Inorganic Chemistry

Controlled Energy Transfer from a Ligand to an Eu^{III} Ion: A Unique Strategy To Obtain Bright-White-Light Emission and Its Versatile Applications

Rajamouli Boddula,[®] Kasturi Singh, Santanab Giri,[®] and Sivakumar Vaidyanathan^{*®}

Department of Chemistry, National Institute of Technology, Rourkela, Odisha 769008, India

Supporting Information

ABSTRACT: A new diphenylamine-functionalized ancillary-ligand-coordinated europium(III) β -diketonate complex showed incomplete photoexcitation energy transfer from a ligand to a Eu^{III} ion. A solvatochromism study led to a balancing of the primary colors to obtain single-molecule white-light emission. Thermal-sensing analysis of the europium complex was executed. The europium complex, conjugated with a near-UV-light-emitting diode (395 nm), showed appropriate white-light-emission CIE color coordinates (x = 0.34 and y = 0.33) with a 5152 K correlated color temperature.

he new single-organic-molecule- or molecular-complexbased white-light-emitting sources are attractive owing to their potential applications in full-color smart displays and lighting sources [including white-organic-light-emitting diodes and solid-state lighting (SSL)].¹ In general, white light can be generated by mixing three primary colors, to cover the entire visible spectrum. At present, several organic fluorophores having the capacity of emitting individual red-blue-green (RGB) color are known. However, white light generated by a single molecule (a single-component approach) has several advantages over that of simple RGB mixing (multicomponent emitters).² The benefits include improved stability, stable Commission International de I'Eclairage (CIE) color coordinates, and a simple fabrication process.³ Stable white-light photo- and electroluminescence released in a single-molecule dyad have been documented.⁴ White-light creation by aggregation-induced emission in a single organic molecule has also been reported.⁵ An iridium-based molecular complex, which emits white light (from 440 to 800 nm in the spectral window), is known.⁶ When the sensitizing/ energy-harvesting capability of a Ir^{III} ion to lanthanides is used, an iridium-europium dyad has been used to release white light (bluish-green emission from the IrIII emissive center and red emission from the Eu^{III} metal center).⁷ However, generating white-light emission from a single-molecular complex is still a stimulating research manifold. The ever-increasing demand of the cumulative global energy crisis is reducing energy sources, and it can be overcome by highly energy-efficient lighting systems (SSL) that can help to conserve energy and reduce the overall lighting costs.8

Recently, ligand-based incomplete/partial energy transfer (ET) to a Eu^{III} metal center leading to white-light generation has become an attractive research task.^{9,1d} However, white-light emission from a single lanthanide complex is limited in its

solution phase, and solid-state white-light emission is quite rare. Very recently, we have explored triphenylamine (TPA)functionalized imidazole-phenanthroline based, a new bipolar ligand for a monochromatic red-light-emitting europium(III) complex.¹⁰ Further, efforts have been made to obtain monochromatic red emission as well as investigate the effect of functionalization [extended the TPA moiety with diphenylamine (DPA)] on the luminescence properties of the complex in detail, where the ET process from a ligand to a Eu^{III} metal ion plays a vital role. The DPA-decorated phenanthroline-fluorene-TPA ligand (Phen-Fl-TPA-DPA) and its corresponding europium-(III) β -diketonate complex [Eu(TTA)₃-Phen-Fl-TPA-DPA, where TTA = thenoyltrifluoroacetone] have been synthesized. The fluorene moiety was used to design the europium complex because its strong $\pi - \pi^*$ absorption will improve the morphological properties and photostability of the complex. The presence of DPA moieties in the ligand widen the absorption outline and can act as light-harvesting units. TTA can act as an antenna, and the presence of fluorine in the ligand can decrease the vibrational quenching and increase the decay time.¹¹ In the presently studied europium(III) complex, ET to a central metal ion from a ligand and an antenna, is expected (Figure 1). The ligand can act as both sensitizer and a yellow-emitting source.



Figure 1. Chemical structure of europium(III) complex.

The detailed experimental procedure for the synthesis of the ligand and corresponding europium(III) complex is given in Scheme S1 and Figures S1–S10, and their thermal stabilities were investigated (Figure S12). The amorphous nature of the complex was confirmed by X-ray diffraction (Figure S11). The UV–visible absorption spectra of the ligand and complex were carried out in solution (CHCl₃, 1.0×10^{-4} mol L⁻¹), thin film, and solid state (Figure S13). The absorption spectrum of the ligand shows absorption ranging from 240 to 450 nm with λ_{max} values at 306 and 280 nm (attributed to the $\pi \to \pi^*$ transitions of

Received: May 16, 2017

the aromatic moieties). This was verified theoretically by the time-dependent density functional theory (TD-DFT) (Figure S14). Similarly, the absorption studies of the europium(III) complex and $Eu(TTA)_3$ ·2H₂O show peak maxima at 340 and 296 nm and at 340 and 275 nm, respectively. The europium(III) complex shows comparable peaks, which are observed for the ligand as well as the $Eu(TTA)_3$ moiety (Table S6), suggesting presence of ligand in the same.

The photoluminescence (PL) emission of the ligand was extended from 400 to 700 nm (covering the entire visible spectral window) with a maxima at 517 nm at different excitation wavelengths (285, 305, and 365 nm) in CHCl₃ (Figure S17). The ligand emission in different solvents was monitored to explain the broadness observed in the ligand emission spectra (Figures S33 and S34 and Table S5). Among all of the solvents, toluene showed a distinct emission behavior. In the case of the europium(III) complex, a characteristic red emission at 612 nm from the Eu^{III} ion was shown; emission belonging to the ligand was also observed from 400 to 600 nm with a peak maximum at 517 nm. The partial ET from a ligand to a central metal ion is responsible for the obtained orange-red emission, instead of pure red (Figure S20). The intensity ratio (2:1) of the red emission was higher than that of the yellow emission from the ligand. According to Latva et al., investigations, i.e., the difference between the ligand $({}^{3}\pi\pi^{*})$ and the europium excited state $({}^{5}D_{0})$, should be >2500 cm⁻¹ for efficient ET.¹² The singlet and triplet energy levels of TTA located at ~25164 (3.12 eV) and 18954 cm⁻¹ (2.35 eV)¹³ and the Eu^{III}-metal-ion radiative excited state ⁵D₀ energy level located at 17500 cm⁻¹ are known (Table S4).¹⁴ However, to understand the process of ET in the europium(III) complex, it is essential to know the exact location/position of the singlet (S_1) and triplet (T_1) energy levels of the ligand.¹¹

To well understand the reason behind the complete or partial ET, the excited-state energy levels were calculated by employing TD-DFT methodology embedded in the *G09* program,¹⁶ and there is strong supporting evidence that the singlet and triplet energy levels are located at 23256 (2.88 eV) and 19960 cm⁻¹ (2.47 eV), respectively (Figure 2a and Table S4 and Figure S30).



Figure 2. (a) Ligand-to-Eu^{III}-metal-ion ET process. (b) Europium(III) complex emission in different solvents and white-light emission in toluene with a CIE color gamut.

This was also confirmed by emission spectra of the gadolinium complex at 77 K (Figure S46). The difference between the triplet excited state and Eu^{III}-metal-ion-excited ⁵D₀ energy level was less than 2500 cm⁻¹ and also singlet excited level was <25000 cm⁻¹. The ligand singlet- and triplet-state energy level, $\Delta E(^{1}\pi\pi^{*}-^{3}\pi\pi^{*})$, difference was found to be 3296 cm⁻¹, which is less than 5000 cm⁻¹. These lower energy levels of the ligand suggest that the excited-state energy can be back-transferred from the Eu^{III} excited state (⁵D₀) to the ligand.¹⁷ Hence, it is clear that both the ligand (yellow) and Eu^{III} ion (red) emissions were observed in the PL spectra of the complex.

The dual (yellow and red) emission behavior was used to generate white light from a single molecule. If color balancing among the ligand broad (BG) emission and the Eu^{III} (R) emission will be proper, white light can be generated from a single-molecule system. In the emission spectra for a europium-(III) complex at different concentrations (1, 10, 20, and 75 \times 10^{-5} mmol) using chloroform, no distinguished result was observed, while for a red shift, an increase in the emission intensity was observed (ligand emission) by exciting with different excitation wavelengths for the europium complex (Figures S24-S26). On basis of ligand emission behavior in different solvents, emission spectroscopy of the europium(III) complex in different solvents has also been carried out, and the strange responses were perplexing. These perplexing outcomes made it extremely difficult to obtain white-light emission with the appropriate CIE [0.31, 0.32; correlated color temperature (CCT) = 6558 K; Figure S23 and Table S3]. The color gamut observed from toluene (Figure 2b) was due to the proper balance between primary colors.

From solvatochromism analysis, it was found that the presently synthesized europium(III) complex is acting as a single white-light-emitting component with tunable emission color with changes in the solvent. An antenna (ligand) present in the complex is responsible for partial sensitization to obtain white-light emission. This is due to less energy difference between the T_1 state of the ligand and Eu^{III} ion excited state. It was expected that the free rotation of the phenyl rings of the DPA molecule is sufficient in a less polar solvent (less density), which leads to a decrease in the excited-state energy level of the ligand. In addition, under the same conditions, theoretical analysis was performed to understand the energy levels by arresting the C-Cbond of DPA [carboxybenzyl (CBZ)]. From the obtained theoretical results, the optimized CBZ moiety with a ligand showed high singlet (25707 cm⁻¹, 3.18 eV) as well as triplet $(21277 \text{ cm}^{-1}, 2.63 \text{ eV})$ energy levels, which was greater than the DPA ligand.^{15b} More polar solvents like acetonitrile (ACN), N,N-dimethylformamide, and dimethyl sulfoxide showed almost pure red emission, revealing the existence of a sufficient energy gap (complete ET). This clearly indicates that the solvent plays a major role and the aromatic ring in toluene is more responsible for white-light emission. Morever, to generate bright-white-light emission (CIE, x = 0.33, y = 0.33), the corresponding europium complex was excited with different exciting wavelengths, and 380 nm found to be proper excitation wavelength (CIE; 0.34, 0.33; CCT = 5152 K; Figures S27–S29).

To study solvent polarity effect on the emission performances of white-light emission, the solvatochromism studies were executed using a mixture of solvents [polar (ACN; pure Eu^{III} emission) and less polar (toluene; both ligand and Eu^{III} emission)] by different ratios from 90:10 to 10:90, respectively (Figure S35a-j). The intensity of the Eu^{III} ion, 612 nm emission peak started to increase from 90:10 to 10:90 toluene-ACN, and the broad emission at the 450–600 nm range started to decrease. The intense Eu^{III} ion red emission was higher in the pure solvent compared to that of a mixture of solvents (CIE shown in Table S12). The decrease of the Eu^{III} emission intensity as well as the increase in the ligand emission was observed by changing the mixture from 90:10 to 10:90 toluene-ethyl acetate (EtOAc) (Figure S36a-j), respectively (CIE shown in Table S10). The above study indicates that the solvent polarity plays a vital role. The characteristic dual-emission behavior of the complex extend their applications for luminescent temperature sensors. The PL measurements were performed in the 283-358 K temperature

Communication

range. It is well documented that the europium(III) complexes with organic ligands also showed high-temperature sensitivity, particularly with β -diketonates.¹⁸ In the present study with increasing temperature, the ligand emission from the complex was found to be enhanced, while the intensity of the 612 nm peak decreased and a change in the emission color was observed from orange-red (283 K) to near-white (303 K) to green (358 K) (Figures 3A and S39). The temperature-dependent PL emission



Figure 3. (A) Europium(III) complex with different temperatures. Inset: Ligand emission from the europium(III) complex. (B) Whitelight emission from the LED (395 nm): (a) LED without coating; (aa) LED with forward bias. (b) 1:10 and (c) 1:50 europium(III)-complexcoated LEDs; (bb and cc) with forward bias.

spectra state that the complex exhibits color tunability. The emission profile in different wavelengths with specific temperatures and their respective CIE color coordinates were investigated and are presented in Figure S38 and Table S11. A comparison study was discussed in the Supporting Information.

It is worth noting that, without DPA, functionalization on the Phen-Fl-TPA ligand in toluene showed emissions ranging from 380 to 530 nm with λ_{max} = 423 nm, blue region.⁹ When the DPA moiety was connected to TPA (TPA-DPA), the emission wavelength was shifted from 300 to 630 nm with a maximum at 480 nm. However, after insertion of the Eu^{III} metal ion into the TPA-DPA ligand; the emission spectrum was found to cover a broad range from 410 to 630 nm (Figure S37). However, similar results were also observed in other solvents (tetrahydrofuran, EtOAc, dichloromethane, trichloromethane). A primary color balance was perceived in only toluene, which leads to white-light emission. To the best of our knowledge, we observed white-light emission from the europium(III) complex with an imidazolebased neutral ligand for the first time. It is also notable that the above-mentioned observation influences the PL quantum yield (PLQY) of the europium(III) complex and is found to be 15.3%. The PLQY indirectly supports the partial ET from a ligand to a central Eu^{III} metal ion. The experimental outcome was supported by the electrochemical (Figure S21 and Table S2), theoretical, diffuse-reflectance spectroscopy (Figure S15), and PL lifetime (Figure S22) studies.

To further understand the ET process and emission contribution (ligand and Eu^{III} ion), PL lifetime measurements with different monitoring wavelengths [517/500 nm (solution/solid) belongs to ligand emission and 612 nm (solution/solid) belongs to Eu^{III} ion emission in the complex] were executed. In addition, different excitation wavelengths (spectral window, 300–400 nm with an interval of 10 nm) were used for the experimental procedure. The lifetimes of the complex in solution with 517 and 612 nm as a monitoring wavelength and $\lambda_{exc} = 300-360$ nm have shown similar outcomes. However, beyond (>360 nm excitation) where the lifetime values started decreasing, found at 390 nm, there was much less contribution ($\lambda_{em} = 612$ nm, shown in Figures S41 and S42). This indicates that the ET

from ligand to Eu^{III} metal ion is efficient only up to 380 nm and partial for 390 nm excitation. These observations reveal that ligand emission from the europium complex supports the brightwhite-light emission. In the case of the solid, no such type (solution) of lifetime difference observation was detected (Figures S43 and S44). The obtained lifetime results (Table S9) clearly support ligand and Eu^{III} emission in solution and no ligand emission (minute) contribution along with Eu^{III} red emission in the solid.

The ligand exhibits a distinct excited-state rotation conformation in different polarity solvents, which might be possible for polarity-dependent fluorophores. Therefore, white-light emission in toluene may come from a mixture of either several excited states or even ground states. Fortunately, weak ligand emission was observed from the complex in solid form, taken as an advantage to fabricate the white-light-emitting diode (LED). The white-LED was fabricated by integrating the complex with 395 nm emitting UV-LED (InGaN) chips under 20 mA forward bias (Figure 3B). The excitation source from LED was fully observed by the europium complex shown at different concentrations [1:10 and 1:50 Eu³⁺–PMMA). The fabricated LED showed white-light emission (PLQY 0.68%) with CIE values of x = 0.34 and y = 0.33, which are close to the National Television Standard Committee (NTSC) standard value.

In conclusion, the newly synthesized europium(III) complex is acting as a single-component white-light emitter, and it is due to the balancing of the primary colors. The combined experimental and TD-DFT calculations support the ET mechanism. The temperature-dependent PL emission color tuning will certainly give directions for using the presently studied europium complex as a temperature sensor. In addition, the complex conjugated with LED (395 nm) showed bright-white-light with appropriate CIE color coordinates. All of these observations have important implications in the design of single-molecule white-light emissive complex and its ability as a temperature sensor.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01255.

Experimental section, NMR, FT-IR, LC-MS, XRD, DSC-TGA, UV, PL, CIE, electrochemical and DFT analysis (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: vsiva@nitrkl.ac.in. Tel: +91-661-2462654.

ORCID 0

Rajamouli Boddula: 0000-0003-0414-715X Santanab Giri: 0000-0002-5155-8819

Sivakumar Vaidyanathan: 0000-0002-2104-2627

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Board of Research in Nuclear Sciences, DAE and Naval Research Board, DRDO, India, for funding and are grateful to the reviewers for their suggestions.

REFERENCES

(1) (a) Li, S.; Zhong, G.; Zhu, W.; Li, F.; Pan, J.; Huang, W.; Tian, H. Dendritic europium complex as a single dopant for white-light electroluminescent devices. J. Mater. Chem. 2005, 15, 3221-3228. (b) Furman, J. D.; Warner, A. Y.; Teat, S. J.; Mikhailovsky, A. A.; Cheetham, A. K. Tunable, ligand-based emission from inorganicorganic frameworks: a new approach to phosphors for solid state lighting and other applications. Chem. Mater. 2010, 22, 2255-2260. (c) Reineke, S.; Lindner, F.; Schwartz, G.; Seidler, N.; Walzer, K.; Lussem, B.; Leo, K. White organic light-emitting diodes with fluorescent tube efficiency. Nature 2009, 459, 234-238. (d) Shelton, A. H.; Sazanovich, I. V.; Weinstein, J. A.; Ward, M. D. Controllable three-component luminescence from a 1,8-naphthalimide/ Eu(III) complex: white light emission from a single molecule. Chem. Commun. 2012, 48, 2749-2751. (e) Kamtekar, K. T.; Monkman, A. P.; Bryce, M. R. Recent advances in white organic light-emitting materials and devices (WOLEDs). Adv. Mater. 2010, 22, 572-582. (f) Shao, G.; Yu, H.; Zhang, N.; He, Y.; Feng, K.; Yang, X.; Cao, R.; Gong, M. Synthesis and photophysical properties of europium(III) $-\beta$ -diketonate complexes applied in LEDs. *Phys. Chem.* Chem. Phys. 2014, 16, 695-702. (g) Wang, Z.; Yang, H.; He; He, Y.; Zhao, J.; Tang, H. A highly-efficient blue-light excitable red phosphor: intramolecular π -stacking interactions in one dinuclear europium(III) complex. Dalton Trans. 2016, 45, 2839-2844.

(2) Kwon, J. B. H.; Jang, H. S.; Yoo, H. S.; Kim, S. W.; Kang, D. S.; Maeng, S.; Jang, D. S.; Kim, H.; Jeon, D. Y. White-light emitting surface-functionalized ZnSe quantum dots: europium complex-capped hybrid nanocrystal. *J. Mater. Chem.* **2011**, *21*, 12812–12818.

(3) Wang, Q.; Ma, D. Management of charges and excitons for high-performance white organic light-emitting diodes. *Chem. Soc. Rev.* 2010, 39, 2387–2398.

(4) Park, S.; Kwon, J. E.; Kim, S. H.; Seo, J.; Chung, K.; Park, S. Y.; Jang, D. J.; Medina, B. M.; Gierschner, J.; Park, S. Y. A. White-light-emitting molecule: frustrated energy transfer between constituent emitting centers. *J. Am. Chem. Soc.* **2009**, *131*, 14043–14049.

(5) Xie, Z.; Chen, C.; Xu, S.; Li, J.; Zhang, Y.; Liu, S.; Xu, J.; Chi, Z. White-light emission strategy of a single organic compound with aggregation-induced emission and delayed fluorescence properties. *Angew. Chem., Int. Ed.* **2015**, *54*, 7181–7184.

(6) Bolink, H. J.; De Angelis, F.; Baranoff, E.; Klein, C.; Fantacci, S.; Coronado, E.; Sessolo, M.; Kalyanasundaram, K.; Gratzel, M.; Nazeeruddin, Md. K. White-light phosphorescence emission from a single molecule:application to OLED. *Chem. Commun.* **2009**, 4672– 4674.

(7) (a) Coppo, P.; Duati, M.; Kozhevnikov, V. N.; Hofstraat, J. W.; De Cola, L. White-light emission from an assembly comprising luminescent iridium and europium complexes. *Angew. Chem., Int. Ed.* **2005**, *44*, 1806–1810. (b) Sykes, D.; Tidmarsh, I. S.; Barbieri, A.; Sazanovich, I. V.; Weinstein, J. A.; Ward, M. D. d→f energy transfer in a series of Ir^{III}/Eu^{III} dyads: energy-transfer mechanisms and white-light emission. *Inorg. Chem.* **2011**, *50*, 11323–11339.

(8) (a) Duan, J. P.; Sun, P. P.; Cheng, C. H. Europium complexes having an aminophenanthroline ligand as red dopants in electroluminescent devices. *Adv. Technol. Mater. Mater. Process.* **2004**, *6*, 95–102. (b) King, R. B. *Adv. Chem. Ser.*, **1967**, *62*, Chapter 21, pp 306–317.10.1021/ba-1967-0062.ch015 (c) Bunzli, J. C. G.; Chauvin, A. S. In Handbook on the Physics and Chemistry of Rare Earths; Bunzli, J. C. G., Pecharski, V. K., Eds.; Elsevier Science Publishers: Amsterdam, The Netherlands, 2014; Vol. *44*, Chapter 261, pp 169–281.

(9) (a) Kar, A.; Kundu, S.; Patra, A. A simple approach to generate efficient white light emission from a ZnO-ionic liquid complex. *RSC Adv.* **2012**, *2*, 4879–4885. (b) Wang, R.; Peng, J.; Qiu, F.; Yang, Y.; Xie, Z. Simultaneous blue, green, and red emission from diblock copolymer micellar films: a new approach to white-light emission. *Chem. Commun.* **2009**, 6723–6725. (c) He, G.; Guo, D.; He, C.; Zhang, X.; Zhao, X.; Duan, C. A color-tunable europium complex emitting three primary colors and white light. *Angew. Chem., Int. Ed.* **2009**, 48, 6132–6135. (d) Zhang, J.; Li, H.; Chen, P.; Sun, W.; Gao, T.; Yan, P. A new strategy for achieving white-light emission of lanthanide complexes: effective

control of energy transfer from blue-emissive fluorophore to Eu(III) centres. J. Mater. Chem. C 2015, 3, 1799–1806.

(10) Rajamouli, B.; Sood, P.; Giri, S.; Krishnan, V.; Sivakumar, V. A dual-characteristic bidentate ligand for a ternary mononuclear europium(III) molecular complex – synthesis, photophysical, electrochemical, and theoretical study. *Eur. J. Inorg. Chem.* **2016**, 2016, 3900–3911.

(11) (a) Zheng, Y.; Lin, J.; Liang, Y.; Lin, Q.; Yu, Y.; Meng, Q.; Zhou, Y.; Wang, S.; Wang, H.; Zhang, H. A comparative study on the electroluminescence properties of some terbium β -diketonate complexes. *J. Mater. Chem.* **2001**, *11*, 2615–2619. (b) De Silva, C. R.; Wang, R.; Zheng, Z. Highly luminescent Eu(III) complexes with 2,4,6-tri(2-pyridyl)-1,3,5-triazine ligand: Synthesis, structural characterization, and photoluminescence studies. *Polyhedron* **2006**, *25*, 3449–3455.

(12) Latva, M.; Takalo, H.; Mukkala, V. M.; Matachescu, C.; Rodriguez-Ubis, J. C.; Kankare. Correlation between the lowest triplet state energy level of the ligand and lanthanide(III) luminescence quantum yield. *J. Lumin.* **1997**, *75*, 149–169.

(13) Xu, H.; Wang, L. H.; Zhu, X. H.; Yin, K.; Zhong, G. Y.; Hou, X. Y.; Huang, W. Application of chelate phosphine oxide ligand in Eu^{III} complex with mezzo triplet energy level, highly efficient photoluminescent, and electroluminescent performances. *J. Phys. Chem. B* **2006**, *110*, 3023–3029.

(14) (a) Shi, M.; Li, F.; Yi, T.; Zhang, D.; Hu, H.; Huang, C. Tuning the triplet energy levels of pyrazolone ligands to match the 5D_0 level of europium(III). *Inorg. Chem.* **2005**, *44*, 8929–8936. (b) Li, T.; Shang, W.; Zhang, F.; Mao, L.; Tang, C.; Song, M.; Du, C.; Wu, Y. Luminescent properties of europium complexes with different long chains in Langmuir-Blodgett (LB) Films. *Engineering* **2011**, *3*, 301–311.

(15) (a) Yang, C.; Fu, L. M.; Wang, Y.; Zhang, J. P.; Wong, W. T.; Ai, X. C.; Qiao, Y. F.; Zou, B. S.; Gui, L. L. A highly luminescent europium complex showing visible-light-sensitized red emission: direct observation of the singlet pathway. *Angew. Chem., Int. Ed.* 2004, *43*, 5010–5013.
(b) Rajamouli, B.; Dwaraka Viswanath, C. S.; Giri, S.; Jayasankar, C. K.; Sivakumar, V. Carbazole functionalized new bipolar ligand for monochromatic red light emitting Europium(III) complex: combined experimental and theoretical study. *New J. Chem.* 2017, *41*, 3112–3123.

(16) D'Aleo, A.; Moore, E. G.; Szigethy, G.; Xu, J.; Raymond, K. N. Aryl bridged 1-hydroxypyridin-2-one: effect of the bridge on the Eu(III) sensitization process. *Inorg. Chem.* **2009**, *48*, 9316–9324.

(17) Pavithran, R.; Reddy, M. L. P.; Junior, S. A.; Freire, R. O.; Rocha, G. B.; Lima, P. P. Synthesis and luminescent properties of novel europium(III) heterocyclic β -diketone complexes with Lewis Bases: structural analysis using the Sparkle/AM1 model. *Eur. J. Inorg. Chem.* **2005**, 2005, 4129–4137.

(18) (a) Allison, S. W.; Gillies, G. T. Remote thermometry with thermographic phosphors: Instrumentation and applications. *Rev. Sci. Instrum.* **1997**, *68*, 2615–2650. (b) Zelelow, B.; Khalil, G. E.; Phelan, G.; Carlson, B.; Gouterman, M.; Callis, J. B.; Dalton, L. R. Dual luminophor pressure sensitive paint: II. Lifetime based measurement of pressure and temperature. *Sens. Actuators, B* **2003**, *96*, 304–314. (c) Borisov, S. M.; Wolfbeis, O. S. Temperature-sensitive europium(iii) probes and their use for simultaneous luminescent sensing of temperature and oxygen. *Anal. Chem.* **2006**, *78*, 5094–5101.