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Versatile Luminescent Europium(III)– β -Diketonate-imidazo-bipyridyl Complexes Intended for White LEDs: A Detailed Photophysical and Theoretical Study

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Supporting Information

ABSTRACT: Three ancillary ligands based on imidazo-bipyridyl with phenyl (Ph), naphthyl (Np), and triphenylamine (TPA) substitution were synthesized and secondhand to formulate the consistent europium(III) ternary complexes using thenoyltrifluoroacetone as an anionic ligand. The complete investigation of spectroscopic, photophysical, and electrochemical properties was carried out. The attained results for all the ancillary ligands and their corresponding Eu complexes were compared with one another. All the Eu complexes reveal a broad excitation band ranging from the near-UV to blue region, along with high intense emission and apposite color purity. To further understand the ligand-to-metal energy transfer (ET) process, the geometry of the ligand was optimized and the energy level location (singlet and triplet) was calculated by using DFT and TD-DFT calculations. On the basis of the theoretical calculation, the ET mechanism was proposed. From PL emission spectra in the solid state, complete ET occurs from Ph, Np based ancillary ligands to the Eu³⁺ ion, which yields a pure red emission,



whereas the TPA functionalized based Eu complex shows incomplete ET. Fortunately, white emission was observed in the TPA based Eu complex in the solid state. The white LED was fabricated by using a white emitting complex integrated with 395 nm emitted LED (InGaN) chips under 20 mA forward-bias current. The excitation source from LED was fully observed by the complex shown for 3Eu and showed yellowish emission in different concentrations (the similar observation also reflected in solid). However, in the case of 1Eu and 2Eu complexes, they showed close to white emission. The Commission International de l'Eclairage (CIE) chromaticity coordinates are close to the National Television Standard Committee standard value for white emission, and in addition, the complex 3Eu coated with the blue LED chip (460 nm) by PMMA (1:10) showed bright white emission with CIE x, y values of 0.30, 0.33, respectively.

INTRODUCTION

Lanthanide based molecular complexes have received a great deal of attention due to their brilliant applications in different provinces, such as biomedical diagnostics, biological labeling, photonic devices, and solar energy conversion.¹⁻⁴ Lanthanide ions are known to emit light in the visible or else near-infrared (IR) spectral region under UV or IR excitation by either a downor up-conversion process. Lanthanides have unique spectral properties, atomic-like or line-like emission bands, and long-lived excited states (microseconds to milliseconds). The 4f electrons can be arranged liberally in any other seven 4f orbitals, resulting in them being able to absorb or emit various wavelengths ranging from the ultraviolet and visible to IR spectral region in the electromagnetic spectrum, excluding for when the 4f sublevels of Ln³⁺ are completely empty or full (La³⁺ and Lu³⁺). By choosing the organic ligand, one can obtain highly luminescent lanthanide complexes by means of the "antenna effect" and populate the emitting levels of the Ln^{3+} ions, as the 4f-4f electronic transition is a parity forbidden one. In other words, accumulating the ligating moieties could shield the central metal ion against the solvent in order to avoid nonradiative deactivation processes. The molecular design of the apt organic antennas/ligands which

can efficiently transfer their excited energy to the lanthanide ions is a stimulating research task. It also plays a vital role in tailoring the photophysical properties of the lanthanide molecular complexes for specific applications. β -Diketones based ligands were considered as an important class of energy harvesters for the Ln^{3+} ions,⁵⁻⁸ as well as they give very volatile, thermodynamically stable, and highly luminescent complexes, which are essential conditions for optoelectronic or lighting applications.^{9,10} Tris- β -diketonate lanthanide complexes are coordinatively unsaturated and usually remain solvated. The solvent molecules contain high energy O-H/C-H oscillators, and these oscillators lead to nonradiative deactivation which has a detrimental impact on Ln luminescence.¹¹ The energy deactivation via a nonradiative process could be prohibited by introducing neutral ancillary ligands, such as phenanthroline (phen), 2,2'-bipyridine (bpy),¹² bis(pyrazolyl)methane (bpm),¹³ and pyrazole,¹⁴ or fully fluorinated β -diketones.¹⁵ These bidentate ancillary ligands replace the solvated water molecules and lead to a coordinately saturated Ln³⁺ complex.¹⁶ It

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is worth to note that the functionalization of ligands (either anionic or ancillary) is apparently based on the problems that need to be addressed. The water insoluble (soluble in polar solvents) molecular complexes are necessary for optoelectronic applications, whereas, in biomedical diagnostics, the molecular complexes should be soluble in aqueous medium and that can be achieved by introducing a polar functional group in the ligand structure.^{17,18} For application, specific molecular design of lanthanide complexes is a striking research task.

The cumulative global energy crisis and climate change are demanding high energy efficient lighting systems (solid state lighting (SSL)) that can help to conserve energy and reduce overall lighting costs. Visible light (near-UV to blue) excited Eu complexes are extremely desirable for the high-efficiency warm white LEDs as a red-emitting phosphor. Design and synthesis of highly efficient europium molecular complexes are expand-²¹ Here, we report photophysical characteristics of three ing.¹ newly synthesized ternary europium complexes [Eu(tta)₃Ph, Ph = 3-phenyl-1-(pyridin-2-yl)*H*-imidazo[1,5-*a*]pyridine] (1Eu), $[Eu(tta)_3Np, Np = N-phenyl-N-(4-(1-(pyridin-2-yl)H-imidazo-$ [1,5-*a*]pyridin-3-yl)phenyl)benzenamine] (2Eu), and [Eu(tta)₃-TPA, TPA = 3-(naphthalen-3-yl)-1-(pyridin-2-yl)H-imidazo-[1,5-*a*]pyridine] (3Eu) with TTA and a bipyridyl (heterocyclic amine) with phenyl (Ph, L-Ph), naphthyl (Np, L-Np), and triphenylamine (TPA, L-TPA) substitution in solutions and in the solid state. The anionic ligand TTA (primary sensitizer) was preferred because of its versatile nature and stability (under ambient conditions) as well as strong absorption in the UV region and could harvest the energy to the central Eu³⁺ ion. Imidazo-bipyridyl as the ancillary ligand is chosen because it is an efficient chromophore (can be easily functionalized), which has the triplet state at the optimum energy level (18 974 cm⁻¹) and stabilizes the molecular structure and reduces the nonradiative channels (in the absence of imidazo-bipyridyl, water molecules would remain associated with the complex). Thus, the existence of bipyridyl in the complex aids a 2-fold purpose, namely, increase thermal stability and red emission enhancement. It is well familiar that the Ln(III) complexes suffer through low thermal stability, limited photostability, and poor mechanical properties in their original state.^{22,23} In this context, the polymers provide a sequence of compensations for the development of molecular materials, for instance, thermal and chemical stability, flexibility, versatility, biocompatibility, hydrophobic-hydrophilic balance, and the characteristic improved luminescence of lanthanide ions.²⁴ Hence, the use of a polymethyl methacrylate (PMMA) matrix is quite common, which will certainly enhance the luminescence properties, versatility, and thermal stability of the newly synthesized complexes.²⁵ To understand the optical properties in the thin film of Eu complexes, we have investigated the optical properties by incorporating in the PMMA matrix with different concentrations. White light generation from a single molecule or component always helps to simplify the device structure and fabrication procedure.²⁶ The generation of white light from a single molecule is rarely observed in Ln containing complexes. Here, the white light is generated by combining the blue emission that is generated from the ligand or an organic molecule with the unique luminescent properties of Ln ions. $^{27-30}$ The use of ternary complexes with Eu(TTA)₃ is very much common in white light generation procedures. The choosing of the ligand always plays an important role as the ligands not only play a role as sensitizers for the Ln(III) ions via an "antenna effect" but also act as bluish-yellow-emitting sources in the complexes. Due to mismatch in the energy levels of the

Ln(III) ions and the ligands, the entity of energy transfer is less. Use of an additional sensitizer always facilitates the energy transfer pathway to the triplet state of the ligands through an intersystem crossing.³¹ Hence, a perfect design of ligand that is suitable with the complex not only helps to emit blue light but also acts as an operative sensitizer is crucial for succeeding highefficiency white light emission. Keeping all of these in mind, efforts have been made to design and synthesize three Eu³⁺ complexes with TTA and imidazo-bipyridyl that are new to the organic electronics and have been reported for the first time. The introduction of various functional groups in an ancillary ligand has given an elegant approach to optimize the lanthanide luminescence with a view to develop high performance luminescent materials for lighting or optoelectronic applications. The enhancement in the hole transporting properties may be anticipated by the attached TPA group and may increase the solubility in common organic solvents and thermal stability of the complex.³² The photophysical and electrochemical studies of the bipolar ligand and its corresponding Eu complexes were studied in detail. In order to further understand the energy transfer process between the ancillary ligand to the central metal ion, we have optimized the ligand structure and calculated the exact location of the singlet and triplet levels by using DFT and TD-DFT. Electrochemical studies have also been carried out for both ligands as well as complexes to find the redox potential (HOMO and LUMO energy gap). The CIE color coordinates were calculated for the complex as well as ligands, and it showed NTSC (National Television Standards Committee) standard values. Among all the complexes, we found that the TPA integrated complex showed white emission in the solid state. We have taken benefit of this characteristic and fabricated a white LED based on an InGaN LED chip (460 nm). In addition, on the basis of the PL emission spectra, we also tried to fabricate the LED by using currently synthesized Eu(III) complexes. The Eu(III) complexes integrated with a near blue LED chip (395 nm) showed nearly white emission for 1Eu and 2Eu and yellow emission for the 3Eu complex. The synthesized bipolar ligand and its corresponding Eu(III) complex structures are represented in Figure 1.

EXPERIMENTAL SECTION

General Information for Synthesis. All reactions were performed under an inert (nitrogen $(N_2)/argon (Ar)$) atmosphere. Solvents (tetrahydrofuran (THF), ethanol (EtOH), dimethyl sulfoxide (DMSO), hexane, etc.) were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents



Figure 1. Structure of the europium complexes.

are used without further purification unless otherwise stated. Benzaldehyde, β -naphthyl, 2,2'-dipyridyl ketone, triphenylamine (TPA), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA), europium(III) chloride hexahydrate (99.99%), and tetrabutyl-ammonium perchlorate (nBu_4NCIO_4) electrolyte were purchased from Sigma-Aldrich chemicals company. Thin-layer chromatography (TLC) was used to monitor all the reactions (silicagel 60 F₂₅₄ aluminum plates, Merk). Column chromatography was carried out using silica gel from Aldrich (70–230 mesh, 60 Å).

Measurements. ¹H and ¹³C NMR spectra were recorded using an AV 400 Avance-III 400 MHz Fourier transform nuclear magnetic resonance (FT-NMR) spectrometer (Bruker Biospin International, Switzerland), in deuterated chloroform/dimethyl sulfoxide solution. Chemical shifts were quoted relative to tetramethylsilane (TMS, standard reference). Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer, USA/RX-I FTIR, spectrophotometer, and elemental analysis was measured by an Elementar Analysen Systeme, Germany/Vario EL spectrometer. Powder X-ray diffraction of ligands and the Eu(III) complex were measured by a powder X-ray diffractometer (XRD) using Cu-K α_1 radiation (Rigaku, ULTIMA IV). The absorption spectra in solution, solid (diffuse reflectance spectroscopy, DRS), and thin film were measured by using a UV-visible spectrometer (Shimadzu Corporation, Japan or UV-2450 PerkinElmer, USA/Lamda 25 and Lamda PerkinElmer). The photoluminescence (PL) emission spectra in solution phase and thin film were recorded by a Horiba Jobin Yvon, USA/Fluoromax 4P spectrophotometer. The relative photoluminescence quantum yield was measured with a Horiba Jobin Yvon, HR 320, and the absolute fluorescence quantum yield was measured with an Edinburgh Instruments, spectrofluorometer, FS5, Integrating Sphere SC-30. The CIE color coordinates were calculated by using PL emission data (MATLAB software). The electrochemical properties of the complex and ligand were measured by using cyclic voltammetry (CV), AUTOLAB 302N Modular potentiostat, at RT in dichloromethane. The working (glass-carbon rod), auxiliary (counter, Pt wire), and reference (Ag/Agcl wire) electrodes were used for CV analysis. The dimethylformamide (DMF) which contains 0.1 M Bu₄NClO₄ was used as the supporting electrolyte, and the scan rate was maintained as 100 mV s⁻¹. The ligand structure (geometry) was optimized within the density functional theory (DFT)³³ framework using the B3LYP/6-31G(d, p) level of theory. After confirming the ground state geometry for the ligand, we have vertically excited the molecule to get the UV-visible spectra and first excited state using TD-DFT.³⁴ To understand PL spectra of the Eu(III) complex, the triplet excited state of the ligand is also obtained by using the same methodology mentioned above. The optimization was carried out in the G09W suit of programs. Lifetimes of the Eu(III) complex as well as ligand were measured at 298 K with an Edinburgh Instruments FLS 980 based on the time correlated single photon counting technology upon the excitation at 380 nm for all complexes and ligands. A pulsed xenon lamp was used as the excitation source, and the signals were detected with a photomultiplier. The triplet energy of the synthesized ligand was estimated by measuring the phosphorescence spectra of the Gd complex of the ligand at 77 K by using an Edinburgh FLS 920 spectrofluorimeter, UK, system that consists of a 450 W xenon lamp (Xe 900) mounted in an air-cooled lamp housing with a built-in de-ozonizer filter. The ozonefree Xe arc lamp emits a continuous radiation from 190 to 2600 nm. Thermal analysis of the complexes was carried out using thermogravimetric/differential thermal analysis (TG/DTA), TMA (Shimadzu).

Materials. The commercially available reactants are used except for (diphenylamino)benzaldehyde (TPA-CHO). The compound TPA-CHO was synthesized by the well-known Vilsmeier–Haack reaction, and the metal compound tris(thenoyltrifluoroacetone)europium(III) (Eu(TTA),·2H₂O) was synthesized by using a well-recognized method.^{35,36}

General Synthesis of Ligand. 2,2'-Dipyridyl ketone (0.5 g, 2.717 mmol) was taken in a round-bottom flask, and to this was added glacial acetic acid (15 mL) at room temperature (RT). To this reaction mixture were subsequently added the aldehyde compound (benzaldehyde/ β -naphthyl/4-(diphenylamino)benzaldehyde) (0.576 g, 5.434 mmol) and

ammonium acetate (1.04 g, 13.58 mmol). Then, the resultant mixture was stirred for 12 h at 110 °C. The progress of the reaction was monitored by TLC (MeOH in chloroform 1:9, R_f - 0.3). The RM was poured into a minimum amount of water and then ammonium hydroxide (NH₄OH) solution was added. The obtained solid was filtered and dissolved in dichloromethane, followed by dried with anhydrous sodium sulfate. The solvent was evaporated to get 0.600 g of crude compound. This was purified with column chromatography by using silica gel (100–200 mesh), eluent with 5% methanol in chloroform. The obtained product was dissolved in a minimum amount of THF solution and an excess amount of THF solvent was added to the same; the pale yellow color solid that was formed is 450 mg (60.0%). The spectra are displayed in Figures S1–S3.

3- \hat{P} henyl-1-(pyridin-2-yl) \hat{H} -imidazo[1,5-a]pyridine (L-Ph). ¹H NMR data (400 MHz, DMSO- d_6): δ 8.68–8.62 (m, 2H), 8.50 (d, 1H, J = 7.2 Hz), 8.15 (dd, 1H, J = 0.4, 1.6 Hz), 7.90 (dd, 2H, J = 1.2, 3.2 Hz), 7.83 (t, 1H, J = 7.6 Hz), 7.60 (t, 2H, J = 7.2 Hz), 7.54–7.50 (m, 1H), 7.22–7.19 (m, 1H), 7.19 (t, 1H, J = 6.4 Hz), 6.85 (t, 1H, J = 7.2 Hz). ¹³C NMR data (100 MHz, DMSO- d_6): δ 159.6, 154.2, 142.5, 141.7, 134.8, 134.6, 134.4, 134.1, 133.9, 133.1, 127.6, 127.1, 125.9, 125.7, 124.2, 119.4. FT-IR data: v (in cm⁻¹) = 3059, 2927, 1663.6, 1590.3, 1534, 1507, 1477, 1443, 1425, 1401, 1351, 1305, 1275, 1248, 1195, 1138, 1122, 1088, 1073, 1031, 1008, 978, 951, 920, 886, 829, 787, 772, 737, 692, 620, 593, 505. ESI-Mass (m/z): 274.3

3-(Naphthalen-3-yl)-1-(pyridin-2-yl)H-imidazo[1,5-a]pyridine (L-Np). ¹H NMR data (400 MHz, DMSO- d_6): δ 8.62–8.78 (m, 3H), 8.54 (S, 1H), 8.20 (d, 1H, *J* = 7.2 Hz), 8.14–8.01 (m, 4H), 7.85 (td, 1H, *J* = 1.6 Hz, 9.6 Hz), 7.62–7.60 (m, 2H), 7.24–7.11 (m, 2H), 6.92 (t, 1H, *J* = 6.4 Hz). ¹³C NMR data (100 MHz, DMSO- d_6): δ 154.9, 148.9, 138.0, 136.2, 133.3, 133.2, 130.7, 130.3, 128.8, 128.2, 127.8, 127.4, 127.2, 126.7, 126.6, 125.8, 121.8, 129.6, 121.1, 120.4, 119.4, 119.9, 114.0. FT-IR data: v (in cm⁻¹) = 3381, 1683, 1601, 1533, 1456, 1408, 1360, 1302, 1186, 1137, 1060, 935, 857, 780, 722, 683, 645, 577, 519. ESI-Mass (*m*/*z*): 322.5

N-Phenyl-*N*-(4-(1-(pyridin-2-yl)*H*-imidazo[1,5-a]pyridin-3-yl)phenyl)benzenamine (*L*-TPA). ¹H NMR data (400 MHz, DMSO- d_6): δ 8.61 (d, 2H, *J* = 5.2 Hz), 8.49 (d, 1H, *J* = 7.2 Hz), 8.12 (d, 1H, *J* = 8 Hz), 7.84–7.78 (m, 2H), 7.72 (d, 1H, *J* = 8.4 Hz), 7.44–7.35 (m, 4H), 7.25– 7.04 (m, 10H), 6.89–6.82 (m, 1H). ¹³C NMR data (100 MHz, DMSO- d_6): δ 149.5, 149.3, 137.7, 137.5, 137.0, 133.3, 133.1, 130.3, 130.0, 129.8, 129.0, 128.8, 128.7, 128.0, 127.3, 127.3, 127.1, 126.9, 126.3, 126.1, 123.3, 122.6, 121.2, 121.1, 119.6, 114.9. FT-IR data: *v* (in cm⁻¹) = 3045, 1585, 1531, 1511, 1487, 1403, 1354, 1334, 1285, 1191, 1176, 1136, 1008, 954, 840, 801, 757, 742, 698, 629, 515. ESI-Mass (*m*/*z*): 438.5

Synthesis of Eu(TTA)₃**R**. A 50 mL two-neck round-bottom flask was taken with a N₂ containing balloon adaptor and followed by pouring $Eu(TTA)_3$ ·2H₂O (0.300 g, 0.352 mmol, 1 equiv) dissolved in dry THF (15 mL). To the above solution was added a mixture of ligand (R) (0.095 g, 0.352 mmol, 1 equiv) in THF (10 mL), and the reaction mixture (RM) was stirred for 12 h at 60 °C. The resulting product was dissolved in a minimum amount of THF and an excess of hexane was added to get a solid product that is a pale yellow color with 285 mg (72.0%).

*Eu(TTA)*₃*Ph*. Elemental analysis: Anal. Calc. for C₄₂H₂₅EuF₉N₃O₆S₃: C, 46.42; H, 2.32; N, 3.87; S, 8.85; Found: C, 46.68; H, 2.23; N, 3.95; S, 8.69%. FT-IR data: v (in cm⁻¹) = 3657, 3110, 2957, 1685, 1606, 1539, 1506, 1451, 1488, 1356, 1305, 1246, 1191, 1138, 1060, 933, 859, 785, 718, 641, 581, 520. ESI-Mass (*m*/*z*): 1087.2.

*Eu(TTA)*₃*Np*. Elemental analysis: Anal. Calc. for C₄₆H₂₇EuF₉N₃O₆S₃: C, 48.60; H, 2.39; N, 3.70; S, 8.46; Found: C, 48.80; H, 2.17; N, 3.82; S, 8.32%. FT-IR data: v (in cm⁻¹) = 3350, 1679, 1604, 1537, 1453, 1415, 1349, 1301, 1188, 1141, 1056, 983, 858, 782, 716, 679, 641, 575, 518. ESI-Mass (*m*/*z*): 1136.8.

*Eu(TTA)*₃*TPA*. Elemental analysis: Anal. Calc. for C₅₄H₃₄EuF₉N₄O₆S₃: C, 51.72; H, 2.73; N, 4.47; S, 7.67; Found: C, 52.02; H, 2.53; N, 4.57; S, 7.47%. FT-IR data: v (in cm⁻¹) = 3106, 3656, 1683, 1594, 1540, 1486, 1361, 1301, 1200, 1139, 1056, 936, 841, 799, 763, 721, 694, 643, 584, 512. ESI-Mass (*m*/*z*): 1255.6.

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Scheme 1. Synthesis Route of the Ligand and Corresponding Eu(III) Complex



Figure 2. UV-vis absorption spectra of ligands (left) and respective complexes (right) in chloroform solution.

Table 1. PL Emission Intensity Ratios as Well as Their Respective CIE Coordinates for 1Eu, 2Eu, and 3Eu in Diverse Polarity of Solvents

	1Eu			2Eu			3Eu		
	CIE		CIE			C	IE		
solvent	asym. ratio	x	у	asym. ratio	x	у	asym. ratio	x	у
acetone	8.0366	0.6611	0.3385	7.4428	0.6610	0.3386	1.5554	0.6365	0.3631
DMSO	6.6740	0.6624	0.3372	11.2561	0.6613	0.3383	2.7005	0.6383	0.3613
DMF	8.8023	0.6635	0.3362	14.8450	0.6651	0.3346	5.3477	0.6573	0.3423
MeOH	3.0356	0.6493	0.3503	13.7521	0.6657	0.3340	1.5675	0.6400	0.3596
EtOAc	8.6639	0.6627	0.3369	12.0440	0.6670	0.3327	1.4387	0.6412	0.3583
CHCl ₃	7.8347	0.6621	0.3376	7.5295	0.6641	0.3355	1.4058	0.6371	0.3624
DCM	6.2596	0.6576	0.3420	13.4092	0.6654	0.3342	2.4239	0.6442	0.3553
THF	9.0502	0.6650	0.3347	13.2930	0.6662	0.3334	2.3467	0.6444	0.3551
ACN	11.2483	0.6623	0.3374	15.0378	0.3333	0.6663	3.9763	0.6500	0.3496
toluene	10.584	0.6652	0.3344	19.1317	0.6643	0.3353	8.5966	0.6622	0.3374

RESULTS AND DISCUSSION

Characterization of the Complex. The synthesis direction method of Eu(III) complexes is summarized in Scheme 1. The compounds are characterized by ¹H and ¹³C NMR, FT-IR, and elemental analysis. All the measurements were completed at RT.

The PXRD study analyses are measured for all the complexes. These results show the amorphous nature of complexes (Figure S4), which are suitable for device fabrication and further analysis. The PXRD data of 1Eu, 2Eu, and 3Eu complexes are also provided in Tables ST1–ST3. FT-Infrared spectroscopy: The FT-IR spectra of ligands and their respective Eu(III) complexes

S. no.	compound	λ_{\max} (abs) (nm) solution ^{<i>a,b</i>}	$\lambda_{\rm ex}^{a}$ (nm)	$\lambda_{\rm em}^{a,c}$ (nm)	I_2/I_1 ratio	fwhm
1	Eu(TTA) ₃ Ph	271, 340	275	580, 592, 612, 652, 702	11.7	8.2
2	Eu(TTA) ₃ Np	270, 340	275, 389, 356	580, 592, 612, 652, 703	10.9	10.8
3	Eu(TTA) ₃ TPA	304, 340	275, 389	580, 592, 612, 652, 703	10.5	11.2
4	L-Ph	243, 323, 385	365	465		
5	L-Np	246, 290, 330, 366	365	465		
6	L-TPA	242, 303, 343	330	440		

Table 2. UV-Absorption and PL Emission Data of Synthesized Ligands and Corresponding Eu(III) Complexes

^aMeasured in chloroform solution at 298 K. ^bAbsorption peaks from the UV-vis absorption spectra. ^cEmission peaks from photoluminescence emission spectra.

were measured in the range of $500-4000 \text{ cm}^{-1}$ (Figures S5 and S6). The FT-IR spectra of the Eu(TTA)₃·2H₂O complex showed a strong carbonyl (C=O) stretching frequency at 1610 cm⁻¹ and the complexes showed around 1600 cm⁻¹. The change in the stretching frequency of the carbonyl group is an indirect evidence to that the β -diketonate (Eu(TTA)₃·2H₂O) compound coordinated with the neutral ligand.^{37,38} In addition, to the same, the imidazole moiety peak at around 1600 cm⁻¹ in the ligand was shifted toward the higher wavenumber. All the above strategies are suggesting that the Eu metal ion was coordinated with the ligand molecule.

Photophysical Properties. UV-Visible Absorption and DRS Studies. The UV-visible absorption spectra of the ligands and the respective Eu(III) complexes were carried out in solution (chloroform solution conc. 1.0×10^{-5} mol L⁻¹) as well as in solid (Figure 2). The absorption spectra of ligands show absorption ranging from 240 to 450 nm with λ_{max} values ~ 242, 330, and 366 nm, respectively. These bands are attributed to the $\pi \to \pi^*$ transitions of the ligands. The absorption studies of Eu(III) complexes and Eu(TTA)₃·2H₂O show the peak maxima at ~340, 270 nm and 340, 275 nm, respectively. Similar spectral features were observed for the Eu(III) complexes as for the ligand as well as Eu(TTA)₃. However, a noticeable change was observed for the peaks maxima of the complexes compared to those of ligands. It is suggesting the presence of the ligand in the corresponding Eu(III) complexes, and the detailed study is listed in Table 2. The theoretically calculated UV absorption of the ligands is interpreted in Figure S7. The absorption maxima of the L-Ph, L-Np, and L-TPA are shown at 305, 348, and 350 nm, respectively. The observed peak maxima from the theoretical calculations are similar to those of the experimental analysis.

The relative study of absorption spectra of the europium(III) complexes in solution and solid shows that the absorption maximum shifts toward the longer spectra range for solid phase as compared to that of complex in solution. The experiential bathochromic shift in the absorption spectra is due to the aggregation of the complex in the solid phase.³⁹ The band gaps for all the ligands and respective complexes were calculated from the DRS with the help of the Kubelka–Munk function (Figures S8 and S9).^{40–42} The attained data from the DRS is adapted to the Kubelka–Munk function, and α is substituted with $F(R_{\infty})$ ($\alpha = F(R_{\infty})$).

$$\alpha h\nu = A(h\nu - E_{\rm g})^n \tag{1}$$

Here, *h*: Planck's constant, α : absorption coefficient, ν : frequency of vibration, *A*: proportional constant, E_g : band gap. Here, *n* values are given, for example, in the case of exponent n = 1/2, 3/2 is for direct transition allowed/forbidden and n = 2, 3 for allowed/forbidden indirect transition, respectively.

Photoluminescence Studies. In the luminescence process of Eu(III) complexes, populating the ligand triplet state as well as

manipulating the excited state of europium(III) complex energy levels is major task. The synthesized ligands, l-L, 2-L, and 3-L showed emission at 465, 465, and 440 nm under excitation wavelengths 365, 365, and 330 nm (Figure 3) in solution,



Figure 3. PL excitation and emission spectra of the ligands in chloroform.

respectively. The corresponding solid state showed emission at 476, 465, and 553 nm for L-Ph, L-Np, and L-TPA, respectively (Figure 4). Among all, L-TPA show distinguished emission,



Figure 4. PL emission spectra of the Eu(III) complexes in solid form.

which consisted of the broad emission which covers the region of primary spectral colors. Obviously, one can expect white light emission from the complex (cf. CIE color coordinates, Figure 12). The peak maxima of ligands in solid were shifted to higher wavelength compared to that of the peak maxima in solution. The red shift is expected due to aggregation of the molecule in the solid state. The ligands L-Ph, L-Np, and L-TPA showed blue emission in solution. The emission spectra of the ligands in different solvents were measured and are given in Figure S10. In the case of solid L-Ph and L-Np, they showed blue emission; however, L-TPA showed greenish-yellow emission. The complexes in ~360 nm excitation wavelength showed intense emission peaks at 612 nm attributed to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, due to electrical dipole (ED) transition in solution as well as solid. The excitation spectra of the ligands as well as complexes in solid form are displayed in Figures S11 and S12.

The Eu(III) complexes characteristic emission peaks are attributed to the intraconfigurational ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 0-4) transitions. The emission peaks appear at 579, 592, 612, 652, and 702 nm, and these emission lines correspond to 4f-4f transitions of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$, and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$, respectively. These results are indirectly indicating that there is energy transfer from ligand (L) to metal (M) ion. The ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition (579 nm) in the emission spectra indicates that all the Eu³⁺ ions occupy a site with the same symmetry. The magnetic character of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is independent of the coordinate environment of the Eu³⁺ ion. The observed transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ at 612 nm is the most intense induced ED transition, and it is clearly indicating that the Eu(III) occupies the site without an inversion center in the complex (Figure 5). The



Figure 5. PL excitation and emission spectra of the Eu(III) complexes in solution form.

calculated narrow fwhm's for 1Eu, 2Eu, and 3Eu in solution are 11.7, 10.9, and 10.5 nm, respectively. In the solid state, fwhm's for 1Eu, 2Eu, and 3Eu are 7.9, 8.1, and 12.8 nm, respectively. The fwhm of the 1Eu showed a better value for solid than the remaining complexes. The highest value of the 3Eu complex is due to expressed dominating character of the ligand emission from the complex.

The solvatochromism effect on ligands as well as Eu(III) complexes was studied, and their Stokes shift, linear fitting was discussed and shown in 2D, 3D spectra (Figures S11–S14; Table

ST4). The observed emission of the ligands (365, 365, and 330 to 475, 465, and 553 nm) showed wavelength moving toward the red spectral region (red shift) in the solution state with increasing the solvent polarity. This might be illuminated as the dipole of the excited state is high in polar solvents and leads to peak shift. The solvatochromism analysis of the Eu(III) complexes is shown in Figure 6, and their respective CIE color coordinates are listed in Table 1. The PL excitation and emission in different solvents with 2D spectra are displayed in Figures S17 and S18. The intensity of the ligand emission in the Eu(III) complexes is high in acetone solution, whereas it is less intense in toluene. The Eu(III) complex in less polar solvent is expected to be have energy levels that are high compared to those of the Eu(III) complex in polar solvent, which leads to intense high emission peak of the ligand along with europium emission (complex emission), observed in polar solvents like acetone, DMF, etc. The CIE color coordinates of the TPA based Eu(III) complex showed nearly white emission and showed close CIE white color coordinates in chloroform solution. This observation are expected as seen from the emission spectrum, where the ligand broad emission covered from blue to green emission in the complex as well as Eu(III) metal ion gives red emission.

The complexes in solution showed red emission at 612 nm along with additional emission peaks at around 420-580 nm regions. It belongs to ligand emission from the complex. It leads to deviating from the red emission of the Eu complexes. However, no emission from the ligand was observed in the solid state for 1Eu and 2Eu complexes (Figure 7) and showed red emission (digital images are shown in the inset of Figure 7). In the case of the TPA conjugated ligand based Eu complex (3Eu), the observation is weird; emissions from both ligand and Eu(III) metal ion were observed. These uncommon emissions were observed from the complex in solution as well as solid (3Eu); this might be due to less energy difference between the triplet state of the ligand and the excited state $({}^{5}D_{0})$ of the Eu(III) metal ion (cf. computational study). The presence of ligand emission in the Eu complex leads to greenish-yellow emission shown under UV light.

To understand the above optical characteristics of the complexes as well as the ligand-to-metal ion energy transfer mechanism, we extended our study to computational. The energy level locations (ligand singlet and triplet) were calculated by using DFT and TD-DFT analysis. The ligands, L-Ph, L-Np, and L-TPA, singlet energy levels were shown at 27 183 (3.37 eV), 268 421 (3.32 eV), and 25 591 (3.17 eV) cm⁻¹, respectively (Figure 8). The corresponding triplet energy levels were shown at 18 974 (2.35 eV), 18 904 (2.34 eV), and 18 582 (2.30 eV) cm^{-1} , respectively. Further, it was confirmed experimentally by the help of phosphorescence emission spectra at 77 K and found to be the triplet energy level, 2.55, 2.53, 2.36 eV for 1Eu, 2Eu, 3Eu, respectively (Figure S19). It is well-known that TTA energy levels are located at 25 164 (singlet) and 18 954 (triplet).⁴³ The excited state of the ${}^{5}D_{0}$ energy level of the Eu(III) metal ion is located at the 17.500 cm^{-1.44} For effective energy transfer from ligand $E(T_1)$ to Eu excited level $E({}^{5}D_0)$, according to the Letva et al. investigation, the energy difference ΔE should be in the range 2500–4000 cm^{-1.45} The present investigation indicates that the complexes 1Eu and 2Eu are satisfying the specified strategy, whereas 3Eu showed less energy difference between singlet and triplet levels as well as the ⁵D₀ level of Eu ion. It is clearly indicating that the complexes, 1Eu and 2Eu, have shown efficient energy transfer; however, the energy mismatch in the 3Eu indicates the inefficient energy transfer between ligand excited



Figure 6. PL emission of the complexes in different solvents (polarity variations).



Figure 7. PL emission spectra of the Eu(III) complexes in solid phase, and digital images under UV light are shown in the inset.

levels to ${}^{5}D_{0}$ Eu^{III} ion. In addition, the overlapping of the absorption spectra of TTA (acceptor) and emission spectra of the ligands indicates that the energy can also transfer from the TTA to the ligand triplet energy and reach to Eu(III) metal ion (interaction in the range of 400–440 nm) (Figure S20).

Photoluminescence Quantum Efficiency. By using the following formulas, the quantum efficiency (φ) can be obtained for the presently investigated complexes.⁴⁶



Figure 8. Energy transfer process from the ligands to center metal (Eu^{3+}) ion.

$$\varphi = \frac{L_0(\lambda) - L_i(\lambda)}{L_0(\lambda)}$$
$$\eta = \frac{E_i(\lambda) - (1 - \varphi)E_0(\lambda)}{E_0(\lambda)\varphi}$$

Here, $L_0(\lambda)$ = integrated excitation profile when the sample is directly excited by the incident beam, $E_0(\lambda)$ and $E_i(\lambda)$ = integrated luminescence of powder caused by direct excitation and by indirect illumination from the sphere, respectively. $L_i(\lambda)$ = integrated excitation profile obtained from the empty integrated sphere (empty holder). PLQYs of the complexes were measured

Table 3. Observed Luminescence Lifetimes τ_{obs} and Intensity Parameters of Synthesized Ligand and Corresponding Eu(III) Complex

		intensity parameters (10^{-20} cm^2)		$ au ({ m ms})^a$					
S. no.	compound	Ω_2	Ω_4	solid	acetone	CHCl ₃	DMF	THF	toluene
1	Eu(TTA) ₃ Ph	6.33	2.16	0.092	0.31	0.24	0.44	0.31	0.36
2	Eu(TTA) ₃ Np	4.78	0.79	0.084	0.32	0.20	0.43	0.30	0.37
3	Eu(TTA) ₃ TPA	5.84	0.13	0.070 ^b	0.005 ^b	0.005 ^b	0.005 ^b	0.005 ^b	0.006 ^b
4	L-ph (10^{-3} ms)			1.64	1.91	2.17	2.76	4.34	2.15
5	L-Np (10^{-3} ms)			3.14	3.63 ^b	3.16 ^b	4.18 ^b	2.16 ^b	2.72 ^b
6	L-TPA (10^{-3} ms)			2.21	2.06 ^b	2.75	2.67 ^b	2.49	2.67

^aThe decay curves for the β -diketonate europium(III) complexes and its ligands. ^bThe decay curves were found to be biexponential for the β -diketonate europium(III) complex and its ligand.



Figure 9. Lifetime of the Eu(III) complexes (1, 2, and 3 complexes) in different solvents and in the form of solid.

in chloroform solution as well as solid state. The PLQYs of the 1Eu, 2Eu, and 3Eu are shown as 6.3, 6.6 and 3.8% in solution and 1.4, 0.42 and 0.1% in solid. However, in the case of the solid, QY was reduced and it can be believed that nonradiative channels are expected to be more in solid. In addition, the PLQY of the complexes in thin film with PMMA doping showed enhanced observations and detailed discussions are given in PMMA film of Eu(III) complexes.

Lifetime and Judd–Ofelt Analysis. The lifetime data of the complexes as well as ligands were fitted with the single exponential function given by the equation, $I(t) = I_0 + A_1$

 $\exp\left(\frac{-t}{\tau}\right)$, where A_1 is the scalar quantity obtained from the curve fitting, t is the time in ms, $I_0 = 0$ is the offset value, and τ is the decay time value for the exponential component. However, among them, some of the complexes are best fitted with the biexponential curve, and details are interpreted in Table 3. Luminescence decay curves of the ${}^{5}D_0$ excited state were measured at 298 K and under 360 nm excitation (Figure 9). To understand the solvent influence on lifetime, the PL lifetime was investigated in various solvents (acetone, CHCl₃, DMF, THF, toluene). The luminescent lifetime values (τ) of 1Eu and 2Eu

ß.

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1Eu	901.85	1.10	9.96	8.36	36	5.54	77.67	16.79
2Eu	148.78	6.72	11.75	1.25	19.84	33.60	50.24	16.15
3Eu	641.60	1.6	13.66	4.4	54.09	7.79	75.78	16.42
Current (I) / µА	-1.08	— L-TP/	1.20 A 1.10	Current (I) / μA	-1.27 -1.14	—— Eu(TTA —— Eu(TTA —— Eu(TTA	0.90 (A) ₃ TPA (1.15 (A) ₃ Np (1.04 (A) ₃ Ph	

1.5

B2

Table 4. Radiat	tive Properties,	Internal Quar	ntum Efficiency	, and Branchi	ng Ratios of the	e Complexes
complex	$A_{\rm md} ({\rm s}^{-1})$	$T_{\rm md}~(\rm ms)$	A_{nr} (ms)	$\eta_{\rm In}$ (%)	$\eta_{\rm cons}$ (%)	β_1

Figure 10. Cyclic voltammetry analysis of the ligands (left) and their corresponding complexes (right).

0.5

1.0

complexes showed high in solution, almost 0.44 ms (in DMF solution), and their solids showed lower lifetime values, respectively. It indicates that the nonradiative relaxation is high in solid for 1Eu and 2Eu complexes. However, in the case of the 3Eu complex, a lower value of lifetime was observed. It could be expected that the presence of the ligand broad emission along with the Eu(III) metal ion emission peak in the 3Eu complex while, in liquid systems, the quenching of lifetime is due to nonradiative relaxation via vibronic coupling.⁴⁷ The complexes, 1Eu, 2Eu, and 3Eu, follow the order of lifetime such as DMF > toluene > THF \approx acetone > CHCl₃ > solid, DMF > toluene > acetone > THF > CHCl₃ > solid, solid > toluene > acetone \approx $CHCl_3 \approx DMF \approx THF$, respectively. In addition, the lifetime of the ligands was also calculated in solution as well as in solid. The details of the lifetime values are interpreted and summarized in Table 3. The lifetimes of the ligands in different solutions are interpreted and shown in Figure S21. The J-O parameter is one of the essential information for Eu(III) ions. The detailed calculation of the J-O parameter is reported elsewhere.³⁸ Parameters of Ω_2 and Ω_4 were calculated for all Eu(III) complexes. The calculated values are tabulated in Table 3. The observed higher Ω_2 value clearly indicates that the Eu(III) ion was located in a more covalent environment.

-0.5

0.0

Potential / V (vs Ag/AgCl)

-1.0

-1.5

Further, to understand the emission behavior by observing the lifetime with monitoring the ligand (465 nm) and Eu(III) metal ion (612 nm) at 340 nm excitation wavelength in the Eu complex was executed (Figure S22). The lifetimes of both monitoring wavelength are well fitted with a monoexponential function. The calculated lifetime values for 1Eu, 2Eu, and 3Eu are 0.243, 0.247, and 0.087 ms at 612 nm as a monitoring wavelength, and 0.0022, 0.0022, and 0.0021 ms at 460 nm as a monitoring wavelength. The lifetime of the Eu complexes at ~465 nm as monitoring wavelength (ligand emission in Eu complex) showed much lesser values than 612 nm monitoring wavelength, and it indicates that the less energy transfer from the ligand and more energy transfer from the Eu(III) metal ion in the complex. These results are clearly indicating the low percentage of ligand emission and high

percentage of Eu(III) presence in the Eu complex, which leads to deviating from red emission.

0.0

Potential / V (vs Ag/AgCl)

0.5

1.0

1.5

-0.5

-1.0

-1.5

The Judd-Ofelt intensity parameters were utilized further to calculate other vital optical properties unlike transition probabilities (A_{rad}, A_{nr}) , radiative lifetime (τ_{rad}) , and branching ratio (β). The total radiative transition probability can be written

$$A_{\rm rad} = \sum_{J} A_{0-J} \tag{2}$$

where $A_{\rm rad}$ is the total radiative transition probabilities. The radiative lifetime of the excited state of the $\operatorname{Eu}^{3\scriptscriptstyle+}$ ion and the total radiative transition probabilities are interrelated, which can be expressed as

$$\tau_{\rm rad} = \frac{1}{A_{\rm rad}} \tag{3}$$

The fluorescence branching ratio (β) for the transitions starting from the ${}^{5}D_{0}$ level can be resulting from the following equation:

$$\beta = \frac{A(0-J)}{A_{\rm rad}(0-J)} \tag{4}$$

The rate of nonradiative relaxation (A_{nr}) can be expressed as

$$A_{\rm nr} = \frac{1}{\tau_{\rm mes}} - \frac{1}{\tau_{\rm cal}}$$

where $\tau_{\rm mes}$ is the measured from the instrument decay curves and τ_{cal} is radiative lifetimes which was calculated from J–O theory, respectively. A_{nr} is the nonradiative relaxation rate which comprises multiphonon relaxation, energy transfer through cross-relaxation, and several other nonradiative processes.

Luminescence quantum efficiency (η) is defined as the ratio of the number of photons emitted to the number of photons absorbed. However, for the system containing lanthanide ion, it can be referred to as the ratio of the experimental lifetime to the

S. no.	compound	voltage $_{\text{onset}}^{\text{Oxi}}$ (V) (E_{LUMO} [eV])	$voltage_{onset}^{Red}$ (V) (E_{HOMO} [eV])	$\lambda_{\text{onset,}} (\text{nm})^{b}$	band gap/energy gap, E_{g}^{opt} , $(eV)^{c}$
1	Eu(TTA) ₃ Ph	1.04 (-5.44)	-0.96 (-3.43)	419	2.96 (2.0)
2	Eu(TTA) ₃ Np	1.15 (-5.55)	-1.13 (-3.26)	454	2.73 (2.29)
3	Eu(TTA) ₃ TPA	0.90 (-5.30)	-1.27 (-3.12)	423	2.93 (2.17)
4	L-Ph	1.23 (-5.63)	-1.04 (-3.35)	451	2.75 (2.28)
5	L-Np	1.09 (-5.49)	-1.06 (-3.33)	446	2.78 (2.16)
6	L-TPA	1.20 (-5.60)	-1.07(-3.32)	464	2.67 (2.27)

 ${}^{a}E_{\text{conset}}^{\text{Red}}$ = the onset reduction potentials, $E_{\text{onset}}^{\text{Oxi}}$ = the onset oxidation potentials, E_{g} = band gap, $E_{\text{g}} = E_{\text{LUMO}} - E_{\text{HOMO}}$. b Calculated from the optical absorption (DRS spectra). c Calculated the onset wavelength of optical absorption (onset) in solid state film (DRS spectra). The energy differences (HOMO and LUMO) values were calculated by cyclic voltammogram and are displayed in parentheses.



Figure 11. HOMO-LUMO energy levels and their calculated band gap of the ligands and their corresponding Eu(III) complexes.

calculated radiative lifetime of the $^5\!D_0$ level and can be expressed as

$$\eta_{\rm Ln}(\%) = \frac{\tau_{\rm mes}}{\tau_{\rm cal}} \times 100$$

The sensitized quantum efficiency (η_{sen}) can be determined from the equation given below

$$\eta_{\rm sen} = \frac{\eta_{\rm overall}}{\eta_{\rm Ln}}$$

where η_{overall} is the total quantum efficiency of the system measured through the standard measurement procedure. The corresponding radiative properties along with the branching ratios were calculated for the complexes, and the same has been tabulated in Table 4.

Electrochemical Properties. The HOMO and LUMO of the complexes are measured by cyclic voltammetry analysis. It gives significant redox properties that can be used to understand the energy levels of the Eu(III) complexes as well as ligand molecules. The observed 1Eu, 2Eu and 3Eu(III) complexes onset potentials are 1.04, 1.15, and 0.90 V; their ligand potentials are 1.23, 1.09, and 1.20 V, respectively (Figure 10). The reduction waves with onset potentials data as well as their obtained band gaps are listed in Table 5. The HOMO and LUMO energy levels were calculated by using the well-reported equation by de Leeuw et al.⁴⁸ The lowest energy gap is observed for 1Eu in cyclic voltammetry analysis, and 2Eu showed more energy gap.

$$E_{\text{HOMO}} = -(E_{\text{onset} \rightarrow \text{SCE}}^{\text{Oxi}} + 4.4) \text{ eV}$$

$$E_{\text{LUMO}} = -(E_{\text{onset} \rightarrow \text{SCE}}^{\text{Red}} + 4.4) \text{ eV}$$

The ground state optimized structures of the ligand were obtained from computational study, and their *xyz* coordinates for L-Ph, L-Np, and L-TPA are listed in Figure S23. The HOMO–LUMO of the ligands have also been calculated by DFT analysis. The obtained results as well as their HOMO and LUMO are listed in Table ST5. The HOMO and LUMO energy levels with respective band gaps of the ligands as well as their singlet and triplet energy levels are listed in Table ST6. The energy levels from HOMO–LUMO and their calculated band gap of the ligands and the corresponding Eu(III) complexes are shown in a pictorial way in Figure 11.

CIE Chromaticity Coordinates. CIE chromaticity coordinates were calculated for ligands and respective Eu(III) complexes from emission spectral data. The CIE color coordinates for 1Eu, 2Eu, and 3Eu are shown to be x = 0.36, y = 0.30; x = 0.42, y = 0.29; and x = 0.38, y = 0.29, respectively, in CHCl₃ solution. In the solid state, the CIEs are shown to be x = 0.64, y = 0.35; x = 0.60, y = 0.35; and x = 0.32, y = 0.44 for 1Eu, 2Eu, and 3Eu, respectively. In addition, the ligand CIEs were also measured in chloroform as well as solid phase. The CIE coordinates in solutions are shown for L-Ph, L-Np, and L-TPA, x = 0.17, y = 0.211; x = 0.18, y = 0.17; and x = 0.18, y = 0.24, respectively. In the case of solid of L-Ph, L-Np, and L-TPA, x = 0.24, y = 0.33; x = 0.38, y = 0.49; and x = 0.20, y = 0.30,



respectively (Figure 12). In the case of solution, the ligands L-Ph, L-Np, and L-TPA showed CIE toward blue emission to pale blue

Figure 12. CIE color coordinates for the 1Eu, 2Eu, and 3Eu complexes and respective ligands in solution as well as solid.

(nearly white). However, in the case of respective complexes, they showed white emission in the CIE color coordinates. 1Eu and 2Eu showed characteristic red emission. However, the 3Eu complex showed greenish-yellow emission. Comparing with solution and solid of the ligands, CIE color coordinates are showing shifting toward nearly white location in the CIE diagram from solution to solid. The same is indicating that the conjugation of the ligands increases with their color tuning toward white emission. It is clearly indirectly indicating that the ligand modification can lead to pure white emission as a single molecular complex. The CIE color coordinates (x, y) for the ligands L-Ph, L-Np, and L-TPA in different solvents are tabulated in Table ST7.

PMMA FILM OF EU(III) COMPLEXES

In order to understand the optical properties in the thin film, we have investigated the optical properties of Eu complexes by incorporating in PMMA matrix with different Eu complex concentrations. All the complexes showed red color PL emission except the TPA based complex. The TPA based complex fortunately showed white light emission at 1% doping (Figure 13). The intensity ratio (asymmetric ratio) as well as corresponding CIE color coordinates is interpreted in Table 6. The PLQYs of the complexes were also measured to understand the variance between the emission in different forms like solution, solid, and thin film. PLQYs of the complexes, 1Eu, 2Eu, and 3Eu, are shown in the case of pure thin film to be 1.44, 0.42, and 0.35%, respectively. The extreme enhanced PLQYs of the



Figure 13. PMMA doped thin films emission spectra for the 1Eu, 2Eu, and 3Eu complexes in different dopant concentrations and their respective CIE color coordinates (right side, down).

Table 6. Intensity Ratios as Well as CIE Color Coordinates for the Eu(III) Complexes in Different Concentration Ratio Doped PMMA

character	rization	1Eu	2Eu	3Eu
I ₂ /I ₁ (% of E	Eu ³⁺)	12.97 (pure) 17.06 (0.1) 16.07 (0.5) 17.00 (1.0)	11.46 (pure) 16.79 (0.1) 16.63 (0.5) 15.55 (1.0)	6.04 (pure) 7.67 (0.1) 8.08 (0.5) 7.55 (1.0)
CIE	x	0.647 (pure) 0.608 (0.1) 0.583 (0.5) 0.589 (1.0)	0.498 (pure) 0.297 (0.1) 0.315 (0.5) 0.355 (1.0)	0.530 (pure) 0.549 (0.1) 0.555 (0.5) 0.580 (1.0)
	у	0.335 (pure) 0.312 (0.1) 0.304 (0.5) 0.305 (1.0)	0.416 (pure) 0.240 (0.1) 0.251 (0.5) 0.301 (1.0)	0.312 (pure) 0.295 (0.1) 0.297 (0.5) 0.304 (1.0)

complexes were observed in the Eu(III) complex doped PMMA matrix. The Eu(III) complex doped with 0.5% in PMMA showed a high value than the remaining percentage of complexes, which are 30.1, 23.8, and 24.8% for 1Eu, 2Eu, and 3Eu, respectively.

Temperature Dependent Emission of the Eu Complex. There have been reports on the use of coordinated Eu(III) β diketone complexes in temperature sensing as well as in laser technologies.49,50 To use the above synthesized dual characteristic emissive Eu complex as a temperature sensing material, the temperature dependent PL spectra of the complexes have been monitored and the same is depicted in Figure 14. For the explanation of temperature sensing behavior of the Eu(III)-TPA complex, we have monitored the PL intensity at 612 nm (i.e., the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ electric dipole transition of the Eu³⁺ ion) versus various temperatures (from 20 to 90 °C) at an interval of 10 °C. The PL emission spectra reveal that the luminescence intensity linearly decreases with increasing temperature; the ligand emission also follows the same behavior and was found to decrease constantly. In addition, the CIE color coordinates for each of the emissions show a color transition from greenish blue toward blue region (CIE diagram in Figure 14, right). These obtained results are indicating that the currently synthesized TPA-Eu complex can serve as a temperature sensor.

Fabrication of LED with Eu Complexes. Light-emitting diodes were fabricated by using a combination of a 395 nm emitting InGaN chip with the complexes in different ratios like 1:10 and 1:50 (Eu(III) complex:PMMA). The complexes were coated by matching the above ratio and dried for 6 h at beyond ambient temperature (40 °C). Figure 15 shows emission of the original naked InGaN LED with a 395 nm chip and emission from the complexes under 20 mA forward-bias current. The excitation source from the LED was fully observed by the complex shown for 3Eu. The 3Eu complex showed yellowish emission at 20 mA forward-bias in both concentrations. The same was reflected in the case of solid also. However, in the case of 1Eu and 2Eu complexes, the observed emission is close to white emission. The obtained results were confirmed by CIE color coordinates and shown for 1Eu are x = 0.28, y = 0.35(1:10); x = 0.26, y = 0.33 (1:50); 2Eu are x = 0.26, y = 0.34(1:10); x = 0.27, y = 0.39 (1:50); and 3Eu are x = 0.41, y = 0.52(1:10); x = 0.46, y = 0.50 (1:50), respectively. In addition, the CIE of the obtained results are interpreted in Figure S24.

The above analysis include discussion about white emission obtained by integrating the 395 nm emitting InGaN chip. However, yellow emission was only obtained in the case of 3Eu instead of pure white or red emission, due to the broad ligand emission. Complex 3Eu has greenish yellow as well as red spectral region range. Due to lack of blue emission in the range of 400–450 nm, there is no white emission observed. On the basis of this criteria, we also coated with the blue LED with PMMA (1:10), and it showed white emission with CIE color coordinates of x = 0.29, y = 0.37 (1:10) (Figure S25). The presence of red emission from Eu(III) ion is very weak, and to improve the same, the percentage of Eu complex (3Eu) was increased. The 3:10 ratio was made to achieve the bright white emission with appropriate CIE color coordinates x = 0.30, y = 0.33 (Figure 16).

In addition, to achieve the white emission from the UVemitted LED, the ligand and Eu complex were conjugated in different ratios. The L-Np and 3Eu were taken in 1:1, 3:6, 6:3, 1:9, and 1:15 ratios in the PMMA. Increasing with concentration of the ligand in the PMMA, emission in the region of bluish green increment was observed and CIE values are shifting toward the blue region. To avoid the same, Eu complex concentration was



Figure 14. Temperature dependent emission spectra of Eu(TTA)₃TPA and their corresponding CIE color coordinates.



Figure 15. Spectra A, B, and C are Eu(III) complexes coated on the 395 nm emitted LED chip. In the inset a is the original 365 nm emitted LED chip; aa is under forward bias. b and c are coated with Eu(III) complexes, and bb and cc are with forward bias, respectively.



Figure 16. Emission spectra of Eu(III) complex with coated on the blue (450 nm) emitted LED chip. In inset **a** is the original 450 nm emitted blue LED chip; **aa** is under forward bias. **b** is coated with Eu(III) complex, and **bb** is with forward bias, respectively (left side). The respective CIE of the 3Eu complex (right side).

increased up to 1–15 ratio and the CIE was found to be x = 0.28, y = 0.34 (Figure S26). Remaining CIE values are x = 0.26, y = 0.51 (1:1); x = 0.19, y = 0.30 (3:6); x = 0.26, y = 0.42 (6:3); and x = 0.22, y = 0.35 (1:9). Further, increment of the Eu complex concentration may lead to bright white emission.

Thermal Study. The thermogravimetric analysis of the complexes, 1Eu, 2Eu, and 3Eu, is measured from ambient temperature to 800 °C under a nitrogen atmosphere (Figure 17). The thermal decomposition of the complexes are shown in three stages in the region of ~134–294 °C (first stage, major), ~300–

513 °C (second stage), and >515 °C (third stage). The major decomposition of the Eu complexes is responsible for the ancillary ligands present in the complex. The second thermal decomposition is due to TTA molecules present in the Eu complex. The minor thermal decomposition that has also been observed in the region of 85–110 °C belongs to the loss of water traces present in the complex. The final decomposition of the complexes is due to the presence of a pyridyl moiety and aromatic phenyl groups. As compared with 2Eu and 3Eu, 1Eu showed that the end of thermal decomposition was found to be



Figure 17. Thermal decomposition analysis of the Eu complexes; the inset shows the end point of the thermal decomposition.

higher, which is shown in Figure 17, inset. However, the thermal decomposition of the Eu complexes is shown to be more than 185 °C. These results indicate that the current synthesized Eu complexes are potential candidates.

CONCLUSIONS

In the summary, the mononuclear Eu(III) metal ion with tris- β diketones and bipyridyl ancillary based ligands (1L-Ph, 2L-Np, 3L-TPA) were synthesized, and the corresponding europium-(III) ternary complexes were prepared. The photophysical properties of the ligands and respective complexes are investigated in solution, thin film, as well as solid. The 1Eu and 2Eu showed efficient energy transfer. The remaining 3Eu complex showed inefficient energy transfer from ligand to Eu(III) metal ion. All the Eu complexes exhibit high intense emission with high color purity. We have optimized the ligand geometry and calculated the energy level location by using DFT and TD-DFT calculations. On the basis of these calculations, the energy transfer mechanism was proposed as a ligand-sensitized luminescence process to the Eu(III) metal ion. The temperature dependent emission behavior of the 3Eu complex was analyzed, and it leads to the 3Eu complex sustaining as a temperature sensor. A white LED was fabricated by integrating the complexes with a naked InGaN LED with a 395 nm chip, and emission was observed from the complexes under 20 mA forward-bias current. The excitation source from the LED was fully observed by the complex shown for 3Eu and it showed yellowish emission. However, in the case of 1Eu and 2Eu complexes, they showed close to white emission and were analyzed by CIE color coordinates (NTSC standard value). In addition, the complex 3Eu coated with the blue LED by PMMA (1:10) showed bright white emission. The work undoubtedly gives a path to discover the visible light/near-UV excited Eu(III) complex and inefficient energy transfer from ligand to metal ion is the key criteria for exploring single component white emissive new Eu(III) complexes for solid state lightings.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01565.

The ¹H and ¹³C NMR spectra of the ligands, powder X-ray diffraction patterns of the complexes and the ligands, detailed solvatochromism studies of the complexes, emission spectra of the ligands L-Ph, L-Np, and L-TPA in different solvents, lifetime of the Eu complexes as well as ligands at different monitoring wavelengths, and HOMO, LUMO energy levels of the ligands and their corresponding complexes (PDF)

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Notes

The authors declare no competing financial interest.

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