 nm decreases monotonously. The decrease in intensity of Eu(III) complex with temperature is generally described as thermal activation of non-radiative decay processes. Even though, the non-radiative procedure delivers a specific quantity of heat, it doesn't influence the temperature of the sample in the process of analysis. Hence, the non-radiative procedure won't affect the temperature-dependent photoluminescence experiment. The

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reversibility of the emission behaviour during cooling also been recorded for the Eu(DBM)$_3$L-mCF$_3$ and the same shown in Fig S27.

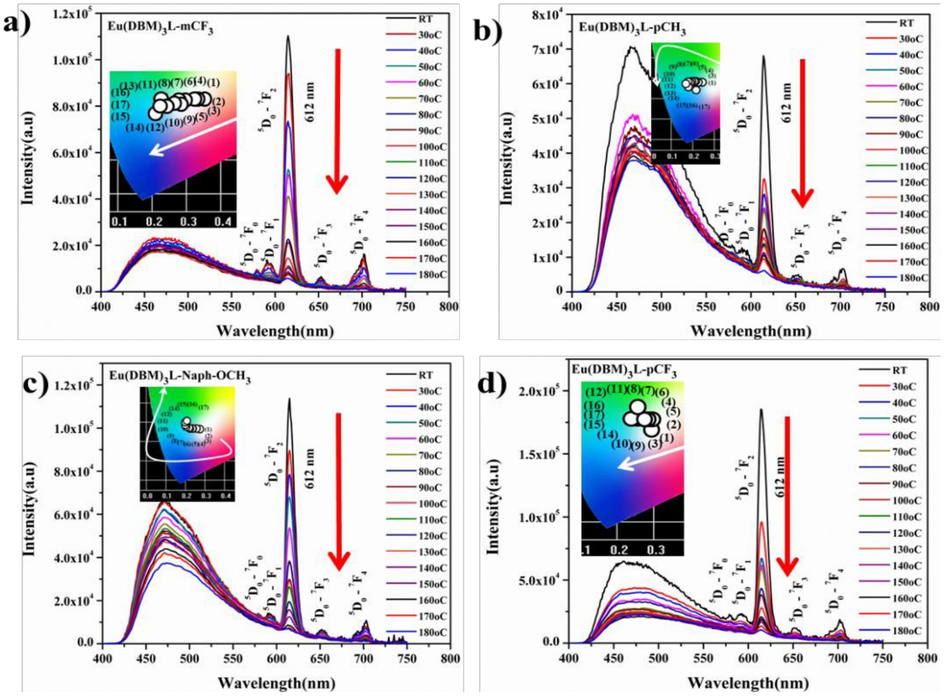

Fig. 11 Temperature dependent emission spectra of Eu(DBM)$_3$L-mCF$_3$, Eu(DBM)$_3$L-pCF$_3$, Eu(DBM)$_3$L-pCH$_3$and Eu(DBM)$_3$L-Naph-OCH$_3$ in acetonitrile (ACN) solvent and their CIE, respectively

The temperature dependent PL of Eu(III) complexes can be better comprehended by the help of intensity ratio of ligand at 465 nm and Eu(III) complex at 612 nm ($\boldsymbol{\Delta} = I_{lig}/I_{Eu}$). The linear relationship between the intensity ratio($\boldsymbol{\Delta}$) and the temperature T are shown in the Fig. 12(b). The fitting curve is shown by the red line, which obeys an empirical formula displayed as eqn.(4)

$$\boldsymbol{\Delta} = \mathbf{0.000738(T)} - \mathbf{0.18776} \ldots\ldots (4)$$

Where, T represents the temperature and $R^2 = 0.9828$ is correlation coefficient, which indicating that Eu(DBM)$_3$L-mCF$_3$ can behave as excellent luminescent thermometer at this temperature range (303−460 K). The relative sensitivity (the relative change of the thermometric parameter

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per degree of temperature change) for the Eu(DBM)$_3$L-mCF$_3$ complex was calculated by the eqn. (5),

$$\boldsymbol{SR} = \frac{\partial\boldsymbol{\Delta}/\partial\boldsymbol{T}}{\boldsymbol{\Delta}}\ldots\ldots\ldots\ldots\ldots\mathbf{(5)}$$

After calculating the relative sensitivity, one can accomplish that the Eu(DBM)$_3$L-mCF$_3$ can behave as a luminescent thermometer at temperature range (303−460 K). The Eu(DBM)$_3$L-mCF$_3$ have the relative sensitivity value of 4.9% K^{-1} at 323 K as represent in the Fig. 12(C) and the values are comparable with the lanthanide functionalized metal–organic frameworks. [22]

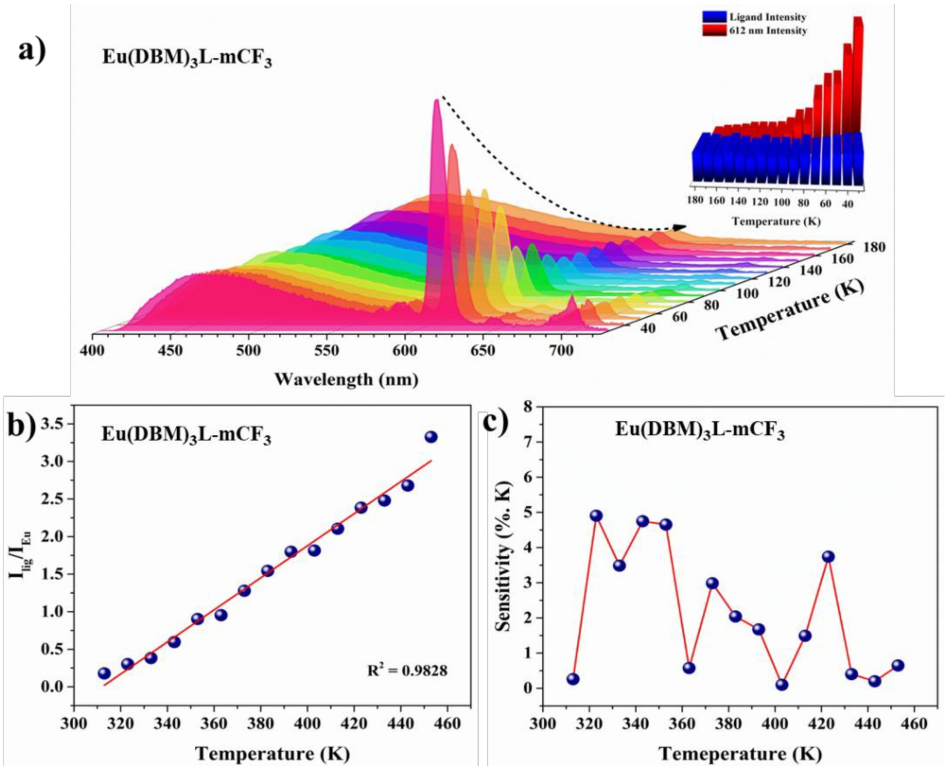

Fig. 12a) Temperature-dependent emission spectra of Eu(DBM)$_3$L-mCF$_3$ complex (inset emission intensity bar graph of ligand and $^5D_0 \rightarrow 7F_2$), b) temperature dependent Δ and linearly fitted curve, and c) temperature dependent relative sensitivity (SR).

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Conclusions:

Series of ancillary ligands were designed by computational modeling and synthesized for europium complexation. White light emission were observed for all the Eu-complexes, due to their energy mismatch between the triplet state of the ligand and excited state of Eu(III) ion (supported by the both experimental and theoretical study). Single component white light emissive LEDs were fabricated and among all $Eu(DBM)_3L$-pCH_3 conjugated with near UV LED showed pure white emission with CIE (0.33, 0.33) and exactly matching with the NTSC standard for natural light. The CRI significantly improved by integrating the Eu-complex with blue LED chip. In addition, the temperature dependent PL study reveals that these complexes can be used for ratiometric temperature sensing applications and the relative sensitivity value found to be 4.9% K^{-1} at 323 K for $Eu(DBM)_3L$-mCF_3 .

Conflicts of interest

There are no conflicts to declare.

Dedicated to Professor U. V. Varadaraju on the occasion of his 65th birthday

Supplementary Information:

General Information for synthesis (Materials, Synthesis, characterization), FT-IR, NMR, MASS, Judd-Ofelt analysis, solvatochromism, electrochemical properties, thermal study, PMMA film study, DFT.

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