Theoretical Modeling (Sparkle RM1 and PM7) and Crystal Structures of the Luminescent Dinuclear Sm(III) and Eu(III) Complexes of 6,6,7,7,8,8,8- Heptafluoro-2,2-dimethyl-3,5-octanedione and 2,3-Bis(2-pyridyl)pyrazine: Determination of Individual Spectroscopic Parameters for Two Unique Eu$^{3+}$ Sites

Aabid Bashir Ganaie and Khalid Iftikhar*

Cite This: ACS Omega 2021, 6, 21207−21226

1. INTRODUCTION

The luminescence of lanthanides being unique in its own nature has made them applicable as lasers,1 sensors,2−5 luminescent materials,6−8 luminescence based tools for the investigation of cellular environments,9 and solar energy conversion devices.10,11 The lanthanide emission bands are very sharp and exhibit long emission decay times.12 The direct optical excitation of lanthanide metal ions results in poor emission quantum yields due to lower absorptivity coefficients in the UV−Visible spectrum. To overcome this problem, the indirect excitation through the organic ligands is used. The choice of the organic ligand for light harvesting and then efficiently transferring the energy to the metal ion is the key for achieving higher quantum yields (antenna effect).13,14 Luminescence can also be intensified by tuning the triplet state of the coordinating ligands to provide a suitable energy gap for effective energy transfer from the triplet state of the ligand to the emissive level of lanthanide ions.15 Of the plethora of the ligands used as sensitizers, β-diketones are one of the most effective ligands16 for the sensitization of the lanthanide ions since the β-diketone derivatives are easy to prepare, have greater stability, and present noticeable luminescence properties.17,18 The fluorines in the fluorinated β-diketones also enhance the overall quantum yield by reducing the non-radiative decay occurring via high energy C−H/N−H vibrations by replacing them with lower energy
C–F vibrations. The fluorinated β-diketone complexes possess greater oxidative and thermal stability (evaporable) while presenting as single molecule magnets and electroluminescent devices. The lanthanide tris β-diketone being coordinatively unsaturated are highly reactive and readily coordinate with the approaching ancillary ligand. The ancillary ligands are proficient in suppression of radiation less transitions by replacing the water molecules in the coordination sphere and therefore intensify the overall luminescence. Voluminous combinations of β-diketones and ancillary ligands have been studied for the subject of luminescence. Along the same lines, our group hitherto has synthesized and studied many mononuclear, dinuclear, and hetero-dinuclear complexes for the purposes of fabricating OLEDs and luminescent materials resulting from various combinations of different fluorinated β-diketones and several ancillary ligands. The luminescence of samarium (pink/orange) and europium (red) complexes/materials has been studied extensively among the lanthanides. The homo-dinuclear heavier lanthanide centers for a polynuclear complex by a classical method provides inconsistent results and, to overcome this problem, the overlap polyhedra method (OPM) has been successfully used for more complicated structures like lanthanide organic frameworks in a reasonable time. 

Table 1. Crystal Structure Data and Structure Refinement of Complexes

| Complex | Sm[Sm(fod)₃]₂(bpp) | Eu[Sm(fod)₃]₂(bpp) |
|---------|--------------------|--------------------|
| CCDC number | 1956378 | 1956379 |
| Empirical formula | C₇₄H₇₀F₄₂N₄O₁₂Sm₂ | C₇₄H₇₀F₄₂N₄O₁₂Eu₂ |
| Formula weight | 1926.62 | 1926.62 |
| Temperature | 100 K | 100 K |
| Wavelength | 0.7107 Å | 0.7107 Å |
| Space group | P1 | P1 |
| Unit cell dimensions | a = 12.384 Å, α = 103.852°, b = 19.821 Å, β = 90.682°, c = 19.834 Å, γ = 102.420° | a = 12.322 Å, α = 103.841°, b = 19.694 Å, β = 90.859°, c = 19.714 Å, γ = 102.307° |
| Volume | 4606 Å³ | 4527 Å³ |
| Density | 1.037 g cm⁻³ | 1.081 g cm⁻³ |
| F(000) | 2280 | 2284.0 |
| Reflections collected | 28958 | 27838 |
| Completeness to theta = 26.5° | 95.2% | 96.7% |
| Final R indices [I > 2σ(I)] | R libr = 0.0878, wR libr = 0.2747 | R libr = 0.0883, wR libr = 0.2317 |
| S | 1.037 | 1.081 |

2. RESULTS AND DISCUSSION

2.1. Experimental (Single-Crystal X-ray Analysis) and Theoretical Structure Elucidation. Pure crystals suitable for single-crystal X-ray analysis were obtained by slow evaporation of ethanol solution of isolated complexes. The single-crystal X-ray analysis data is presented in Table 1. The single-crystal structure analysis reveals that Sm³⁺ and Eu³⁺ complexes are dinuclear, in which the two metal centers are bridged by the bpp ligand. Both the complexes crystallize in the triclinic P1 space group and have similar unit cell dimensions. Each unit cell contains two independent moieties of [Sm(fod)₃(bpp)] (Sm = Sm and Eu). These complexes are isomorphous, in which each metal center is surrounded by six oxygen atoms (from three fod ligands) and two nitrogen atoms (from the bpp ligand) resulting in an eight-coordinate structure (Figures 1 and 2). Each metal center in these complexes (Sm and Eu) is coordinated to one pyridyl and one pyrazine nitrogen on each side of bpp. The metal–N and metal–O bond distances are presented in Table 2. It is interesting to mention that the average Eu–O (2.35 Å) and Eu–N (2.62 Å) bond distances are shorter than Sm–O (2.38 Å) and Sm–N (2.65 Å), which could be the result of the smaller size of Eu³⁺ ions. The intermetallic distances between the two metal centers are 7.96 Å (Sm–Sm) and 7.90 Å (Eu–
Eu). The longer Sm–Sm intermetallic distance can also be related to the larger size of Sm$^{3+}$. The Eu–N bond lengths and Eu–Eu intermetallic distance for the present complex under study are shorter than those reported for the bpp bridged dinuclear complex [Eu(tta)$_3$(bpp)] (tta = 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione). It could be due to the presence of perfluoryl group in the fod moiety, which increases the residual acidity of europium, making it a better complexing site for the incoming donors. Therefore, the europium ions attract the bpp more strongly, resulting in shorter Eu–Eu and Eu–N distances. However, the Eu–O (2.35 Å) and Eu–N (2.62 Å) bond distances for the [Eu(fod)$_3$(μ-bpp)Eu(fod)$_3$] complex are longer than the Eu–O (2.33 Å) and Eu–N (2.57 Å) bond distances reported for mononuclear [Eu(tdh)$_3$(bpp)] (tdh is 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione). Both Sm$^{3+}$ and Eu$^{3+}$ complexes are stabilized by the π–π stacking interactions between the two pyridine rings of bpp with interplanar distances of 4.11 Å (Figures 1b and 2b). Similar interplanar π–π interactions are also reported between the rings of indazole in the complexes [Eu(hfaa)$_3$(indazole)$_3$] and [Dy(hfaa)$_3$(indazole)$_3$]. The torsion angle of two pyridine rings with respect to the pyrazine ring has been reported to be 5.4°.

Figure 1. (a) Molecular structure of [Sm(fod)$_3$(μ-bpp)Sm(fod)$_3$], (b) π–π stacking between two molecular units, (c) shapes of the polyhedra of coordination sphere around the two metal ions in [Sm(fod)$_3$(μ-bpp)Sm(fod)$_3$], and (d, e) the unit cell views of the complex from two perpendicular directions.
in the crystal structure of free bpp. However, this angle is 17.9° (C10−C3−C4−C5) in the Sm3+ complex and 19.1° (C10−C3−C4−C5) in the Eu3+ complex. In addition to the torsion induced into the bpp upon coordination with the Ln(fod)3 moieties (Ln = Sm3+ and Eu3+), the pyrazine ring is also more deviated from its planarity than it had in the free bpp.

The optimized structure of the complexes was obtained using Sparkle RM1 and PM7 (Figures S1−S4). The average bond lengths predicted by Sparkle RM1 and PM7 for metal to oxygen and metal to nitrogen are in close agreement to the results found from the crystal structure analysis for the complexes (Table 3). The Sparkle RM1 and PM7 optimized structures of the Eu3+ complex show the root mean square deviation (RMSD) of 2.217 and 2.878 Å, respectively, from the crystal structure. Similarly, the RMS deviation of Sparkle RM1 and PM7 optimized structures from the crystal structure of the Sm3+ complex is 2.675 and 2.564 Å, respectively. In both cases, the RMS deviation values are lower than those reported for the Sparkle/RM1 optimized structure of the tetra-europium centered molecule (5.07 Å) with respect to its crystal structure. The lower RMSD values for the optimized structures indicate the accuracy of the Sparkle RM1 and PM7 in predicting the structures of the complex structures.

2.2. **Shape Analysis.** The shape analysis was performed using the reported method by Haigh. For the eight-coordinate metal centers, the most encountered shapes are square antiprism (SAP), bicapped trigonal prism (BCTP), and dodecahedron (D). These shapes have 16, 17, and 18 edges, respectively. The two adjacent atoms depicting an edge subtend an angle at the central metal atom (Figure S5). Therefore, there are 16, 17, and 18 angles, respectively, subtended by the 16, 17, and 18 edges of square antiprism, bicapped trigonal prism, and dodecahedron shapes at the central metal atom. The total number of angles in an eight-coordinate polyhedron subtended at the central metal atom by all the possible pairs of the coordinated 8 ligand atoms is 28 (including both adjacent and non-adjacent pair of atoms). For
the shapes (vide supra), the angles subtended by the edges at the central metal atom must be the smallest of the total number (28) of angles and the change between the two consecutive angles among them must be very small. Therefore, for square antiprism 16, for bccapped trigonal prism 17, and for dodecahedron 18, angles must be the smallest of the total 28 angles in ascending order. All the possible 28 angles of the individual polyhedron of the complexes of Sm3+ and Eu3+ in the ascending order are presented in Tables S1 and S2. In the case of the Sm1 center of the Sm3+ complex and Eu1 center of the Eu3+ complex, the 17th angle abruptly increases compared to the smaller 16th angle (Tables S1 and S2). The difference between the 16th and the 17th angle is 21.1° (Sm1 center of the Sm3+ complex) and 20.4° (Eu1 center of the Eu3+ complex). These values suggest that the arrangement of the ligand atoms around it while the other center has a triangular dodecahedron geometry (Figures S6 and S7). However, the Sparkle RM1 optimized structures show that, in the case of the Eu3+ complex, the shape around both Eu3+ centers is square antiprismatic while the shape around the two unique metal centers in a given complex is not similar, with one metal center having a square antiprismic arrangement of ligand atoms around it while the other center has a triangular dodecahedron geometry (Figures S8 and S9). It is not in the agreement with the experimental results obtained from the single-crystal X-ray analyses. Therefore, it is concluded that the Sparkle RM1 does not work satisfactorily for the complexes investigated here. The distortions calculated from the ideal eight-coordinate geometries using SHAPE software66 for Sparkle PM7 and RM1 are presented in Tables S5–S8.

2.3. 1H NMR Spectra. The one-dimensional (1H NMR) and two-dimensional (1H-1H COSY) spectra were used to assign the NMR signals of the bpp and the complexes. The chemical shifts of the free ligand and the complexes are presented in Table 4. The 1H NMR spectra (1D and COSY correlation) of the free ligand 2,3-bis(2-pyridyl)pyrazine (bpp) exhibit four resonances at 8.68, 8.36, 7.76, and 7.21 ppm (δ) in the intensity ratio of 1:1:2:1 (Figures S10 and S11). The pyrazine ring protons (H-1) resonate as a singlet at 8.68 ppm (δ). The other three signals are due to the protons of the pyridine rings. The H-2 protons that are nearer to pyridyl nitrogen appear at 8.38 ppm (δ) as a doublet. The H-4 and H-5 protons appear as a combined multiplet at 7.76 ppm (δ), and the H-3 protons resonate as an asymmetric triplet at 7.21 ppm (δ). The proton resonances of free bpp assigned by 1H-1H COSY conform with the report available in the literature.52 The NMR spectra of the complexes are consistent with the presence of coordinated bpp. The NMR spectra of the diamagnetic complexes [La(fod)3(bpp)] (Figure S12) and [Lu(fod)3(μ-bpp)Lu(fod)3]66 (Figures 3 and 4) show four signals for the coordinated bpp and one resonance each for methine and t-butyl group of the β-diketone. The methine and

| Table 2. Bond Lengths between Metal Ions and Atoms around the Coordination Sphere of the Complexes |
|-----------------------------------------------|
| [Sm(fod)3(μ-bpp)Sm(fod)3] | [Eu(fod)3(μ-bpp)Eu(fod)3] |
| Sm1–O7 | 2.403 | Eu1–O7 | 2.331 |
| Sm1–O8 | 2.379 | Eu1–O8 | 2.358 |
| Sm1–O9 | 2.403 | Eu1–O9 | 2.371 |
| Sm1–O10 | 2.377 | Eu1–O10 | 2.319 |
| Sm1–O11 | 2.405 | Eu1–O11 | 2.350 |
| Sm1–O12 | 2.355 | Eu1–O12 | 2.374 |
| Sm1–N3 | 2.625 | Eu1–N1 | 2.594 |
| Sm1–N4 | 2.626 | Eu1–N2 | 2.593 |
| Sm2–N1 | 2.688 | Eu2–N3 | 2.656 |
| Sm2–N2 | 2.650 | Eu2–N4 | 2.622 |
| Sm2–O1 | 2.348 | Eu2–O1 | 2.332 |
| Sm2–O2 | 2.407 | Eu2–O2 | 2.350 |
| Sm2–O3 | 2.385 | Eu2–O3 | 2.396 |
| Sm2–O4 | 2.376 | Eu2–O4 | 2.336 |
| Sm2–O5 | 2.358 | Eu2–O5 | 2.346 |
| Sm2–O6 | 2.368 | Eu2–O6 | 2.358 |

| Table 3. Average Bond Lengths |
|--------------------------------|
| Sm1–O | Sm1–N | Sm2–O | Sm2–N | Eu1–O | Eu1–N | Eu2–O | Eu2–N |
| crystal structure | 2.387 | 2.625 | 2.374 | 2.669 | 2.351 | 2.594 | 2.353 | 2.639 |
| sparkle/RM1 | 2.412 | 2.587 | 2.414 | 2.588 | 2.388 | 2.519 | 2.385 | 2.522 |
| sparkle/PM7 | 2.382 | 2.559 | 2.380 | 2.561 | 2.382 | 2.559 | 2.382 | 2.555 |
butyl resonances appear in a 1:9 intensity ratio. The magnitude of the inductive effect of coordination in the case of the Lu$^{3+}$ complex is stronger and is manifested by the larger downfield shifts of H-1 and H-2 protons, which are closer to the Lu$^{3+}$.

The NMR spectra of the paramagnetic complexes are more interesting where the bpp signals are shifted to higher fields (in the case of the Sm$^{3+}$ complex) as well as to the lower fields (in the case of the Eu$^{3+}$ complex). The NMR spectra of the Sm$^{3+}$ complex display six resonances in the intensity ratio of 1:1:1:4:1:27, which have been assigned by 2D$^1$H-$^1$H COSY (Figures 5 and 6). Similarly, the NMR spectra of the Eu$^{3+}$ complex display six resonances in the intensity ratio of 2:1:1:3:27 (Figures S13 and S14). In both the paramagnetic complexes, the largest shift is noted for H-2 followed by H-1 protons, supporting the view that the bpp is acting as the bridge between the Ln(fod)$_3$ units through the nitrogen atoms of pyrazine and pyridine rings. In the case of [Sm(fod)$_3$(μ-bpp)Sm(fod)$_3$], the methine resonance coalesce with the H-4 proton signal of bpp and appears at 7.04 ppm. The other signals due to bpp protons, except H-5, are shifted to upfield with H-2 showing the highest shift followed by and H-1 due to their proximity to the metal ion. In the Eu$^{3+}$ complex, all resonances of coordinated bpp are shifted to downfields with the largest downfield shift for H-2 followed by H-1. Meanwhile, the methine proton signal has moved to the upfield side. The t-butyl could not be shifted to the higher field instead has been de-shielded and appears at the lower field. Such exceptions are available in the literature.$^{67}$ This result and reports available in the literature$^{68,69}$ suggest that the induced paramagnetic shifts are dipolar in nature. The NMR spectra of the complexes show no resonance for free bpp or free β-diketone; no change in signal line width or position is noted even on keeping the solutions for a few days.

### 2.4. UV/Visible Absorption Spectra

The absorption spectra of the 10$^{-5}$ M solution of free ligands and Sm and Eu

| Chemical Shifts$^{a}$ and Paramagnetic Shifts$^{b}$ of the Complexes |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | H-1             | H-2             | H-3             | H-4             | H-5             | CH              | Bu$^t$          |
| bpp            | 8.68(s)         | 8.38(d)         | 7.21(t)         | 7.76(m)         | 7.76(m)         | 5.88            | 1.05            |
| [La(fod)$_3$(bpp)] | 8.99(s)         | 8.86            | 7.40(m)         | 7.70(t)         | 7.39(m)         | 5.88            | 1.06            |
| [Lu(fod)$_3$(μ-bpp)Lu(fod)$_3$] | 9.32            | 9.25            | 7.49            | 7.67            | 7.47            | 5.87            | 1.08            |
| [Sm(fod)$_3$(μ-bpp)Sm(fod)$_3$] | 7.16(−2.16)     | 6.23(d)(−3.02)  | 7.21(t)(−0.28)  | 7.04(−0.63)     | 8.11(0.64)      | 7.04(1.17)      | 1.01(−0.05)     |
| [Eu(fod)$_3$(μ-bpp)Eu(fod)$_3$] | 16.98(7.61)     | 17.72(8.47)     | 15.14(7.44)     | 11.78(4.39)     | 10.23(2.84)     | 2.59(−3.29)     | 1.41(0.36)      |

$^{a}$Chemical shifts are presented in parts per million (ppm) relative to the internal standard tetramethylsilane (TMS). Positive and negative chemical shifts are plotted downfield and upfield, respectively. $^{b}$The paramagnetic shift, given in parentheses, is the difference between chemical shifts of a given proton in the paramagnetic complex and diamagnetic Lu complex.

Figure 3. 500 MHz $^1$H NMR spectra at 298 K of [Lu(fod)$_3$(μ-bpp)Lu(fod)$_3$], (a) enlarged portion from 7.2 to 9.7 ppm of spectra.
complexes are presented in Figure 7. The free ligands absorb in the range of 240−330 nm, and the maxima ($\lambda_{\text{max}}$) appear at 296 nm (Hfod) and 286 nm (bpp). The absorption band of the ligands are shifted in the complexes and appear as a single band in the range of 240−380 nm with the maxima ($\lambda_{\text{max}}$) appearing at 293 nm. This band in the complexes is assigned to the $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition. The shift of the band is due to coordination of the ligands to the metal ion. The molar extinction coefficients of $[\text{Sm}(\text{fod})_3(\mu\text{-bpp})\text{Sm}(\text{fod})_3]$ (1.10 × $10^4$ L mol$^{-1}$ cm$^{-1}$) and $[\text{Eu}(\text{fod})_3(\mu\text{-bpp})\text{Eu}(\text{fod})_3]$ (2.63 × $10^4$ L mol$^{-1}$ cm$^{-1}$) are higher than those of Hfod (8.10 × $10^3$ L mol$^{-1}$ cm$^{-1}$) and bpp (3.95 × $10^3$ L mol$^{-1}$ cm$^{-1}$). The increase in the molar extinction coefficient of the complexes than the ligands provides strong evidence that the Hfod and bpp have coordinated to the metal ions. The spectra of the $[\text{Sm}(\text{fod})_3(\mu\text{-bpp})\text{Sm}(\text{fod})_3]$ and $[\text{Eu}(\text{fod})_3(\mu\text{-bpp})\text{Eu}(\text{fod})_3]$ complexes were also obtained from 10−3 M chloroform solutions (Figure S15) in order to observe metal-based absorptions (4f-4f absorption are parity forbidden, therefore have very low absorptivity coefficients). It is noteworthy that the 4f-4f transitions appearing in the absorption spectra are also present in the excitation spectra of the complexes.

2.5. Luminescence. The luminescence spectra in the visible region are investigated in the solid state, solution (chloroform, dichloromethane, ethanol, and acetone), and PMMA polymer thin films. The emission spectra with the most intense emission peaks for the Sm$^{3+}$ and Eu$^{3+}$ complexes were obtained by recording the emission spectra of the chloroform solutions at different excitation wavelengths (Figures S16 and S17). The excitation spectra were also obtained from 10$^{-3}$ M chloroform solutions in order to observe metal-based absorptions (4f-4f absorption are parity forbidden, therefore have very low absorptivity coefficients). It is noteworthy that the 4f-4f transitions appearing in the absorption spectra are also present in the excitation spectra of the complexes. The emission spectra of the samarium complex display three characteristic emission peaks $^4G_{5/2} \rightarrow ^6H_{5/2}$ (561 nm), $^4G_{5/2} \rightarrow ^6H_{7/2}$ (596 nm), and $^4G_{5/2} \rightarrow ^6H_{9/2}$ (642 nm) in each solvent and hybrid thin films (Figure S16 and S17). The excitation spectra are obtained by monitoring the most intense emission peak of the complexes. These are at 642 nm ($^2G_{5/2} \rightarrow ^2H_{9/2}$) for the Sm$^{3+}$ complex and 614 nm ($^2D_{9/2} \rightarrow ^2F_{7/2}$) for the Eu$^{3+}$ complex. The excitation spectra of the complexes in different solvents (Figure 8) appear in the range of 325−430 nm with maxima ($\lambda_{\text{max}}$) at 351 nm (acetone), 363 nm (chloroform), 359 nm (dichloromethane), and 361 nm (ethanol) for the Sm$^{3+}$ complex and 358 nm (acetone), 364 nm (chloroform), 361 nm (dichloromethane), and 361 nm (ethanol) for the Eu$^{3+}$ complex. These are $\pi \rightarrow \pi^*$ transitions ($S_0 \rightarrow S_1$) of the organic ligands (fod and bpp). The maximum wavelength ($\lambda_{\text{max}}$) was used to obtain the emission spectra in the respective solvents. The excitation bands in the case of solid complexes are more intense and much broader than those observed for the solution (Figures 8 and 9). The excitation bands for the solid complexes extend up to 440 nm with maxima at 354 nm (Sm$^{3+}$ complex) and 261 nm (Eu$^{3+}$ complex). The excitation spectra of the thin films (Figures S18 and S19) show broad bands in the range of 230−360 nm (for the Eu$^{3+}$ complex) and 330−460 nm (for the Sm$^{3+}$ complex). The excitation spectra of thin films broaden and show red shift on increasing the concentration of complexes in the PMMA polymer. These results corroborate with those reported for $[\text{Eu}(\text{fod})_3(\text{H}_2\text{O})_2]$-doped PMMA films.70 The excitation spectra mimic the absorption spectra, suggesting that the energy is absorbed through the $\pi \rightarrow \pi^*$ transitions ($S_0 \rightarrow S_1$) of the organic ligands (fod and bpp) and then transferred to the metal ion.

The emission spectra of the samarium complex display three characteristic emission peaks $^4G_{5/2} \rightarrow ^6H_{5/2}$ (561 nm), $^4G_{5/2} \rightarrow ^6H_{7/2}$ (596 nm), and $^4G_{5/2} \rightarrow ^6H_{9/2}$ (642 nm) in each solvent and hybrid thin films (Figure 11 and Figure S20). The emission spectrum of the solid complex (Figure 10) displays an additional peak at 561 nm $^2G_{5/2} \rightarrow ^2H_{11/2}$,71,72 The electric-dipole transition $^2G_{5/2} \rightarrow ^2H_{9/2}$ is the most intense, followed by $^4G_{5/2} \rightarrow ^2H_{7/2}$ (magnetic-dipole) and $^4G_{5/2} \rightarrow ^6H_{5/2}$ transitions. This indicates that the samarium complex lacks...
an inversion center. It is reported that the intensity of the magnetic-dipole transition \(4G5/2 \rightarrow 6H7/2\) is higher than the electric-dipole transition in centrosymmetric complexes.\(^7\) Furthermore, the \(4G5/2 \rightarrow 6H7/2\) transition shows stark splitting. The higher intensity of the electric-dipole transition and stark splitting in the magnetic-dipole transition are indicative of the fact that the complex has a distorted geometry, which results in higher asymmetry of the field around samarium. This corroborates with the results obtained from the shape analysis of the crystal structure. The coordination symmetry around the \(\text{Sm}^{3+}\) ion in a complex is determined by measuring the experimental energy parameter \(\eta_{\text{sm}}\), which represents the ratio of the integrated area under the peaks of \(4G5/2 \rightarrow 6H9/2\) (electric-dipole) and \(4G5/2 \rightarrow 6H5/2\) (magnetic-dipole) transition.\(^7\) The \(\eta_{\text{sm}}\) of the solid complex and its solutions in different solvents are 8.71 (solid complex), 5.85 (chloroform), 4.92 (acetone), 4.6 (ethanol), and 4.31 (dichloromethane). It appears that the highest asymmetry of the field prevails in chloroform followed by acetone, ethanol, and dichloromethane. The highest asymmetry around the samarium is noted for the solid complex (\(\eta_{\text{sm}} = 8.71\)), which is evident from the very prominent stark splitting of the magnetic-dipole transition.

The emission spectra of the europium complex display five emission peaks, \(5D_0 \rightarrow 7F_0\) (578 nm), \(5D_0 \rightarrow 7F_1\) (590 nm), \(5D_0 \rightarrow 7F_2\) (614 nm), \(5D_0 \rightarrow 7F_3\) (651 nm), and \(5D_0 \rightarrow 7F_4\) (694 nm), in different solvents, the solid state, and thin films (Figures 10 and 11 and Figure S21). The electric-dipole transition \(5D_0 \rightarrow 7F_2\) transition is hypersensitive and is the most intense. The higher intensity of the \(5D_0 \rightarrow 7F_2\) transition is directly related to the asymmetry around the europium ion and higher polarizability of the ligands.\(^7\) The bright red emission reflected in CIE coordinates of the europium complex is due to the highly intense \(5D_0 \rightarrow 7F_2\) transition. The intensity ratios \(\eta_{\text{Eu}}\) of \(5D_0 \rightarrow 7F_2/5D_0 \rightarrow 7F_1\) transitions for the europium complex in acetone, chloroform, dichloromethane, and ethanol are 13.29, 12.80, 12.38, and 12.29, respectively. This intensity ratio \(\eta_{\text{Eu}}\) in the solid state is 11.54, and those in thin hybrid films are 11.67 (at 5\%(w/w)) and 12.28 (at 10\%(w/w)). The \(5D_0 \rightarrow 7F_2/5D_0 \rightarrow 7F_1\) intensity ratio in all solvents, the solid state, and thin films is greater than that reported\(^7\) for \([\text{Eu}(\text{fod})_3(\text{H}_2\text{O})_2]\) with \(\eta_{\text{Eu}} = 7.96\), indicating that the intensity of \(5D_0 \rightarrow 7F_2\) has remarkably increased on complex formation with bpp. It reflects that bpp is a good sensitizer and effectively populates the emitting level of europium. The higher intensity ratio indicates that the ligand environment around the europium is highly polarized.\(^7\) The Stark splitting of the \(5D_0 \rightarrow 7F_2\) transition is prominent in dichloromethane and in the solid state with three stark components. The band shape and stark components of the \(5D_0 \rightarrow 7F_2\) transition are typical of the fodo complexes reported in the literature,\(^7\) which could be due to the asymmetry of the tris fodo \(\text{Eu}^{3+}\) complexes. The room temperature line width at half maximum (FWHM) of the \(5D_0 \rightarrow 7F_0\) transition in acetone, chloroform, dichloromethane, ethanol, the solid state, and in thin films at 10\%(w/w) and 5\%(w/w) are 2.68, 2.21, 2.22, 2.28, 1.67, 1.51, and 1.52 nm, respectively (Figures S22 and S23). Only one line is observed for the non-degenerate
5D0 → 7F0 transition, suggesting that only one type of Eu3+ species is emitting in the solution and the two Eu3+ sites are equivalent in the complex. This corroborates with the NMR results where only one set of signals is observed, suggesting that only one species is present in the solution. The presence of only one asymmetric shaped 5D0 → 7F0 transition line in the solid state shows that the ligand symmetry around the two europium ions are similar with smaller structural difference.

The small width of FWHM of the 5D0 → 7F0 transition indicates that the europium complex could be a potential material to be used in optoelectronic devices. The splitting of the 5D0 → 7F1 transition into two Stark components indicates that the environment around both the europium ions is asymmetric. It gets strong support from the results of shape analysis where both the Eu3+ centers have been found with distorted geometries (square antiprism and dodecahedron).

2.6. Decay Curves, Quantum Yield, and CIE Chromaticity. The decay curves at 300 K of the solutions, solid state, and thin films of both Sm3+ and Eu3+ complexes are fitted by a mono-exponential function (Figure 12 and Figures S24−S35). The mono-exponential functions indicate that there is only a single type of emitting centers in the complexes. It contrasts with the findings of the shape analysis, which predicts two distinct geometrical arrangements (square antiprism and dodecahedron) around the two metal centers in a given complex. There could be two reasons for the antithesis: (i) the emission and lifetime measuring instruments could not resolve the differences due their detecting limitations and (ii) the geometries of the two polyhedrons in a complex are not that dissimilar. The lifetime decay was monitored at 648 nm (4G5/2 → 5H9/2) in the case of the Sm3+ complex and at 610 nm (5D0 → 7F2) in the case of the Eu3+ complex. The emission lifetimes of the 4G5/2 → 5H9/2 transition of the Sm3+ complex in different media are 28.58 μs (chloroform), 29.33 μs (dichloro-
Figure 8. Excitation spectra of (a) [Sm(fod)\(_3\)(μ-bpp)Sm(fod)\(_3\)] and (b) [Eu(fod)\(_3\)(μ-bpp)Eu(fod)\(_3\)] in different solvents. Concentration = 5 \times 10^{-5} \text{ M}.

Figure 9. Solid-state excitation spectra of (a) [Sm(fod)\(_3\)(μ-bpp)Sm(fod)\(_3\)] and (b) [Eu(fod)\(_3\)(μ-bpp)Eu(fod)\(_3\)].

Figure 10. Emission spectra of (a) [Sm(fod)\(_3\)(μ-bpp)Sm(fod)\(_3\)] and (b) [Eu(fod)\(_3\)(μ-bpp)Eu(fod)\(_3\)] in the solid state.
methane), 25.97 μs (acetone), 21.58 μs (ethanol), and 38.74 μs (solid state). The higher lifetime in the solid state suggests that the impact of vibrational oscillators upon the decay of the excited state is lower in the solid state due to restricted degrees of freedom. The emission lifetime of the \(^{4}G_{5/2} \rightarrow ^{5}H_{9/2}\) transition for the Sm\(^{3+}\) complex in dichloromethane (29.33 μs) is greater than the lifetime of this transition reported for 2-thienyll trifluoroacetone (ttta)-based complexes\(^8^1\) in the same solvent. The lifetime of the \(^{5}D_{0} \rightarrow ^{7}F_{2}\) transition in different media of the Eu\(^{3+}\) complex is 695.98 μs (chloroform), 584.34 μs (dichloromethane), 505.71 μs (acetone), 421.97 μs (ethanol), and 713.62 μs (solid state) (Table 5). The lifetime of the \(^{5}D_{0} \rightarrow ^{7}F_{2}\) transition of the Eu\(^{3+}\) complex is much higher than bpp containing the mononuclear complex \([\text{Eu}(\text{tdh})_3\text{bpp}]\) (300–414 μs) obtained in the temperature range of 323–273 K.\(^6^3\) It is also higher than the lifetime of the same transition reported for Eu(fod)\(_3\) (330 μs in chloroform and 620 μs in the solid state)\(^8^2\) and \([\text{Eu}(\text{fod})_3\text{phen-N-O}]\).\(^8^3\) The lifetimes of the \(^{5}D_{0} \rightarrow ^{7}F_2\) transition of PMMA-doped films of \([\text{Eu}(\text{fod})_3(\mu-\text{bpp})\text{Eu}(\text{fod})_3]\) are 512.79 μs (10%(w/w)) and 520.30 μs (5%(w/w)). These are lower than that found for the solid

![Figure 11. Emission spectra of (a) \([\text{Sm}(\text{fod})_3(\mu-\text{bpp})\text{Sm}(\text{fod})_3]\) and (b) \([\text{Eu}(\text{fod})_3(\mu-\text{bpp})\text{Eu}(\text{fod})_3]\) in different solvents. Concentration = 5 × 10\(^{-5}\) M.](image)

![Figure 12. Emission decay curve of (a) \([\text{Sm}(\text{fod})_3(\mu-\text{bpp})\text{Sm}(\text{fod})_3]\) and (b) \([\text{Eu}(\text{fod})_3(\mu-\text{bpp})\text{Eu}(\text{fod})_3]\) in the solid state.](image)

### Table 5. Lifetime and Intrinsic Quantum Yield of Some Europium Complexes

| complex | lifetime (ms) | Q\(_{\text{Eu}}\) % | reference |
|---------|--------------|-------------------|-----------|
| \([\text{Eu}(\text{fod})_3(\mu-\text{bpp})\text{Eu}(\text{fod})_3]\) | 0.71 | 56.99 | present work |
| \([\text{Eu}(\text{fod})_3\text{H}_2\text{O}]\) | 0.62 | 26.5 | 88 |
| \([\text{Eu}(\text{fod})_3\text{phen}]\) | 0.85 | 51 | 88 |
| \([\text{Eu}(\text{fod})_3(\text{phen N-O})]\) | 0.37 | 43 | 84 |
| \([\text{Eu}(\text{fod})_3\text{tptz}]\) | 0.22 | 34 | 90 |
| \([\text{Eu}(\text{fod})_3\text{indazole}]\) | 0.71 | 54.30 | 24 |
| \([\text{Eu}(\text{fod})_3\text{impy}]\) | 0.85 | 47.07 | 24 |
| \([\text{Eu}(\text{fod})_3\text{phen}]\) | 0.79 | 60.61 | 24 |
| \([\text{Eu}(\text{ttta})_3(\text{H}_2\text{O})_1]\) | 0.26 | 29 | 91 |
| \([\text{Eu}(\text{dbm})_3(\text{H}_2\text{O})]\) | 0.06 | 3.44 | 92 |
| \([\text{Eu}(\text{dbm})_3(\text{impy})]\) | 0.42 | 9.0 | 92 |
| \([\text{Eu}(\text{tfaa})_3(\text{phen})]\) | 0.87 | 35.98 | 93 |
| \([\text{Eu}(\text{tfaa})_3(\text{H}_2\text{O})]\) | 0.33 | 20.83 | 94 |
| \([\text{Eu}(\text{tfaa})_3(\text{bpy})]\) | 0.87 | 31.56 | 95 |
| \([\text{Eu}(\text{tfaa})_3(\text{mpy})]\) | 0.98 | 32 | 96 |
| \([\text{Eu}(\text{tfaa})_3(\text{pyz})]\) | 0.40 | 9.86 | 97 |

\(^1\)The lifetimes of the \(^{5}D_{0} \rightarrow ^{7}F_2\) transition of the Eu\(^{3+}\) complex is much higher than bpp containing the mononuclear complex \([\text{Eu}(\text{tdh})_3\text{bpp}]\) (300–414 μs) obtained in the temperature range of 323–273 K.\(^6^3\) It is also higher than the lifetime of the same transition reported for Eu(fod)\(_3\) (330 μs in chloroform and 620 μs in the solid state)\(^8^2\) and \([\text{Eu}(\text{fod})_3\text{phen-N-O}]\).\(^8^3\) The lifetimes of the \(^{5}D_{0} \rightarrow ^{7}F_2\) transition of PMMA-doped films of \([\text{Eu}(\text{fod})_3(\mu-\text{bpp})\text{Eu}(\text{fod})_3]\) are 512.79 μs (10%(w/w)) and 520.30 μs (5%(w/w)). These are lower than that found for the solid
complex (713.62 μs), suggesting that the host polymer has a detrimental effect on the lifetime of the excited state. This is more pronounced in the case of PMMA-doped hybrid films of [Sm(fod)(μ-bpp)Sm(fod)], where the lifetime is much smaller for the polymeric films (6.73 μs 5%;w/w and 2.28 μs 10%;w/w) than the lifetime in the solid state. Similar results are reported for [Eu(fod)(H₂O)] where the lifetime in the PMMA film is smaller (440 μs) than the value in the solid state (620 μs). It is interesting to note that, for both the complexes, the lifetime in non-coordinating solvents (chloroform and dichloromethane) are higher than those observed in coordinating solvents (acetone and ethanol). This could be related to (i) the presence of a large number of C−H oscillations in the coordinating solvents (acetone and ethanol), which depopulate the excited state of the Sm³⁺ and Eu³⁺ metals through high energy C−H and O−H vibrations and (ii) invasion of the coordination sphere. A similar result is reported for the Eu(fod). The intrinsic quantum yield for the samarium complex is calculated using the equation Q_{Sm} = τ_{experimental}/τ_o (τ_{experimental} is the experimentally measured radiative lifetime and τ_o is the calculated average natural lifetime (3.25 ms) of Sm³⁺). The quantum yields calculated for the samarium complex in acetone, chloroform, dichloromethane, and ethanol are 0.80%, 0.88%, 0.90%, and 0.66%, respectively. The quantum yield, in the case of the solid state, is 1.19%, which is higher than those obtained from the solution. Similarly, for the Eu³⁺ complex, the quantum yield in the solid state is greater than those obtained from the solutions and thin hybrid films (Table 5). The higher intrinsic quantum yield of the complexes in the case of the solid state could be due to loss of energy of excited states through the dipole−dipole coupling interactions with the solvent or PMMA molecules. The intrinsic quantum yield of the Eu³⁺ complex is much higher than its precursor [Eu(fod)₃(H₂O)] (Q_{Eu} % = 26.5), which indicates that the radiative emission from the excited state ⁵D₀ of the europium complex is very intense.

The CIE color coordinates of Sm³⁺ and Eu³⁺ complexes in solutions, the solid state, and thin films were calculated using LUMPAC software (Table 6). The Sm³⁺ complex shows orange color emission with its color coordinates greatly influenced by the host medium (Figure 13a and Figure S36). The europium complex shows red emission, and the color coordinates are nearly similar in all media (Figure 13b and Figure S37). The overall intensity of emission lines of the samarium ion is lower than the europium ion, which means that ligand fluorescence is influencing the CIE coordinates more in the case of the Sm³⁺ complex.
Table 7. Experimental Intensity Parameters of [Eu(fod),(μ-bpp)Eu(fod)]_3 in Different Solvents, Thin Films, and the Solid State

|     | Ω1 (10^{-38} cm^2) | Ω2 (10^{-38} cm^2) | Ω3/Ω4 | τ_μ (μS) | τ_rad (μS) | A_rad (S^-1) | A_rad (S^-1) | Q_{Eu}% |
|-----|-------------------|-------------------|--------|----------|-----------|--------------|--------------|---------|
| acetone | 23.33            | 2.45              | 9.52   | 505.71   | 1714.74   | 583.18       | 1394.28     | 29.49   |
| chloroform | 22.35            | 5.51              | 4.06   | 695.67   | 1042.58   | 712.97       | 724.44      | 49.60   |
| ethanol | 21.66            | 2.11              | 10.12  | 584.34   | 1602.92   | 623.86       | 1087.59     | 36.45   |
| dichloromethane | 21.60            | 2.33              | 9.27   | 421.96   | 1831.13   | 546.11       | 1823.56     | 23.05   |
| solid state | 20.19            | 9.98              | 2.02   | 713.62   | 1252.08   | 798.67       | 602.68      | 56.99   |
| TF10  | 21.45            | 2.77              | 7.74   | 512.79   | 1358.84   | 735.92       | 1214.16     | 37.74   |
| TF5   | 20.39            | 3.07              | 6.64   | 520.30   | 1412.36   | 708.03       | 1213.94     | 36.84   |

2.7. Experimental and Theoretical Intensity Parameters. The electronic transitions within 4f subshells are strictly forbidden under parity law. However, the mixing of upper shell wave functions with 4f subshells under the influence of odd parameters of ligand field induces some even parity in 4f subshells. This results in states of mixed parity through which electric-dipole transitions can be forced to occur. These transitions are sharp with small bandwidths and are used as a source of laser. The intensity of magnetic-dipole transition is field-independent and can be calculated from the wave functions of free ions. However, for induced electric-dipole transitions, calculation of wave functions is difficult, and parameterization is necessary, which is provided in the Judd–Olfet theory.

The Judd–Olfet intensity parameters (Ω₁, 2, 4, and 6) in the case of Eu can be deduced from the intensity of emission transitions. Since the absolute intensity of transitions could not be calculated, therefore, the intensity of the 5D₀ → 7F₁ magnetic-dipole transition is used as a reference with dipole transition originating from 5D₀ with A = 9.6 × 10^{-39} cm^2 and the parameters of other transitions are calculated relative to it.²⁸ The Ωₐ parameters are calculated using eq 1

\[ Ωₐ = \frac{D_{md}ν_j^3}{ε^2ν_j^3[(µ_j|U|µ_j')|^2]} \frac{9n^3}{4π^2} \frac{∫Iν dν}{∫Iν dν} \]

where ν₁ and ν₂ are the average wave numbers of 5D₀ → 7F₁ and 5D₀ → 7F₂ transitions, respectively, ε is the electronic charge, Jν dν/νdν is the ratio of the integrated intensity of 5D₀ → 7F₁ to the 5D₀ → 7F₂ transition, and nν = (ν(ν^2 + 2))/(η(η^2 + 2)) is the Lorentz local field correction and η is the refractive index of the medium. The values of square reduced matrix elements [(µ_j|U|µ_j')|^2] were obtained from the literature.⁹⁹,¹⁰⁰

The coherence in bonding in the first coordination sphere is directly related to the Ω₂ parameter, and the larger value is an indication of the larger covalent character in the bonding. The higher value of the Ω₂ parameter is also indicative of the higher hypersensitive behavior of the 5D₀ → 7F₂ transition.¹⁰¹ The Ω₃ parameter provides information regarding the rigidity of the host medium in which Ln(III) ions are located.¹⁰² The 5D₀ → 7F₂ transition is not observed experimentally; thus, the Ω₅ experimental parameter could not be obtained and is neglected in calculations.

The radiative transition probability (A), radiative lifetime τ_rad and emission quantum efficiency Q_{Eu} for the transition of Eu³⁺ in both solution and solid states were calculated using both the Judd–Olfet theory and experimental results. The radiative transition probability (A) between two manifolds j and j’ is given by eq 2

\[ A(ψ_j, ψ_j') = \frac{64π^4ν^3}{3h(2j + 1)}[\chi D_{sd} + η^3D_{md}] \]

where D_{sd} and D_{md} are the dipole strength of electric and magnetic dipoles, respectively, η is the refractive index, χ is the Lorentz local field correction equaling to (nν(ν² + 2))/(η(η² + 2)), and ν is the average wave number of the transition.

We calculated the radiative transition probability (A) for a transition originating from 5D₀ with j equaling to zero to 7F₉ with j equaling λ = 0, 1, 2, 3, 4, 5, and 6 from the emission spectra using eq 3

\[ A_{0→λ} = A_{0→1} S_{0→1} σ_0 \]

where S₀→₁ and σ₀ are the area under the 0 → λ transition of emission spectra and its energy barycenter, respectively. A₀→₁ is the Einstein coefficient for the 0 → 1 magnetic-dipole transition, and its reported value is 50 s⁻¹.¹⁰³ The relationship between lifetime and the transition probabilities (radiative or non-radiative) is given by eq 4

\[ A_{tot} = \frac{1}{τ} = A_{rad} + A_{nrad} \]

where A_{rad} is the summation of all the radiative probabilities for transitions between 5D₀ → 7F₉ with λ = j (eq 5)

\[ A_{rad} = ∑ A_{0→j} \]

The inverse of A_{rad} gives the radiative lifetime τ_rad of the 5D₀ level and the emission quantum efficiency of the 5D₀ level labeled as intrinsic quantum yield Q_{Eu} is given by eq 6

\[ Q_{Eu} = A_{rad} \]

The results obtained show that Ω₂ is much higher than Ω₄ in any given solvent, solid state, and thin hybrid films, indicating that the 5D₀ → 7F₂ transition is strongly hypersensitive (Table 7). The ratio of Ω₂:Ω₄ is the lowest for the solid state, indicating that the ligand environment around Eu³⁺ is less polarized in the solid state than in thin hybrid films and solution. This also reflects that the ligand environment around Eu³⁺ is relatively less asymmetric in the solid complex, which agrees with the results obtained from the shape analysis of the crystal structure where the polyhedra around Eu³⁺ ions are less asymmetric. The Ω₄ for the solid Eu³⁺ complex is higher than those in solution and thin films. The higher value could be due to the rigid nature of the solid complex.¹⁰² The relatively smaller value of Ω₄ in the case of solution and hybrid films is indicative of the fact that the lower rank components of the crystal field and dynamic coupling interactions are more
influential than the higher rank components of the crystal field.\textsuperscript{76,104}

Experimentally, intensity parameters ($\Omega_i$) ($\lambda = 2, 4, \text{and} 6$) of the Eu\textsuperscript{3+} complex are calculated from the Judd–Ofelt theory using the emission spectra and lifetime. Theoretically, the Judd–Ofelt intensity parameters ($\Omega_i$) are calculated using eqs 7 and 8

$$\Omega_i = (2\lambda + 1) \sum_p \sum_{t \in \alpha} \left| \vec{B}_{tp} \right|^2$$

where the parameter $B_{tp}$ is expressed as

$$B_{tp} = \frac{2}{\Delta E} \left( r_{tp} \right) \left( \frac{\lambda + 1}{2\lambda + 1} \right)^{1/2} \left[ \sum_{\text{odd}} \left( 2\lambda + 3 \right) \frac{\beta_j}{R_j^{t+1}} \right]$$

The theoretical intensity parameters are calculated by adjusting the charge factor ($g$) and polarizabilities ($\alpha$) appearing in eqs 9 and 10, respectively, to reproduce the phenomenological (experimental) values for $\Omega_2$ and $\Omega_4$.

$$g_j = \left( \frac{4\pi}{2t + 1} \right)^{1/2} \frac{1}{R_j^{t+1}} \sum_{\text{odd}} \frac{\beta_j}{\sigma_j} \left( \frac{\lambda + 1}{2\lambda + 3} \right)$$

$$\alpha_j = \left( \frac{4\pi}{2t + 1} \right)^{1/2} \sum_{\text{odd}} \frac{\alpha_j}{R_j^{t+1}} \left( \frac{\lambda + 1}{2\lambda + 3} \right)$$

For mononuclear europium complexes, the process of the calculation of theoretical intensity parameters of an optimized structure is a straightforward task and could be obtained by adjusting the charge factor ($g$) and polarizabilities ($\alpha$) appearing in eqs 1 and 2, respectively, to reproduce the experimental intensity parameters. However, in the case of complexes containing two or more unique europium centers, the calculation of individual intensity parameters for the unique europium centers by classical procedure produces inconsistent results. The solution to this problem has been presented recently in the form of a theoretical methodology named “overlapped polyhedra method” (OPM).\textsuperscript{42} In this method for a di-nuclear molecule, the individual europium coordination polyhedra are overlapped (Figure 14) to reproduce spherical coordinates for all the coordinating atoms with respect to one overlapped europium centers. The charge factor ($g$) and polarizabilities ($\alpha$) are then adjusted to reproduce the experimental intensity parameters. Finally, the adjusted charge factor ($g$) and polarizabilities ($\alpha$) for individual centers are used to calculate the intensity parameters for the individual centers. The spherical atomic coordinates adjusted charge factor ($g$) and polarizabilities ($\alpha$) for the overlapped polyhedra of the crystal structure, Sparkle PM7 and Sparkle RM1, are presented in Tables S9–S11. The calculated intensity parameters, radiative decay probabilities ($A_{rad}$), non-radiative decay probabilities ($A_{nrad}$), and intrinsic quantum yields obtained for each polyhedron for the crystal structure, Sparkle PM7 and Sparkle RM1, are presented in Table 8 and

| Table 8. Experimental and Theoretical Intensity Parameters from the OPM, Radiative and Non-radiative Decay Rates ($A_{rad}$ and $A_{nrad}$), and Intrinsic Quantum Yields |
|---------------------------------|----------------|----------------|----------------|----------------|
|                                 | experimental  | overlapped     | individual     | adjustment     |
|                                 | method        | method         | method         |                |
| $\Omega_2$                      | 20.19         | 20.19          | 5.93           | 6.59           |
| $\Omega_4$                      | 9.98          | 9.98           | 4.19           | 7.72           |
| $\Omega_6$                      | 1.7230        | 1.7230         | 0.9195         | 0.8270         |
| $A_{rad}$ ($S^{-1}$)             | 798.67        | 758.67         | 242.29         | 364.84         |
| $Q_{rad}$ %                     | 56.99         | 54.14          | 17.29          | 26.03          |

Figures S12 and S13. The intrinsic quantum yields for the individual Eu\textsuperscript{3+} centers of the crystal structure are 17.29% and 26.03%, and their sum is 43.32%. Similarly, the $A_{rad}$ values calculated for the individual Eu\textsuperscript{3+} centers of the crystal structure are 242.29 and 364.84 and their total is 607.13. The total intrinsic quantum yield and $A_{rad}$ are close to the experimental values (Table 7). The agreement between the theoretical and experimental values validates the overlap polyhedron method (OPM) as a reliable tool for the prediction of individual spectroscopic parameters. Similar results where the theoretically calculated values are in agreement with the experimentally obtained data are reported for the dinuclear and trinuclear europium complexes. For the optimized (PM7 and RM1) structures, the theoretically calculated total intrinsic quantum yield and $A_{rad}$ are dissimilar to the experimental values, which is due to the different ligand symmetry around the metal ions (Tables S12 and S13). The shapes of the polyhedra around the two Eu\textsuperscript{3+} centers predicted by Sparkle PM7 are similar to those obtained by single-crystal X-ray analysis. However, these are not identical. Sparkle RM1 predicts square antiprismatic geometries around the two Eu\textsuperscript{3+} centers; therefore, the values of the total intrinsic quantum yield and $A_{rad}$ are different from the experimental values.

The radiative branching ratios $\beta_{\psi_i}$ ($\psi_i, \psi_f$) could be calculated from the radiative transition probabilities of every transition from the Judd–Ofelt theory using emission spectra and lifetime of the europium complex. The branching ratio of each transition is the ratio of radiative transition probability of that transition to the overall radiative transition probability of the metal ion; in other words, it gives the relative intensity of the transitions and is given as

![Figure 14. Overlapped polyhedra of the two metal centers.](https://doi.org/10.1021/acsomega.0c05976)
hybrid fi Eu3+ sites in the dinuclear [Eu(fod)3(μ-bpp)Eu(fod)]

Agreement. The overlap polyhedra method (OPM) was used experimentally and theoretically and are found to be in agreement. The overlap polyhedra method (OPM) was used to calculate the individual spectroscopic parameters of two di(Eu) complexes. The results show that the Sm3+ and Eu3+ complexes emit orange and red in di(CIE) chromaticity coordinates of the spectra of the complexes.

In summary, the dinuclear complexes of Sm3+ and Eu3+ bridged by the bpp ligand were synthesized in good yield. The 1H NMR and 1H-1H COSY techniques were used to assign the proton resonances for the complexes. The shifts induced by paramagnetic centers are dipolar in nature. The photoluminescence of Sm3+ and Eu3+ complexes was studied in di(CIE) chromaticity coordinates of the spectra of the complexes. The results of the shape analysis using the magnitude of angles method indicate similar results obtained from SHAPE software, indicating that the method is efficacious for shape analysis. The work is in progress and other complexes of the series containing lanthanides are under investigation, and their structures and properties would be reported in future papers.

### 3. CONCLUSIONS

In summary, the dinuclear complexes of Sm3+ and Eu3+ bridged by the bpp ligand were synthesized in good yield. The 1H NMR and 1H-1H COSY techniques were used to assign the proton resonances for the complexes. The shifts induced by paramagnetic centers are dipolar in nature. The photoluminescence of Sm3+ and Eu3+ complexes was studied in di(CIE) chromaticity coordinates of the spectra of the complexes. The results of the shape analysis using the magnitude of angles method indicate similar results obtained from SHAPE software, indicating that the method is efficacious for shape analysis. The work is in progress and other complexes of the series containing lanthanides are under investigation, and their structures and properties would be reported in future papers.

### 4. EXPERIMENTAL SECTION AND COMPUTATIONAL METHODS

#### 4.1. Materials

The lanthanide oxides (Ln2O3, Ln = La, Sm, Eu and Lu; Sigma-Aldrich 99.9%) were converted into corresponding chlorides LnCl3·nH2O (n = 6–7) by adding an appropriate amount of hydrochloric acid and drying out the product on water bath. 6,6,7,7,8,8,8-Heptfluoro-2,2-dimethyl-3,5-octanedione (Hfod) and 2,3-bis(2-pyridyl)pyrazine (bpp) were also purchased from Sigma-Aldrich. Poly(methyl methacrylate) (PMMA) with an average molecular weight of 120,000 (Aldrich) was used. AR/spectroscopic grade solvents were used in the study.

#### 4.2. Synthesis

The hydrated Ln(fod)3 chelates (Ln = La, Lu, Sm, and Eu) were synthesized by the literature method. The complexes were synthesized by allowing the ethanol solutions of equimolar amounts of chelate and bpp to react (Figure 15). All the complexes were synthesized by a similar method. The synthesis of the Eu3+ complex described here is the representative. The reaction of Eu(fod)3 (800 mg; 77.15 × 10⁻³ moles) and bpp (187.66 mg; 77.15 × 10⁻⁵ moles) in equimolar ratio was carried out in 20 mL of ethanol. The reaction mixture was continuously stirred on a magnetic stirrer-cum hot plate at 40 °C for about 8 h. Then, it was left at room temperature for slow evaporation of the solvent. After 3 days, the solid product appeared, which was isolated. The crystals obtained were washed with cold ethanol twice and dried in vacuo over P2O5. The decanted portion of the reaction mixture was also left out at room temperature for complete evaporation of the solvent. Upon complete evaporation of the poured-out liquid, the solid obtained was found to be unreacted bpp since it melts between 168 and 170 °C (the melting point of bpp is in the range of 168–170 °C). The amount left was around 50% of the initial amount used. It suggests that only one mole of bpp reacts with two moles of [Eu(fod)3] and the reaction takes place in a 1:2 molar ratio (bpp:Eu(fod)3), resulting in the formation of dinuclear complexes. However, in the case of the lanthanum complex, no unreacted bpp was recovered, suggesting a 1:1 reaction between [La(fod)3] and bpp.

#### 4.3. Characterization

Elemental analysis of the complexes was carried out on an Elementar modern elemental analyzer type vario EL cube. Melting points were obtained by a conventional capillary method and DSC of the samples (DSC 6220 SIINT, Japan). The TGA/DTA results of the complexes were obtained in an inert atmosphere under nitrogen gas (N2) with a heating rate of 10 °C per minute on an Exstar 6000 TGA/DTA from SIINT, Japan. The infrared spectra were recorded on a BRUKER FT-IR spectrophotometer in the range of 600–4000 cm⁻¹. The mass spectra of the complexes in positive ion reflector mode were recorded on a Bruker spectrometer.
The strong O–H stretching vibrations appearing in the range of 3500–3700 cm−1 in the IR spectra of the complexes have disappeared from the spectra of the complexes, suggesting that the water molecules present in the chelates are replaced by the ancillary ligand upon coordination (Figures S38–S41). It is strong evidence that the bpp ligand has coordinated to the metal. The strong bands appearing in the complexes at 1515 ± 5 cm−1 and 1620 ± 5 cm−1 are assigned to C=O and C=O stretching vibrations and are characteristics of lanthanide β-diketonate complexes.108 These bands are shifted toward the lower energy side as compared to their position in the chelates. Similarly, the bands appearing around 1550, 1405, 1062, 870, and 787 cm−1 in the complexes have also been shifted in the complexes. Most of the characteristic IR bands of the bpp could not be observed since these are obscured by the strong chelate absorptions. The characteristic C=N and C=O ring stretching vibrations of free bpp appearing at 1583 cm−1110 has been reported to shift to a higher wave number when bpp acts as the bridging ligand by exploiting the two NN chelating sites.112 We could not observe this stretching vibration, perhaps it has merged with the strong band appearing at 1620 cm−1. This is consistent with the binding of the bpp to two metal centers through its two NN chelating sites.112 The strong bands112 appearing in the region of 1108–1278 cm−1 are assigned to the C–F stretching vibrations of the β-diketone. These C–F bands show a smaller shift from their positions in the chelates on complex formation, which could be due to the non-proximity to the metal.

The thermograms (TGA and DTA) of the complexes are recorded in the temperature range of 40–500 °C and are shown in Figures S47 and S48. The lanthanide complexes with fluorinated β-diketone like Hfod and hexafluorocycloacetone (HfFac) are found to be thermally stable and evaporate without decomposition.21–26 The complexes under study do not show any thermal degradation and evaporate in the temperature range of 300–340 °C. The single-step volatilization reveals that the complexes do not dissociate, and the ancillary ligand and β-diketone moieties remain coordinated in the vapor. The DTA curves of the complexes show two endothermic peaks: one at the lower temperature represents melting of the complexes (phase transformation) and the other between 321 °C and 324 °C represent the volatilization. The melting points noted from the DTA and DSC (Figure S49) curves are well in line with those obtained from the conventional capillary method.

4.4. Single-Crystal Structure Analysis. Single-crystal X-ray data collection was performed on a Bruker SMART APEX CCD diffractometer equipped with a fine focus 1.75 kW sealed-tube Mo Kα X-ray source (λ = 0.71073 Å) with increasing ω (width of 0.3° per frame) at a scan speed of 5 s frame−1. All measurements were performed at liquid nitrogen temperature, 100 K. Intensity data were collected using the ω–2θ scan mode and corrected for Lorentz-polarization and absorption effects.116 The structures were solved with the ShelXT (Sheldrick, 2015),117 using olex2 software.118 The structure solution using a direct method were obtained with SHELXL-2018/3.119 The non-hydrogen atoms were refined with anisotropic displacement coefficients, and their coordinates were permitted to ride on their respective carbon atoms. For all the atoms, the atomic positions, for all the non-hydrogen atoms, the anisotropic thermal parameters, and for all the hydrogen atoms, the isotropic thermal parameters, were included in the final refinement. The perspective views were obtained using ORTEP.120 The crystal code provided by CCDC are 1956378 for [Sm(fod)3(µ-bpp)Sm(fod)3] and 1956379 for [Eu(fod)3(µ-bpp)Eu(fod)3]. The crystal model showed signs of disorder, and some alternative positions were
found for terminal groups. The higher R1 and wR2 values for the complexes are mostly due to the disorder in the tertiary butyl and perfluoryl groups of the fod moiety. These observations are similar to those reported for the crystal structures of the complexes containing fod, [Eu(fod)3(phen)],18 [Dy(fod)3(phen)],20 and other similar complexes.

4.5. Computational Details. The ground state geometry of samarium and europium complexes were elucidated using Sparkle/PM736 and RM137 implemented in the MOPAC2016 software package.122 The input structures were drawn and were pre-optimized by the molecular mechanics (AMBER model) implemented in Gabedit software.123 The vibrational frequencies of all the optimized structures were calculated to check that the optimized structures are at the local minimum. The keywords used were GNORM = 0.25; PRECISE; GEO-OK; XYZ (for Cartesian coordinates); T = 10D; ALLVEC; SPARKLE BFGS; and ISCF for MOPAC2016 to not change the impact of that model on the quantum chemical modeling of the complexes. The reason for the selection of a particular Sparkle model depends upon the comprehensive structure of the complexes. The reason for the need to optimize the starting crystallography geometry. Of the various Sparkle models implemented in the MOPAC2016, the Sparkle RM1 and PM7 provided the most reliable results. The keywords used were GNORM = 0.25; PRECISE; GEO-OK; XYZ (for Cartesian coordinates); T = 10D; ALLVEC; SPARKLE BFGS; and ISCF for MOPAC2016 to not change the impact of that model on the quantum chemical modeling of the complexes. The reason for the selection of a particular Sparkle model depends upon the comprehensive structure of the complexes. The reason for the need to optimize the starting crystallography geometry. Of the various Sparkle models implemented in the MOPAC2016, the Sparkle RM1 and PM7 provided the most reliable results.

4.6. Thin Film Formation. Thin hybrid films of the complexes were obtained by the drop casting technique on the glass slides.97 The quartz glass slides were first washed with a solution of NH3 and H2O2 (50%: 50%) and then were dipped in the complex.38 solution of NH3 and H2O2 (50%: 50%) and then were dipped into concentrated HCl for 10 min, and finally, these were washed thoroughly with double distilled water. The 5% and/or 10% (w/w) solution of the complex and PMMA was prepared in chloroform.

ACKNOWLEDGMENTS

A.B.G. thanks CSIR (Govt. of India) for a Senior Research Fellowship. The authors are thankful to Dr. M. Kausar Raza of Indian Institute of Science (IISc), Bangalore, for providing the single-crystal X-ray structures of the complexes, and we are also grateful to Dr. Neetu Singh of Advance Instrumentation Research Facility (AIRF), JNU, New Delhi, for time-resolved fluorescence. The Central Instrumentation Facility (CIF) of Jamia Millia Islamia is also gratefully acknowledged for extending FT-IR and steady-state luminescence facility. This work was not funded by any agency.

REFERENCES

(1) Bradley, J. D. B.; Pollinau, M. Erbium-Doped Integrated Waveguide Amplifiers and Lasers. Laser Photon. Rev. 2011, 5, 368–403.
(2) Sage, I.; Bourhill, G. Triboluminescent Materials for Structural Damage Monitoring. J. Mater. Chem. 2001, 11, 231–245.
(3) Fuego-González, E.; García-Fernandez, E.; Martínez, D.; Infantes, L.; Orte, A.; González-Vera, J. A.; Herranz, R. Smart Lanthanide Antennas for Sensing Water. Chem. Commun. 2020, 56, 5484–5487.
(4) Parker, D.; Williams, J. A. G. Getting Excited About Lanthanide Complex Chemistry. J. Chem. Soc. Dalton Trans. 1996, 18, 3613–3628.
(5) Amoroso, A. J.; Pope, S. J. A. Using Lanthanide Ions in Molecular Bioimaging. Chem. Soc. Rev. 2015, 44, 4723–4742.
(6) Chen, J.; Xie, Z.; Meng, L.; Hu, Z.; Kuan, X.; Xie, Y.; Lu, C. Z. Luminescence Tunable Europium and Samarium Complexes: Reversible On/Off Switching and White-Light Emission. Inorg. Chem. 2020, 59, 6963–6977.
(7) Yang, Y.; Chen, L.; Jiang, F.; Yu, M.; Wan, X.; Zhang, B.; Hong, M. A Family of Doped Lanthanide Metal-Organic Frameworks for Wide-Range Temperature Sensing and Tunable White Light Emission. J. Mater. Chem. C 2017, 5, 1981–1989.
(8) Lapaev, D. V.; Nikiforov, V. G.; Lokvob, V. S.; Knyazev, A. A.; Galyametdinov, Y. G. A Photostable Vitrified Film Based on a Terbium(III) β-Diketonate Complex as a Sensing Element for Reusable Luminescent Thermometers. J. Mater. Chem. C 2016, 8, 9475–9481.
(9) Mathieu, E.; Sipos, A.; Demeyere, E.; Phipps, D.; Sakaveli, D.; Borbas, K. E. Lanthanide-Based Tools for the Investigation of Cellular Environments. Chem. Commun. 2018, 54, 10021–10035.
(10) Bünzl, J.-C. G.; Piguet, C. Taking Advantage of Luminescent Lanthanide Ions. Chem. Soc. Rev. 2005, 34, 1048.
(11) Bünzl, J.-C. G. Benefiting From The Unique Properties of Lanthanide Ions. Acc. Chem. Res. 2006, 39, 53–61.
(12) Bünzl, J.-C. G. Lanthanide Photonics: Shaping the Nanoworld. Trends Chem. 2019, 1, 751–762.
(13) Weissman, S. I. Intramolecular Energy Transfer: The Fluorescence of Complexes of Europium. J. Chem. Phys. 1942, 10, 214–217.
(14) Kalyakina, A. S.; Utochnikova, V. V.; Zimmer, M.; Dietrich, F.; Kaczmarek, A. M.; Van Deun, R.; Vashchenko, A. A.; Goloveshkin, A. S.; Nieger, M.; Gerhardt, M.; et al. Remarkable High Efficiency of Red Emitters Using Eu(III) Ternary Complexes. Chem. Commun. 2018, 54, 5221–5224.
(15) Manzur, J.; Poblete, C.; Morales, J.; De Santana, R. C.; Queiroz Maia, L. J.; Vega, A.; Fuentalba, P.; Spodine, E. Enhancement of Terbium(III)-Centered Luminescence by Tuning the Triplet Energy Level of Substituted Pyridylamino-4-R-Phenoxo Tripodal Ligands. Inorg. Chem. 2020, 59, 5447–5455.
(16) Binnemans, K. Rare-Earth Beta-Diketonates. In Handbook on the physics and chemistry of rare earths; 2005; Vol. 35, pp. 107–272.
(17) Malta, O. L.; Brito, H. F.; Menezes, J. F. S.; Gonçalves e Silva, F. R.; De Mello Donegâ, C.; Alves, S. J. Experimental and Theoretical Emission Quantum Yield in the Compound Eu-

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05976.

Single-crystal X-ray details for the Sm3+ complex (CIF)

Single-crystal X-ray details for the Eu3+ complex (CIF)

The characterization spectra and data tables, Sparkle RM1 and PM7 optimized structures, photophysical spectra and data tables, lifetime spectra, and CIE color coordinate diagrams (PDF)

AUTHOR INFORMATION

Corresponding Author

Khalid Iftikhar — Lanthanide Research Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India; orcid.org/0000-0002-5987-3901; Email: kiftikhar@jmi.ac.in

Author

Aabid Bashir Ganaie — Lanthanide Research Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05976

Notes

The authors declare no competing financial interest.

https://doi.org/10.1021/acsomega.0c05976

ACS Omega 2021, 6, 21007−21226
Europium Complexes. Designing Simple Tridentate Ligands for Highly Luminescent \([\text{Ln}_2(\text{HL})(\text{L})]\) (Ln = SmIII, EuIII, GdIII, TbIII).

Properties. Sensitization and the Effect of Solvent Polarity on Their Luminescent Properties.

Complexes by Mixing Ligands: Microwave-Assisted Synthesis and Substantial Intensification of the Quantum Yield of Samarium(III) in PMMA. Evaporable Lanthanide Single-Ion Magnet.

Lanthanide Complexes for Fabricating Red, Green, and Yellow OLEDs. Inorg. Chem. 2015, 54, 11209–11225.

Ahmed, A.; Ifthikhar, K. Efficient Layers of Emitting Tinry Lanthanide Complexes for Fabricating Red, Green, and Yellow OLEDs. Inorg. Chem. 2018, 57, 15421–15429.

Marques, L. F.; Formiga, A. L. B.; Mazali, I. O.; de Bettencourt-Dias, A.; Sigoli, F. A. Estimating the Donor-Acceptor Distance to Tune the Emission Efficiency of Luminescent Lanthanide Compounds. Inorg. Chem. 2001, 40, 11191–11200.

Rodrigues, M. O.; da Costa Júnior, N. B.; de Simone, C. A.; Araújo, A. A. S.; Brito-Silva, A. M.; Paz, F. A. A.; Mesquita, M. E.; Júnior, S. A.; Freire, R. O. Theoretical and Experimental Studies of the First Highly Luminescent Binuclear Hydrocinnamate of Eu(III), Tb(III) and Gd(III) with bideterminate 2,2′-bipyridine Ligand. J. Lumin. 2014, 148, 307–316.

Montero, J. H. S. K.; Dutra, J. D. L.; Freire, R. O.; Formiga, A. L. B.; Mazali, I. O.; de Bettencourt-Dias, A.; Sigoli, F. A. Estimating the Individual Spectroscopic Properties of Three Unique EuIII Sites in a Coordination Polymer. Inorg. Chem. 2018, 57, 15421–15429.

Dutra, J. D. L.; Ferreira, J. W.; Rodrigues, M. O.; Freire, R. O. Theoretical Methodologies for Calculation of Judd–Ofelt Intensity Parameters of Polyeuropium Systems. J. Phys. Chem. A 2013, 117, 14095–14099.

Rodrigues, M. O.; da Costa Júnior, N. B.; de Simone, C. A.; Araújo, A. A. S.; Brito-Silva, A. M.; Paz, F. A. A.; Mesquita, M. E.; Júnior, S. A.; Freire, R. O. Theoretical and Experimental Studies of the Photo/electroluminescent Europium (I) Complexes Constructed with 6-(Diphenylphosphoryl)Picolinilate. J. Inorg. Chem. 2020, 59, 8800–8808.

Ullmann, T.; Hahn, P.; Blömer, L.; Mehnert, A.; Laube, C.; Abel, B.; Kersting, B. Dinuclear Lanthanide Complexes Supported by a Hybrid Salicylidinamido/[4]Arene-Ligand: Synthesis, Structure, and Magnetic and Luminescence Properties of \([\text{Ln}_2(\text{HL})(\text{L})]\) \((\text{Ln} = \text{SmIII}, \text{EuIII}, \text{GdIII})\). Dalton Trans. 2019, 48, 3839–3805.

Ullmann, T.; Hahn, P.; Mini, P.; Tuck, K. L.; Kahnt, A.; Abel, B.; Gutierrez Suburu, M. E.; Strassert, C. A.; Kersting, B. Mixed-Ligand Lanthanide Complexes Supported by Ditopic Bis(imino-Methyl)-Phenol/Caix[4]Arene Macrocycles: Synthesis, Structure, and Luminescence Properties of \([\text{Ln}_2(\text{L})(\text{MeOH})]\) \((\text{Ln} = \text{La}, \text{Eu}, \text{Th}, \text{Yb})\). Dalton Trans. 2020, 49, 11179–11191.

Shavalev, N. M.; Eliseeva, S. V.; Scopelliti, R.; Bünzli, J.-C. G. Designing Simple Tridentate Ligands for Highly Luminescent Europium Complexes. Chem. - Eur. J. 2009, 15, 10790–10802.

Lo, W.-S.; Zhang, J.; Wong, W.-T.; Law, G.-L. Highly Luminescent Sm III Complexes with Intraligand Charge-Transfer Sensitization and the Effect of Solvent Polarity on Their Luminescent Properties. Inorg. Chem. 2015, 54, 3725–3727.

Melo, L. L. S.; Castro, G. P.; Jr.; Gonçalves, S. M. C. Substantial Intensification of the Quantum Yield of Samarium(III) Complexes by Mixing Ligands: Microwave-Assisted Synthesis and Luminescence Properties. Inorg. Chem. 2019, 58, 3265–3270.

Cuan, J.; Yán, B. Luminescence Lanthanide-Polyoxometalates Assembling Zirconia-Alumina-Titania Hybrid Xerogels through Task-Specified Ionic Liquid Linkage. RSC Adv. 2014, 4, 1735–1743.
(51) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. Luminescent and Redox-Active Polynuclear Transition Metal Complexes. Chem. Rev. 1996, 96, 759−834.

(52) Campagna, S.; Denti, G.; De Rosa, G.; Sabatino, L.; Ciano, M.; Balzani, V. Syntheses, Absorption Spectra, Luminescence Properties, and Electrochemical Behavior of Mono- and Binuclear Ruthenium(II) Complexes of Isomeric Bis(2-Pyridyl)Pyrazines. Inorg. Chem. 1989, 28, 2565−2570.

(53) Ruminski, R. B.; Wallace, J. Synthesis and Characterization of Chromium and Tungsten Tetracarbonyl Bound to the Bridging Ligand 2,3-Bis(2-Pyridyl)Pyrazine (Dpp). Polyhedron 1987, 6, 1673−1676.

(54) Thomas, N. C.; Cox, J. Syntheses of Monometallic and Bimetallic 2,2′-Bipyridine and 2,3-Bis(2-Pyridyl)Pyrazine Complexes of Rhenium(I) complexes bound to the bridging ligand 2,3-bis(2-Pyridyl)Pyrazine (Dpp) as Bridging Ligand; Syntheses, Crystal Structures and Magnetic Properties. Inorg. Chim. Acta 2000, 310, 217−226.

(55) Grove, H.; Julve, M.; Lloret, F.; Kruger, P. E.; Tornroos, K. W.; Sletten, J. Syntheses, Crystal Structures and Magnetic Properties of Copper(II) Polynuclear and Dinuclear Compounds with 2,3-Bis(2-Pyridyl)Pyrazine (Dpp) and Pseudohalide as Ligands. Inorg. Chim. Acta 2001, 325, 115−124.

(56) Grove, H.; Julve, M.; Lloret, F.; Kruger, P. E.; Tornroos, K. W.; Sletten, J. Syntheses, Crystal Structures and Magnetic Properties of Copper(II) Polynuclear and Dinuclear Compounds with 2,3-Bis(2-Pyridyl)Pyrazine (Dpp) and Pseudohalide as Ligands. Inorg. Chim. Acta 2001, 325, 115−124.

(57) Shavaleev, N. M.; Moorcroft, L. P.; Pope, S. J. A.; Bell, Z. R.; Faulkner, S.; Ward, M. D. Sensitized Near-Infrared Emission from Complexes of Yb(III), Nd(III), and Er(III) by Energy-Transfer from Covalently Attached Piπ-Based Antenna Units. Chem. - Eur. J. 2003, 9, 5283−5291.

(58) Kennedy, F.; Shavaleev, N. M.; Koulourou, T.; Bell, Z. R.; Jeffery, J. C.; Faulkner, S.; Ward, M. D. Sensitised Near-Infrared Luminescence from Lanthanide(III) Centres Using Re(II) and Pt(II) Dime ines as Energy Donors in d−f Dinuclear Complexes Based on 2,3-Bis(2-Pyridyl)Pyrazine. Dalton Trans. 2007, 4922−4929.

(59) Sultan, R.; Gadamsetti, K.; Swavey, S. Synthesis, Electrochemistry and Spectroscopy of Lanthanide(III) Homodinuclear Complexes Bridged by Polyamide Ligands. Inorg. Chim. Acta 2006, 359, 1233−1238.

(60) Viviani, S.; Fratini, A.; Swavey, S. The Effect of the Lanthanide Contraction on Coordination with the Polyam ide Bridging Ligan d 2,3-Bis(2-Pyrid yl)Pyrazine (Dpp). Inorg. Chem. Commun. 2012, 24, 29−31.

(61) Swavey, S.; Fratini, A.; Grewal, J.; Hutchinson, A. Monometallic Europium, Terbium, and Neodymium Complexes Formed from the Bridging Ligand 2,3-Bis(2-Pyridyl)Pyrazine: Crystal Structure and Temperature Dependent Luminescent Properties. Inorg. Chim. Acta 2015, 428, 27−31.

(62) Huang, N. T.; Pennington, W. T.; Petersen, J. D. Structure of 2,3-Bis(2-Pyridyl)Pyrazine. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 1991, 47, 2011−2012.

(63) Haigh, C. W. A New Simple Criterion for Distinguishing the Types of Structures in Eight-Coordinate Complexes: The Pattern of Bond Angles. Polyhedron 1995, 14, 2871−2878.

(64) Llunell, M.; Casanova, D.; Cirera, J.; Boill, P. A. SHAPE (version 2.1); Barcelona, 2013.

(65) Ifthikhar, K. Mixed-Ligand Lanthanide Complexes-IX NMR Spectral Study of the Adducts of Ln(fod), with 2,2′-Bipyridyl and 1,10-Phenanthroline. Polyhedron 1996, 15, 1113−1120.

(66) Bleaney, B. Nuclear Magnetic Resonance Shifts in Solution Due to Lanthanide Ions. J. Magn. Reson. 1972, 8, 91−100.

(67) Eaton, D. R. The Nuclear Magnetic Resonance of Some Paramagnetic Transition Metal Acetylacetonates. J. Am. Chem. Soc. 1965, 87, 3097−3102.

(68) Foro, M.; Wa da, M.; Ishihara, K.; Eguchi, M.; Zhang, G.; Ishikawa, T.; Watanabe, A.; Wang, L.; Ogata, N. Fabrication and Characterization of Rare-Earth Metal-Chelate-Doped Plastic Film and Fiber Materials: Eu(3+)-Chelate-Doped PMMA. Mater. Devices Opt. Wireless Commun. 2002, 4905, 126.

(69) Karabulut, Y.; Ayvacikli, M.; Canimoglu, A.; Guene, J. G.; Kotan, Z.; Ek达尔, E.; Akuyz, O.; Can, N. Synthesis and Luminescence Properties of Trivalent Rare-Earth Element-Doped Calcium Stannate Phosphors. Spectrosc. Lett. 2014, 47, 630−641.

(70) Zucchi, G.; Le Goff, X. F. Magneto-Structural and Photophysical Investigations on a Dinuclear Sm(III) Complex Featuring 2,2′-Bipyridimine. Inorg. Chim. Acta 2012, 380, 354−357.

(71) Monteiro, J. H. S. K.; Mazali, I. O.; Sigoli, F. A. Determination of Judd-Olfet Intensity Parameters of Pure Samarium(III) Complexes. J. Fluoresc. 2011, 21, 2237−2243.

(72) Horrocks, W. D.; Albin, M. Progress in Inorganic Chemistry; Lippincott, S. J. Ed.; Progress in Inorganic Chemistry; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1984.

(73) Kirby, A. F.; Richardson, F. S. Detailed Analysis of the Optical Absorption and Emission Spectra of Europium(3+) in the Trigonal (C3) Eu(dmb)3·H2O System. J. Phys. Chem. 1983, 87, 2544−2556.

(74) Görlitz-Walrand, C.; Binnemans, K. Chapter 167 Spectral Intensities of jf Transitions; 1998; Vol. 25, pp. 101−264.

(75) dos Santos, E. R.; dos Santos, M. A. C.; Freire, O. R.; Júnior, S. A.; Barreto, L. S.; de Mesquita, M. E. On the Use of Theoretical Tools in the Study of Photophysical Properties of the New Eu(fod) Complex with Diphenylpyridine. Chem. Phys. Lett. 2006, 418, 337−341.

(76) Iftikhar, M.; Ifthikhar, K. New Dinuclear Lanthanide(III) Complexes Based on 6,6,7,7,8,8,8-Heptafluoro-2,2-Dimethyl-3,5-Octanediene and 2,2′-Bipyridimine. Inorg. Chem. Commun. 2009, 12, 296−299.

(77) Iftikhar, M.; Ifthikhar, K. New Hetero-Dilanthane Complexes Containing Ln′(fod) and Ln′′(fod) Fragments (Ln=Pr−Nd; Nd-Sm; Eu-Tb and Ho-Er) Linked by Bis-Diimine Bridging Ligand. Inorg. Chem. Commun. 2010, 13, 694−698.

(78) Bleaney, B. Nuclear Magnetic Resonance in Solution Due to Lanthanide Ions. J. Magn. Reson. 1972, 8, 91−100.

(79) Eaton, D. R. The Nuclear Magnetic Resonance of Some Paramagnetic Transition Metal Acetylacetonates. J. Am. Chem. Soc. 1965, 87, 3097−3102.
Tris(Dibenzoylemethanido)(1,10-Phenanthroline)Samarium(III). Pol-
yhedron 2010, 29, 2511–2515.
(88) dos Santos, E. R.; Freire, R. O.; da Costa, N. B., Jr.; Paz, F. A. A.; de Simone, C. A.; Júnior, S. A.; Araujo, A. A. S.; Nunes, L. A. O.; de Mesquita, M. E.; Rodrigues, M. O. Theoretical and Experimental Spectroscopic Approach of Fluorinated Ln5−β-Diketonate Com-
plexes. J. Phys. Chem. A 2010, 114, 7926–7936.
(89) Dutta, J. D. L.; Bispo, T. D.; Freire, R. O. LUMPAC Lanthanide Luminescence Software: Efficient and User Friendly. J. Comput. Chem. 2014, 35, 772–775.
(90) Leal, J. P.; Oitus, M; Casimiro, M. H.; Ferreira, L. M.; Fernandes, F.; Monteiro, B.; Laia, C. A. T.; Pereira, C. C. L. A Case of Self-Organization in Highly Emissive Eu3+ Ionic Liquids. Eur. J. Inorg. Chem. 2017, 3429–3434.
(91) Kai, J.; Felinto, M. C. F. C.; Nunes, L. A. O.; Malta, O. L.; Brito, H. F. Intermetallic Energy Transfer and Photostability of Luminescence-Tunable Multicolour PMMA Films Doped with Lanthanide-β-Diketonate Complexes. J. Mater. Chem. 2011, 21, 3796–3802.
(92) Hasan, N.; Iftikhar, K. Synthesis, Crystal Structure and Photoluminescence Studies of [Eu(dbm),(Impy)] and Its Polymer-Based Hybrid Film. New J. Chem. 2019, 43, 2479–2489.
(93) Ilmi, R.; Iftikhar, K. Structure Elucidation by Sparkle/RM1, Effect of Lanthanide Contraction and Photophysical Properties of Lanthanide(III) Trifluoroacetacetonate Complexes with 1,10-Phenanthroline. J. Photochem. Photobiol., A 2016, 325, 68–82.
(94) Ilmi, R.; Iftikhar, K. Optical Emission Studies of New Europium and Terbium Dinuclear Complexes with Trifluoroacetacetonate and Bridging Bipyrimidine. Fast Radiation and High Emission Quantum Yield. Polyhedron 2015, 102, 16–26.
(95) Ilmi, R.; Iftikhar, K. Photophysical properties of Lanthanide(III) 1,1,1-trifluoro-2,4-pentanedionato complexes with 2,2’-Bipyridyl: An experimental and theoretical investigation. J. Photochem. Photobiol., A 2017, 333, 142–155.
(96) Dar, W. A.; Ganaie, A. B.; Iftikhar, K. Synthesis and Photoluminescence Study of Two New Complexes [Sm(HFa)(Impy)] and [Eu(HFa)(Impy)] and Their PMMA Based Hybrid Films. J. Lumin. 2018, 202, 438–449.
(97) Dar, W. A.; Iftikhar, K. Phase Controlled Colour Tuning of Samarium and Europium Complexes and Excellent Photostability of Their PVA Encapsulated Materials. Structural Elucidation, Photophysical Parameters and the Energy Transfer Mechanism in the Eu3+-Complex by Sparkle/PM3 Calculations. Dalton Trans. 2016, 45, 8956–8967.
(98) Werts, M. H. V.; Jukes, R. T. F.; Verhoeven, J. W. The Emission Spectrum and the Radiative Lifetime of Eu3+ in Luminescent Lanthanide Complexes. Phys. Chem. Chem. Phys. 2002, 4, 1542–1548.
(99) Carnall, W. T.; Fields, P. R.; Rajnak, K. Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. IV. Eu3+. J. Chem. Phys. 1968, 49, 4430–4435.
(100) Carnall, W. T.; Crosswhite, H.; Crosswhite, H. M. Energy Level Structure and Transition Probabilities in the Spectra of the Trivalent Lanthanides in LaF3 Argonne, IL (United States), 1978.
(101) Kodaira, C. A.; Brito, H. F.; Malta, O. L.; Serra, O. A. Luminescence and Energy Transfer of the Europium (III) Tungstate Obtained via the Pechini Method. J. Lumin. 2003, 101, 11–21.
(102) Ferhi, M.; Bouzidi, K.; Horchani-Naifer, K.; Elhouichet, H.; Ferid, M. Judd-O'Leff Analysis of Spectroscopic Properties of Eu3+-doped KLa(PO4)3. J. Lumin. 2015, 157, 21–27.
(103) de Sá, G. F.; Malta, O. L.; de Mello Donégà, C.; Simas, A. M.; Longo, R. L.; Santa-Cruz, P. A.; da Silva, E. F. Jr. Spectroscopic Properties and Design of Highly Luminous Lanthanide Coordination Complexes. Coord. Chem. Rev. 2006, 196, 165–195.
(104) Walsh, B. M. Judd-O'Leff Theory: Principles and Practices. In Advances in Spectroscopy for Lasers and Sensing; Springer Netherlands: Dordrecht, 2006; pp. 403–433.
(105) Jiang, H. D.; Wang, J. Y.; Zhang, H. J.; Hu, X. B.; Liu, H. Optical-Transition Properties of the Nd3+ Ion in Gd4d3 La2O3: VO4 Crystal. 2007, 3647–3650, DOI: 10.1063/1.150568.