New europium complexes and their use in red light-emitting diodes and vapoluminescent sensors

Rachna Devi, Rajamouli Boddula, Kasturi Singh, Satendra Kumar and Sivakumar Vaidyanathan

Department of Chemistry, National Institute of Technology Rourkela, Rourkela, Odisha, India; Analytical Chemistry and Spectroscopy Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, India

ABSTRACT
Three novel trivalent europium [Eu(III)] complexes – Eu(DBM)_3Phen-Ph-Ph, Eu(DBM)_3Phen-mCF_3-Ph, and Eu(DBM)_3Phen-pCF_3-Ph – were designed, synthesized, and characterized using various spectroscopic methods. Then their photophysical characteristics were investigated. The Eu complexes in the solid phase showed a pure red emission (due to the electric dipole transitions of the Eu^{3+} ion). In a solution, they had multiple emissions due to their ligand contribution. The solvatochromism studies revealed that the Eu(III) complexes in the methanol and DMSO solutions had both metal ion and ligand emissions with similar intensities, which yielded a white emission. Of all the Eu(III) complexes, Eu(DBM)_3Phen-mCF_3-Ph showed the best quantum yield. In addition, the fluorinated mCF_3 ligand had an unusually high lifetime value. Its remarkable linear decrease in luminescence intensity with increasing temperature opens a new window for its use as a sensitive temperature sensor at the 30–80°C range. The CIE color coordinates of the fabricated red LEDs (InGaN) are very close to the standard NTSC CIE color coordinates for bright red emissions, and the color purity as well as the LER values of the fabricated red LEDs are also very good. The Eu(III) complexes exhibited on-off photoluminescence switching via the vapoluminescent process and responded best to the acid-base (HCl-NH_3) vapors. All these features suggest that the synthesized Eu(III) complexes are efficient candidates for red-emitting LEDs and vapoluminescent sensors.

CONTACT
V. Sivakumar
vsiva@nitrkl.ac.in

This article has been corrected with minor changes. These changes do not impact the academic content of the article.

ISSN (print): 1598-0316; ISSN (online): 2158-1606

Supplemental data for this article can be accessed here. https://doi.org/10.1080/15980316.2021.1879960

© 2021 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group on behalf of the Korean Information Display Society. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
1. Introduction

Light-emitting diode (LED) lights are exceptionally excellent light sources and have been broadly used for solid-state lighting because of their numerous benefits over traditional incandescent and fluorescent lamps, such as their high efficiency, long service life, low energy consumption, and environment-friendliness [1–4]. All these advantages of LEDs over incandescent lights are furthering the development of LEDs for lighting [5,6]. However, LEDs also have some drawbacks such as their need for extensive cooling due to their high power requirement (which ultimately limits the maximum power of each LED chip). To overcome this drawback, high-quality colored or white LEDs are required. There are numerous ways to fabricate LEDs that deliver a white light emission, which is optimal for the sensitive human eye. In the present red LED technology, the red-emitting component is used to produce a pure white light emission, which can also be generated by blue LED with yellow-emitting phosphor [7]. However, white LED generated by blue LED with yellow-emitting phosphor has a low color-rendering index (CRI), low color reproducibility, and low luminous efficiency because of its deficiency in red emission light [8]. It is difficult to design and synthesize stable red-emitting phosphors that can be excited by a 465 nm blue-emitting InGaN chip [9]. Also, the white light emission can be generated by the combination of near UV LED with tricolor [blue, green, and red (RGB)] phosphors. The latter method showed improved performance, an enhanced color rendering index, and a wide range of color temperatures. Eu(III) complexes have been used as red phosphors in the fabrication of white LEDs because of their wide excitation band (the absorption of coordinated organic chromophores can be finetuned as per the requirement of LEDs), high quantum yield, and good color purity (due to their narrow-band or line-like emission) [10,11].

The Eu(III) β-diketonate complex is known for its excellent red emission under near UV irradiation due to the efficient energy transfer from the β-diketonate ligand to the central Eu(III) ions. However, the coordinated water molecule could quench the luminescence and decrease the overall quantum yield or energy transfer efficiency (from the ligand to the europium ion) of the complex. Thus, replacement of the water molecule with the purposely synthesized ancillary ligand is necessary and plays a key role in enhancing the overall performance of the trivalent europium complex quantum yield. The red LED produced by Eu(III) β-diketonate complexes enables them to emit highly monochromatic red light at 615 nm with a full width at half maximum (FWHM) of only 5–10 nm due to the $^5D_0 \rightarrow ^7F_2$ electronic transitions, and can enhance the overall performance of the white LEDs (due to their narrow-band red emission that is ideal for the sensitive human eye) [13,11,12]. In our previous research, some Eu(III) β-diketonate complexes were used as the red component of white LEDs based on their near UV-emitting chips [14,15]. In this study, 2-Thenoyltrifluoroacetone (TTA) was used as an antenna for the trivalent europium ion in the complex. However, the energy transfer efficiency was still comparatively less due to the location of the single and triplet energy levels as well as the synergy with the europium-excited levels ($^5D_{0,1,2}$) [16,17].

It is also worth noting that the TTA singlet energy can harvest the energy to the Dibenzoylmethane (DBM) triplet level in the conjugate energy transfer process and should have a difference of more than 5,000 cm$^{-1}$, according to Latva et al. [18]. Keeping this in mind, we used DBM as an antenna. Its singlet and triplet excited energy levels were extremely favorable to the Eu(III) metal ion. In addition, temperature-dependent photoluminescence is one of the important techniques for studying the defects related to non-radiative processes, localized states, and carrier transport dynamics [19,20].

In this study, we synthesized new Eu(III) β-diketonate complexes [Eu(DBM)$_3$Phen-Ph-Ph, Eu(DBM)$_3$Phen-mCF$_3$-Ph, and Eu(DBM)$_3$Phen-pCF$_3$-Ph] based on N1-functionalised [with phenyl moieties (Ph, m-CF$_3$, and p-CF$_3$ groups)] phenanthro-imidazole ancillary ligands for LED and vapoluminescent sensing applications (Figure 1). The detailed photophysical properties, thermal stability, and energy-transfer mechanism of the synthesized Eu-complexes were examined. Fluorinated ligands play

![Chemical structures of the Eu(III) complexes with the respective substitutions.](image-url)
J. INF. DISP. 139

a significant role in the energy transfer process because they reduce the triplet state energy and improve the overall efficiency of the complex [21–23]. Not only the fluorination of the coordinated ligands is vital, but also where it is located (since it can influence the excited level of the ligands). Since p-CF₃ has extended conjugation, unlike m-CF₃, which may be due to energy transfer or states, the π-conjugation length may be interrupted due to these bulky CF₃ groups in the ligands, which also act as withdrawing groups. In other words, p-CF₃ can reduce the vibrational quenching due to the presence of the C-F bond and the feasibility of improving its photoluminescence quantum efficiency [24,25]. Also discussed in this paper were the recyclable on-off-on vapoluminescent sensor and temperature-dependent PL emissions. Finally, a red-emitting LED was fabricated by integrating the complex into a 395 nm radiating InGaN chip. The chemical structure of the Eu-complexes is shown in Figure S1.

2. Results and Discussion

2.1. Characterization

All the synthesized ligands and their corresponding complexes were confirmed by different spectroscopic methods such as ¹H and ¹³C NMR, FT-IR, Mass, and elemental analysis (Figure 2, S1-S11). The photophysical study of the Eu(III) complexes and ligands was characterized by UV-Vis absorption and PL analyses. Electrochemical and theoretical analyses were also performed to gain more information on the energy levels. The synthetic route of the ligands [15, 26] and their respective complexes are shown in Scheme 1. The detailed experimental procedure and characterization are discussed in the supplementary information.

2.2. Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared (FT-IR) spectra of all the ancillary ligands and their corresponding Eu(III) complexes are shown in Figure 2. In the Eu(III) complexes, the stretching vibration peaks at ~1,596 cm⁻¹ are due to the C = O group of DBM, and the band at ~1,410 cm⁻¹ corresponds to the asymmetric stretching vibration of C = N in the phenanthroimidazole-based ancillary ligands. The strong bending vibration peaks out of the plane from the C-H bonds in the phenanthroimidazole-based ancillary ligands are shown as 811 and 723 cm⁻¹. In addition, the new peak at ~518 cm⁻¹ is ascribed to the Eu-N vibration, which indicates that the phenanthroimidazole-based ancillary ligands were successfully coordinated with the Eu(III) ion in the molecular Eu complex.

![Figure 2. FT-IR spectra of (a) the ligands and (b) their corresponding Eu(III) complexes.](image-url)
3. Photophysical Studies

3.1. UV-Vis spectroscopy

The normalized UV-vis absorption spectra of all the Eu(III) complexes in CHCl₃ (1 × 10⁻⁵ mol/L conc) are shown in Figure 3. All the Eu(III) complexes had two absorption bands at ≈ 282 nm and 372 nm, which correspond to the π−π⁎ transition of the phenanthroimidazole derivative and the DBM anion, respectively [27]. The absorption spectra of all the Eu(III) complexes are virtually comparable to the free ligands, which demonstrate that the singlet excited by ancillary ligands was not influenced upon coordination with the Eu(III) metal ion. In addition, the ligand peaks in the Eu-complexes also indicate that the ligands are connected to the Eu-metal ion in the molecular complex. To further understand the above approach, the results of the study of the absorption of the ligand and the respective complexes are shown in Figures S12 and S13. The Eu(DBM)₃Phen-mCF₃-Ph complex showed two clear absorption peaks at ≈ 270 nm and 350 nm. The Eu(DBM)₃.2H₂O complex showed the maximum absorption band at ≈ 340 nm. Therefore, the presence of two absorption peaks in the final Eu(III) complexes implies the presence of Eu(DBM)₃.2H₂O and the ancillary ligand in the complex. The molar absorption of the m-CF₃ complex was moderately high compared to that of the p-CF₃ complex, and in fact, did not show much difference. The molar extinction coefficients (ε) were as follows: for Eu(DBM)₃Phen-Ph-Ph, 35,200 M⁻¹ cm⁻¹ > Eu(DBM)₃Phen-mCF₃-Ph, 34,550 M⁻¹ cm⁻¹ > Eu(DBM)₃Phen-pCF₃-Ph, 34,230 M⁻¹ cm⁻¹). These show that the electron-withdrawing groups have less ε value than the other group (Figure S13). The absorption, excitation, and emission of the ligands and the corresponding complexes are shown in Table 1.

3.2. Photoluminescence

The photoluminescence excitation and emission spectra of all the Eu(III) complexes in the solid and solution (CHCl₃, 1 × 10⁻⁵ mol/L conc) phases are shown in Figures 4 and 5. The excitation spectra of all the Eu(III) complexes in the solid state as well as in the solution state were measured by monitoring the 5D₀→7F₂ (612 nm) emission peak of the Eu(III) metal ion [Figure 5(a) and Figure 6]. In the solid state, the observed broadband in the excitation spectra of all the Eu(III) complexes in the 300–475 nm region due to the π−π⁎ transition of the coordinated DBM ligand. DBM in a pure condition showed maximum absorption at ≈ 350 nm (Figure S13a) while covering the region to up to 400 nm ranges [28, 29]. Also, a weak peak at ≈ 464 nm (7F₂→5D₀) was observed, which indicates the coordination of the ligand with the Eu(III) metal ion [30]. However, in the solution phase, all the Eu(III) complexes showed excitation at 380 nm. PL emission spectra of all the Eu(III) complexes in a solid state as well as in a solution (CHCl₃, 1 × 10⁻⁵ mol/L conc) state were recorded at 384 nm. As shown in Figure 4(b) and Figure 5(b), the emission window of the Eu(III) complexes covered the spectral region from 400 to 725 nm. The characteristic emission peak of the Eu(III) ion was observed due to the radiative transition attributed to 5D₀→7F₇ (J = 0–4) at around 579, 592, 612, 650, and 695 nm. The 4f-4f radiative transition in the Eu(III) complexes was generally partly forbidden. It mainly produced the two important transitions: (i) the magnetic dipole transition (MD/5D₀→7F₁) and (ii) the induced electric dipole (ED/5D₀→7F₂) transition.

Table 1. Absorption, excitation, and emission of the ligands and the corresponding complexes in the solution and solid states.

| S. No. | Compound          | λ_max (abs) (nm) | λ_ex (nm) | λ_em (nm) | I₂/I₁ Ratio | FWHM (nm) |
|-------|-------------------|-----------------|-----------|-----------|-------------|-----------|
|       | Solution[^a]      |                 |           |           |             |           |
| 1     | Eu(DBM)₃Phen-Ph-Ph | 276             | 385/403   | 613/612   | 5.2/10.91   | 10.93/12.88 |
| 2     | Eu(DBM)₃Phen-mCF₃-Ph | 266, 340     | 385/393   | 614/611   | 5.4/17.25   | 9.00/9.84  |
| 3     | Eu(DBM)₃Phen-pCF₃-Ph | 271           | 386/408   | 614/613   | 4.8/7.82    | 9.09/16.20 |

[^a]Measured in the chloroform solution at 298 K.
[^b]Absorption peaks from the UV-Vis absorption spectra. Emission peaks from the photoluminescence emission spectra.
Figure 4. (a) PL excitation and (b) emission spectra of the complexes in a solid form. The inset shows the CIE color coordinates.

Figure 5. (a) PL excitation and (b) emission spectra of the complexes in solution (CHCl$_3$ $1 \times 10^{-5}$ mol/L conc) form. The inset shows the CIE color coordinates.

The presence of a single weak peak at $^5D_0 - ^7F_0$ (579 nm) in the emission spectra indicates the existence of a single chemical environment around the Eu(III) metal ion [31–33]. A moderately strong magnetic dipole transition peak, $^5D_0 - ^7F_1$ (592 nm), was also observed, which was not dependent on the ligand field environment around the Eu(III) metal ion. Among all the radiative transitions, $^5D_0 - ^7F_2$ (612 nm) was the hypersensitive electric dipole transition responsible for the red luminescence of the Eu(III) complex. Two broad peaks at $^5D_0 - ^7F_3$ (650 nm) and $^5D_0 - ^7F_4$ (695 nm) were also observed in the PL emission spectra. The asymmetric ratio (ED/MD, $I_2/I_1$) of the complexes was found to have been in the range of 5.2-4.8. The highest ratio observed was for the electron-withdrawing free complex, which was 5.2, and the m-CF$_3$ and p-CF$_3$ complexes, which were 5.4 and 4.8, respectively. The observed highest ratio clearly indicated that this Ph-complex had a more hypersensitive electric dipole momentum than the rest of the complexes (Table 1). In other words, the local site symmetry around the trivalent europium ion was distorted (a non-centrosymmetric site). The CIE color coordinates of the complexes in the solid phase showed a bright pure red emission, with $x = 0.66$ and $y = 0.33$ (612 nm).

Further, to understand the effect of the polarity of the solvents on the PL emission spectra of all the Eu(III) complexes, a solvatochromism study was performed. Its results are shown in Figure 6. All the Eu(III) complexes showed the ligand peak along with the Eu(III) peak in the MeOH solution. This was also clearly confirmed.
Figure 6. PL emission spectra of the Eu(III) complexes, Eu(DBM)$_3$Phen-Ph-Ph, Eu(DBM)$_3$Phen-mCF$_3$-Ph, and Eu(DBM)$_3$Phen-pCF$_3$-Ph, in different solvents and their respective CIEs.

by the observed color of the solution (the complex in methanol), from which a nearly white light emission was observed. The CIE color coordinates of all the complexes in different solutions are shown in the inset in Figure 6. The solvatochromism analysis that inferred more polar solvents showed the highest intense emission at the 400-500 nm range. Along with the peak of the Eu(III) metal ion, the ligand emission peak appeared intensely in methanol and DMSO. The CIE color coordinates from the solvatochromism study of the Eu(III) complex in solvents with different polarities are shown in Figures S14–16. The difference between the electron-withdrawing group complexes was measured using the FWHM and was insignificant, i.e., below 10.

### 3.3. Photoluminescence quantum yield (PLQY)

The absolute overall quantum yield is defined as the ratio of the number of photons emitted to the number of photons absorbed. The quantum yield is a significant parameter for calculating the emission efficiency of Eu(III) complexes. The quantum yield calculation for all the complexes in solid form was completed using the integrating sphere [34].

\[
\varphi = \frac{L_0(\lambda) - L_i(\lambda)}{L_0(\lambda)} \tag{1}
\]

\[
\varphi = \frac{E_0(\lambda) \varphi - (1 - \varphi)E_0(\lambda)}{E_0(\lambda)\varphi} \tag{2}
\]

In the above equations, $L_0(\lambda)$ is the integrated excitation profile (the sample is directly excited by the incident beam) and $L_i(\lambda)$ is the integrated excitation profile attained from the empty integrated sphere. $E_0(\lambda)$ is the integrated luminescence of the powder caused by the direct excitation and $E_i(\lambda)$ is the indirect illumination from the sphere. The obtained quantum yield (in...
the solid) for all the Eu(III) complexes, Eu(DBM)$_3$Phen-Ph-Ph, Eu(DBM)$_3$Phen-mCF$_3$-Ph, and Eu(DBM)$_3$Phen-pCF$_3$-Ph, were 4.0, 5.06, and 2.67, respectively, upon excitation at $\lambda = 384$ nm. The observed PLQY confirms the occurrence of energy transfer from the ligand to the Eu(III). Also, the fluorinated phen-mCF$_3$-Ph ligand showed a high lifetime value, which is one of the reasons for its less non-radiative transition. To support the same purpose, the radiative properties of the fluorinated complexes showed reduced non-radiative transition compared to the non-fluorinated complex. In the deep scene of the comparative study between the fluorinated complexes, p-CF$_3$ showed less non-radiation and m-CF$_3$ showed a moderate overlay.

3.4. Judd-Ofelt parameters

The Judd-Ofelt intensity parameters ($\Omega_2$ and $\Omega_4$) for all the Eu(III) complexes were calculated from the well-reported Equation (3) [35]. $\Omega_2$ and $\Omega_4$ are very important parameters in calculating the chemical bonding nature around the central Eu(III) metal ion.

$$\Omega_\lambda = \frac{3hC^2A_{0-\lambda}}{4e^2\omega^3\chi < 5D_0||U(\lambda)||^2FJ^2>^2}$$

The intensity parameters $\Omega_2$ and $\Omega_4$ were calculated from the $^5D_2-^7F_0$ and $^5D_4-^7F_0$ transitions, respectively. The obtained values from the J-O calculation for all the Eu(III) complexes are summarized in Tables 2 and 3. The complexes Eu(DBM)$_3$Phen-mCF$_3$-Ph and Eu(DBM)$_3$Phen-pCF$_3$-ph had the highest $\Omega_2$ value, which indicates the more covalent character of the Eu(III) metal ion. The radiative ($A_{\text{rad}}$) and non-radiative ($A_{\text{nr}}$) properties of the radiative, lifetime ($\tau_{\text{rad}}$), and branching ($\beta_{1-3}$) ratios for the all the Eu(III) complexes were determined with the J-O intensity parameter according to the reported method. All the obtained values are summarized in Table 2.

Figure 7. Decay curves of the luminescence of the Eu(III) complexes at $\lambda = 612$ nm.

3.5. Lifetime study

The lifetime decay curves of all the Eu(III) complexes are shown in Figure 7. They were recorded at the 384 nm excitation wavelength by monitoring the hypersensitive $^5D_0-^7F_2$ (612 nm) emission peaks of the Eu(III) complexes. The obtained lifetime outcomes showed the best fit with the single exponentials model according to the well-reported equation $I(t) = I_0 + A_1\exp(-t/\tau)$. The fitting curve is shown in the inset of Figure 7 and a better resolution is incorporated in Figure S22. The single ligand field environment around the Eu(III) metal ion is basically responsible for the mono-exponential fit. The luminescence lifetime decays of the Eu(III) complexes, Eu(DBM)$_3$Phen-Ph-Ph, Eu(DBM)$_3$Phen-mCF$_3$-Ph, and Eu(DBM)$_3$Phen-pCF$_3$-Ph, at the excited $^5D_0$ level emission were 0.234, 0.453, and 0.325 ms. The radiative properties of the fluorinated complexes showed reduced non-radiative transition compared to that in reported literature [15]. In addition, it revealed the best performance of the fluorinated complexes using radiative transition.

Table 2. Calculated luminescence lifetimes $\tau_{\text{obs}}$ and intensity parameters of the ligands and the corresponding Eu(III) complexes.

| Compound                  | $\Omega_2$ (10$^{-20}$ cm$^2$) | $\Omega_4$ (10$^{-20}$ cm$^2$) | $A_{0-1}$ in S$^{-1}$ | $A_{0-2}$ in S$^{-1}$ | $A_{0-4}$ in S$^{-1}$ | $\tau$ (ms) for the Eu Complexes |
|---------------------------|-------------------------------|-------------------------------|------------------------|------------------------|------------------------|----------------------------------|
| Eu(DBM)$_3$Phen-Ph-Ph     | 0.6854                        | 1.83                          | 50                     | 573.244                | 73.657                 | 0.234                            |
| Eu(DBM)$_3$Phen-mCF$_3$-Ph| 1.055                         | 2.744                         | 50                     | 885.402                | 108.427                | 0.453                            |
| Eu(DBM)$_3$Phen-pCF$_3$-Ph| 1.759                         | 4.331                         | 50                     | 1463.751               | 171.006                | 0.325                            |

Table 3. Radiative properties and branching ratios of the complexes.

| Complex                  | $A_{\text{rad}}$ (S$^{-1}$) | $\tau_{\text{rad}}$ (ms) | $A_{\text{nr}}$ (ms) | $\eta_{\text{on}}$ (%) | $\eta_{\text{sen}}$ (%) | $\beta_1$ | $\beta_2$ | $\beta_4$ |
|---------------------------|-------------------------------|----------------------------|------------------------|------------------------|------------------------|-----------|-----------|-----------|
| Eu(DBM)$_3$Phen-Ph-Ph     | 696.90                        | 1.434                      | 3.575                  | 16.31                  | 95.0                   | 7.174     | 82.256    | 10.569    |
| Eu(DBM)$_3$Phen-mCF$_3$-Ph| 1043.82                       | 0.958                      | 1.164                  | 47.28                  | 65.5                   | 4.790     | 84.822    | 10.387    |
| Eu(DBM)$_3$Phen-pCF$_3$-Ph| 1684.75                       | 0.593                      | 1.389                  | 54.92                  | 54.2                   | 2.967     | 86.882    | 10.150    |
and indicated that DBM can enhance the radiative transition comparably with the TTA antenna. In fact, the DBM triplet state location was the same for all the Eu(III) complexes, but the ligand triplet state is a key factor for efficient energy transfer. The effective intersystem crossing enhanced the phosphorescent lifetime of the complexes. Such phenomenon could be explained by the energy states of TTA and DBM, because the DBM triplet energy state (20,408 cm\(^{-1}\)) follows the rules in the study of Latva et al. for reaching the Eu(III) metal ion. In the case of TTA, there was a smaller difference between the Eu(III) \(^5D_0\) to the triplet state of TTA [36, 37]. This observed energy difference supported the efficient energy transfer better than did TTA. In addition, the \(I_2/I_1\) ratio of the fluorinated complexes was too high and indicated that the 612 nm (\(^5D_0-^7F_2\)) emission became brighter when the MD transition was suppressed at 592 nm (\(^5D_0-^7F_1\)).

### 3.6. Energy transfer process

The Eu(III) complexes were made of ligand molecules and DBM moiety. These two efficient candidates were responsible for the energy transfer process to reach the Eu(III) central metal ion. The ancillary and anionic ligand molecules were extremely followed to attain efficient energy transfer by utilizing their singlet and triplet states. The difference between the singlet energy state and the triplet energy state was more than 5,000 cm\(^{-1}\) (0.619 eV), and the triplet to the \(^5D_0\) of Eu(III) was more than 2,500 cm\(^{-1}\) (0.30996 eV). These confirmations show that the presently studied complexes are efficient and can be utilized for optoelectronic materials. In fact, they also showed the TTA energy levels for the comparative statement in Figure 8. In addition, to understand the more profound process of energy transfer in the complex from the ligand and DBM to reach the Eu(III) metal ion, a possible energy pathway was designed and is shown in Figure S17. The singlet energy of DBM was located \(\sim 6,000\) cm\(^{-1}\) above the triplet state of the ligand and was able to more feasibly transfer the absorbed energy to the ligand triplet states. Moreover, the excited triplet energy levels were calculated (confirmed) experimentally with a phosphorescence emission using the respective Gd(III) complexes at 77 K. The obtained experimentally calculated triplet was found at 22,472 (2.786), 22,370 (2.774), and 22,167 (2.748) cm\(^{-1}\) (eV) for 1 L, 2 L, and 3L, respectively (Figure S18). They are similar to the theoretical calculations.

### 3.7. PMMA film study of the Eu\textsuperscript{III} complexes and the CIE color coordinates

All the Eu(III) complexes were embedded into the PMMA polymer at different proportions of 0.1, 0.5, 1, and 5% (w/w) [Eu(III):PMMA], which makes them the best candidates for use in a wide range of new applications such as optoelectronics. Figure 9 shows that the luminescence emissions of all the Eu(III) complexes doped with the PMMA matrix and excited at 385 nm exhibited well-defined emission peaks characteristic of the \(^5D_0-^7F_1\) (\(J = 0–4\)) transition of the Eu(III) ion in the 550-715 nm wavelength region. It was observed from the emission spectra of the Eu(III) complexes that the intensity of the emission at 612 nm increased linearly with the enhancement of the concentration of the Eu(III) ion. Similar observations were reported in the fluorinated complexes, which also explained the clear view of the 612 nm emission peaks in the normalized spectral analysis mentioned in Figure S19. The complexes did not show the concentration quenching effect up to the 5% load of the Eu complex in the PMMA matrix [38, 39]. This indicates that the synthesized complexes are potential candidates for further analysis and that 5% (w/w) [Eu(III):PMMA] represents high intense emission peaks because PMMA can reduce the collisional quenching of the ligand triplet state in the polymer matrix. This ultimately results in efficient intermolecular energy transfer through the donor (ligand) and acceptor process in the Eu-complex and due to the long chain of PMMA as well as due to its rigidity.

### 3.8. Electrochemical properties

The electrochemical properties of the synthesized Eu(III) complexes were measured using cyclic voltammetry (CV). The CV (potential vs. current) curves of all the Eu(III) complexes are shown in Figure 10. The CV curve of each Eu(III) complex was measured three times but the...
same redox potential values were observed, which indicates that all the Eu(III) complexes were electrochemically stable. The obtained redox (oxidation/reduction) potential values are shown in Table 4. According to Equation (4), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels for all the Eu(III) complexes were successfully calculated [40]. Also, the calculated band gaps of the Eu-complexes from the reflectance (absorption) are shown in the supporting information in Figure S12a.

$$E_{HOMO} = - (E_{Onset}^{Ox} + 4.4) eV$$
$$E_{LUMO} = - (E_{Onset}^{Red} + 4.4) eV$$  \hspace{1cm} (4)

### 3.9. Fabrication of LED using the Eu complexes

The emission spectra of the LED fabricated with the Eu(III) complexes at different mass ratios (1:10 and 1:50) of phosphor to PMMA are shown in Figure 11 (Figures S23 and S24). The small emission peak near the UV chip in the LED emission spectra shows that the ligand efficiently absorbed the energy and successfully
Table 4. Onset oxidation and reduction potentials of the ligands and complexes.

| S. No. | Compound                        | $\text{Voltage}_{\text{Ox}}$ $[E_{\text{HOMO}}] (V)$ | $\text{Voltage}_{\text{Red}}$ $[E_{\text{LUMO}}] (V)$ | Energy Gap (eV) | Wavelength (nm) |
|--------|---------------------------------|--------------------------------------------------|--------------------------------------------------|----------------|-----------------|
| 1.     | Eu(DBM)$_3$Phen-Ph-Ph           | 1.300 (−5.69)                                   | −1.490 (−2.91)                                   | 2.78           | 444.5           |
| 2.     | Eu(DBM)$_3$Phen-mCF$_3$-Ph      | 1.454 (−5.85)                                   | −1.615 (−2.78)                                   | 3.06           | 405.1           |
| 3.     | Eu(DBM)$_3$Phen-pCF$_3$-Ph      | 1.234 (−5.63)                                   | −1.215 (−3.18)                                   | 2.50           | 506.0           |

Figure 11. Emission spectra of the Eu(III) complex coated with the InGaN (395 nm)-emitted LED chip. The inset shows the forward bias coated with the Eu(III) complex.

transferred it to the Eu(III) metal ion. The CIE color coordinates of the Eu(III) complex showed a red emission that was very close to the NTSC standard values for red ($x = 0.67$ and $y = 0.33$). The bright red digital image of the fabricated LED shows that the synthesized Eu(III) complexes are good red components for fabricating near UV-based white LEDs. The color purity of the Eu-complexes was calculated using this formula:

$$
\text{color purity} = \sqrt{\left(\frac{x-x_i}\right)^2 + \left(\frac{y-y_i}\right)^2 + \left(\frac{x-d-x_i^2}{y-d-y_i^2}\right)^2},
$$

wherein $(x, y)$, $(x_i, y_i)$, and $(x_d, y_d)$ refer to the color coordinates of the emission light, the equal energy point, and the dominant wavelength points, respectively. The calculated color purity of the Eu-complexes was very high ($> 95\%$), as shown in Table 4. In addition, the luminous efficiency of the radiation (LER), which describes how bright the radiation is that is perceived by the average human eye in lumens per watt (lm/W), was calculated for the red LED based on the Eu(III) complexes. The LERs for the Eu(DBM)$_3$Phen-Ph-Ph complex were $\sim 281$ and $275$ lm/W at 1:10 and 1:50, respectively. Similarly, the LER was calculated for the two other complexes, and the results are shown in Table 4. Of all the complexes, the Eu(DBM)$_3$Phen-mCF$_3$-Ph complex showed the best LER value (287 lm/W). The results are comparable with the reported values Table 5 [41].

3.10. Temperature-dependent PL emission study of the Eu(III) complex

In this study, we recorded the PL emission spectra of all the Eu(III) complexes at different temperatures (30–80°C) in a solution, as shown in Figure 12. In addition, based on the ligand emission intensity in the Eu(III) complex, the highly suppressed (acetonitrile, ACN) as well as the more intense (MeOH) ligand in the Eu(III) complex were studied. From the observation data, we found that the luminescence intensity showed sensitivity to temperature in that it decreased with increasing temperature. The PL emission intensity of the Eu(III) complexes decreased because of quenching, because the Eu(III) complex lost more energy from the thermal vibration with increasing temperature, and as a result, the absorbed energy transferred to the Eu(III) complex decreased. This remarkable linear decrease in luminescence intensity with increasing temperature opens up a new window for the use of this material as a sensitive temperature sensor in the temperature range of 30–80°C. The CIE color coordinates of the Eu(III) complexes at the temperature range of 30–80°C are shown in Figure S20. Similarly, the CIE color coordinates of the Eu(III) complexes at the temperature range of 30–60°C in methanol are shown in Figure S20. The CIE values of the complexes deviated from the pure red emission with increasing temperature. In addition, the high intense ligand emission in the Eu(III) complex due to MeOH was studied in the range of 30-60°C, as shown in Figure S21. The use of methanol for the same temperature range made the emission white. Compared to the above results for

Table 5. CIE, color purity, and LER of the Eu complexes-based red LEDs.

| Name of Complex                  | CIE Color Coordinates ($x, y$) | Color Purity | LER       |
|---------------------------------|-------------------------------|--------------|-----------|
|                                 | 1:10                          | 1:50         | 1:10      | 1:50      |
| Eu(DBM)$_3$Phen-Ph-Ph           | 0.662,0.337                   | 96.98        | 281       | 275       |
| Eu(DBM)$_3$Phen-mCF$_3$-Ph      | 0.623,0.375                   | 87.47        | 273       | 287       |
| Eu(DBM)$_3$Phen-pCF$_3$-Ph      | 0.666,0.333                   | 97.88        | 267       | 247       |
ACN, wherein the ligand emission was suppressed in the Eu complex, the complex in methanol showed a drastic deviation from a red to a near white light emission. That was due to the flexible intensity of the ligand emission in the complex in methanol, which balanced the primary color coordinates \((x = 0.32 \text{ and } y = 0.29)\). The CIE color coordinates of the Eu(III) complexes are shown in Figure S12.

3.11. Ratiometric temperature sensor of the Eu(III) complex \([\text{Eu(DBM)}_3\text{Phen-Ph-Ph}]\)

The temperature-dependent PL of the Eu(III) complexes can be better comprehended with the help of the intensity ratio of the ligand at 465 nm and of the Eu(III) complex at 612 nm \((\Delta = I_{\text{lig}}/I_{\text{Eu}})\). The linear relationship between the intensity ratio \((\Delta)\) and the temperature \(T\) are shown in Figure 13(a). The fitting curve is shown by the red line,
Figure 14. (a, b, and c) Emission spectra ($\lambda_{ex} = 385$ nm) of the Eu(III) complexes. (b, d, and f) Responses of the 612 nm emission intensity of the Eu(DBM)$_3$Phen-pCN-mCF$_3$ complex during the HCl-NH$_3$ exposure cycles (left inset). (b1, d1, and f1) Photographs of the Eu(III) complex during its exposure to NH$_3$-HCl vapors under UV light ($\lambda_{ex} = 365$ nm) and luminescence changes before and after exposure to NH$_3$ vapors.
which corresponds with the following empirical formula:

\[ \Delta = 0.000738(T) - 0.18776, \]  

(5)

wherein T represents the temperature and \( R^2 = 0.96708 \) is the correlation coefficient. The results signify that Eu(DBM)\(_3\)L-mCF\(_3\) can behave as a luminescent thermometer at the 303–460 K temperature range. The relative sensitivity (the relative change in the thermometric parameter per degree of temperature change) of the Eu(DBM)\(_3\)L-mCF\(_3\) complex was calculated as follows.

\[ SR = \frac{\partial \Delta}{\partial T} \]  

(6)

The obtained relative sensitivity of Eu(DBM)\(_3\)Phen-Ph-Ph indicates that this complex can be used as a luminescent thermometer at the 303–460 K temperature range. Eu(DBM)\(_3\)Phen-Ph-Ph had the relative sensitivity value of 1.969% K\(^{-1}\) at 313 K, as shown in Figure 13(b).

### 3.12. Recyclable on-off-on vapoluminescence sensor

The on-off-on switching of the solid-state luminescence of lanthanides [including of the Eu (III) complexes] in the presence of an external source (HCl-NH\(_3\) or acid-based vapors) has triggered much apprehension in the field of research and applications because of the fascinating associated optical properties [41]. Luminescence switching of Ln(III) complexes is caused by numerous factors such as changes in pH [42, 43] and the microenvironment [44, 45]. Specifically, luminescent materials that show on-off switching in the presence of acid-based gas can be potentially applied in sensors, biochemical assays, and display devices [46–49]. In this study, we explored the switching of the luminescence of mononuclear Eu(III) complexes in the presence of acid-based (HCl-NH\(_3\)) vapors. As shown in Figure 14, on-off switching of the photoluminescence of the Eu(III) complexes was performed after the exposure of the complexes to acidic vapors. When the Eu(III) complex was exposed to HCl gas in a closed system, the red color vanished from the naked eye (under a handheld 365 nm UV lamp). After consecutive exposure of the non-luminescent Eu(III) complex to NH\(_3\) gas, the red luminescence became visible again to the naked eye. This clearly indicates that the synthesized Eu complexes are potential vapoluminescent sensors. This can be easily understood from the mechanism involved. The quenching of the red emission of the Eu(III) complexes in the acidic vapors environment and the reappearance of the same in the basic vapors environment depend on the protonation of DBM in the presence of HCl vapors, which causes the incomplete coordination of the Eu(III) complexes that decreases or diminishes the emission intensity (to 612 nm) in the presence of the HCl vapors. However, in the presence of NH\(_3\) vapors, the deprotonation of DBM takes place through neutralization, which favors the complete coordination of the Eu(III) ion that enhances the emission intensity to 612 nm. To further understand the mechanism of the vapoluminescent sensor, an FT-IR study of Eu complexes exposed to acid-based vapors was performed. The FT-IR spectra of DBM, an ancillary ligand (Phen-pCN-pCF\(_3\)), and an Eu(III) complex were recorded in the presence and absence of HCl-NH\(_3\) vapors (Figure S25). After the ancillary ligand was treated with HCl vapors, an N-H peak appeared at \(~3,384 and 1,632\) cm\(^{-1}\), which vanished after the ancillary ligand was exposed to NH\(_3\) vapors. Similarly, when the Eu(DBM)\(_3\)Phen-pCN-1Naph complex was treated with HCl vapors, an N-H peak appeared at \(~3,358\) and 1,631 cm\(^{-1}\), but it vanished after the complex was exposed to NH\(_3\) vapors (Figure S25). Also, the =C-H stretching frequency was observed at 3,077 cm\(^{-1}\), but it disappeared in the presence of HCl vapors (Fig.S25). This study confirmed that the protonation of the ligand in the Eu complex plays a vital role in the sensing behavior of the complex.

### 4. Conclusion

Ancillary ligands connected to the Eu complexes Eu(DBM)\(_3\)Phen-Ph-Ph, Eu(DBM)\(_3\)Phen-mCF\(_3\)-Ph, and Eu(DBM)\(_3\)Phen-pCF\(_3\)-Ph were synthesized and structurally characterized, and their photophysical properties were studied. The excited energy of the ligand was fully transferred to the Eu-metal ion in the complexes at a solid state (pure red emission) and with a slight deviation in the solution form (red to white emission). High polar solvents increased the ligand emission intensity in the Eu complexes, which was used to measure the temperature-dependent emission properties. The fabricated InGaN-based LED (395 nm) showed an efficient red emission at the ratio of 1:50 (\(x = 0.67\) and \(y = 0.33\)) and the red LED also showed good color purity and LER values. In addition, it exhibited on-off photoluminescence switching via the vapoluminescence process and responded best to the acid-based (HCl-NH\(_3\)) vapors. These efficient red-emitting candidates can be used for LEDs and sensors.

### Conflicts of Interest

The author declares that there is no conflict of interest.
Dr. Rajamouli Boddula received his Ph.D. from the Department of Chemistry, National Institute of Technology, Rourkela, India. He is currently working as an assistant professor at Department of Chemistry, Uka Tarsadia University, Surat, Gujarat. His research direction is luminescent EuII complexes and their application in solid-state lighting sensors: combined experimental and theoretical investigations.

Mrs. Rachna Devi is a Ph.D. candidate in the Department of Chemistry, National Institute of Technology, Rourkela, India. She received her M.Sc. in chemistry from Banasthali Vidyapith Jaipur, India in 2014. Her research direction is Exploration of New Eu(III) complexes and their application in Light Emitting Diodes and Sensors: Combined Experimental and Theoretical Investigations.

Dr. Kasturi Singh received her PhD and Master’s degrees in Chemistry from the Department of Chemistry, National Institute of Technology, Rourkela, India. Her research interest focused on Lanthanide activated phosphor materials and molecular complexes for solid state lighting applications. Currently she is working as a Research Associate at NIT Rourkela.

Dr. Satendra Kumar received his doctoral degree from Homi Bhabha National Institute, Mumbai. He is working as a scientist in IGCAR, Department of Atomic Energy, Kalpakkam, India. His research area of interest includes luminescence spectroscopy, laser spectroscopy, analytical chemistry and coordination chemistry of lanthanides/ actinides complexes.

Prof. Sivakumar Vaidyanathan received his Bachelor’s and Master’s degrees in Chemistry from Muthurangam Government Arts College, Vellore (affiliated to the University of Madras) and his PhD in Solid-State Chemistry (2007) from the Indian Institute of Technology, Madras, with Prof. U. V. Varadaraju. Then, he moved to Prof. Duk Young Jeon’s group at the Korea Advanced Institute of Science and Technology, Republic of Korea, as a Brain Korea 21 postdoctoral research fellow (2007–2009). He also worked as a postdoctoral fellow at the Commissariat a’ l’Energie Atomique (CEA), Saclay, France, for a year. After spending a year in NIT Calicut as a faculty member in the Department of Chemistry, he moved to the Department of Chemistry at the National Institute of Technology Rourkela. His research focuses on lanthanide photochemistry and photophysics, molecular materials (including deep blue) for OLEDs, phosphors for LEDs (solid-state lighting), and organic fluorophores for diverse applications.

**Notes on contributors**

Mrs. Rachna Devi is a Ph.D. candidate in the Department of Chemistry, National Institute of Technology, Rourkela, India. She received her M.Sc. in chemistry from Banasthali Vidyapith Jaipur, India in 2014. Her research direction is Exploration of New Eu(III) complexes and their application in Light Emitting Diodes and Sensors: Combined Experimental and Theoretical Investigations.

Dr. Rajamouli Boddula received his Ph.D. from the Department of Chemistry, National Institute of Technology, Rourkela, India. He is currently working as an assistant professor at Department of Chemistry, Uka Tarsadia University, Surat, Gujarat. His research direction is Luminescent EuII complexes and their application in solid-state lighting sensors: combined experimental and theoretical investigations.

Dr. Kasturi Singh received her PhD and Master’s degrees in Chemistry from the Department of Chemistry, National Institute of Technology, Rourkela, India. Her research interest focused on Lanthanide activated phosphor materials and molecular complexes for solid state lighting applications. Currently she is working as a Research Associate at NIT Rourkela.

Dr. Satendra Kumar received his doctoral degree from Homi Bhabha National Institute, Mumbai. He is working as a scientist in IGCAR, Department of Atomic Energy, Kalpakkam, India. His research area of interest includes luminescence spectroscopy, laser spectroscopy, analytical chemistry and coordination chemistry of lanthanides/actinides complexes.

Prof. Sivakumar Vaidyanathan received his Bachelor’s and Master’s degrees in Chemistry from Muthurangam Government Arts College, Vellore (affiliated to the University of Madras) and his PhD in Solid-State Chemistry (2007) from the Indian Institute of Technology, Madras, with Prof. U. V. Varadaraju. Then, he moved to Prof. Duk Young Jeon’s group at the Korea Advanced Institute of Science and Technology, Republic of Korea, as a Brain Korea 21 postdoctoral research fellow (2007–2009). He also worked as a postdoctoral fellow at the Commissariat a’ l’Energie Atomique (CEA), Saclay, France, for a year. After spending a year in NIT Calicut as a faculty member in the Department of Chemistry, he moved to the Department of Chemistry at the National Institute of Technology Rourkela. His research focuses on lanthanide photochemistry and photophysics, molecular materials (including deep blue) for OLEDs, phosphors for LEDs (solid-state lighting), and organic fluorophores for diverse applications.

**References**

[1] R.J. Xie, N. Hirosaki, K. Sakuma, and N. Kimura, J. Phys. D: Appl. Phys. 41, 144013–144018 (2008). doi:10.1088/0022-3727/41/14/144013

[2] J. Lim, S. Jun, E. Jang, H. Baik, H. Kim, and J. Cho, Adv. Mater. 19, 1927 (2007). doi:10.1002/adma.200602642

[3] Z. Wang, H. Liang, M. Gong, and Q. Su, J. Alloys. Compd. 432, 308 (2007). doi:10.1016/j.jallcom.2006.06.008

[4] S. Kasturi, and V. Sivakumar, Mater. Chem. Front. 1, 550–561 (2017). doi:10.1039/C6QM00118A

[5] C.W. Tang, and S.A. Van Slyke, Appl. Phys. Lett. 51, 913 (1987). doi:10.1063/1.98799

[6] B. Rajamouli, and V. Sivakumar, New J. Chem. 41, 1017–1027 (2017). doi:10.1039/C6NJ03014A

[7] G.R. Choppin, and D.R. Peterman, Coord. Chem. Rev. 174, 283–299 (1998). doi:10.1016/S0010-8545(98)00125-8

[8] R. Devi, and S. Vaidyanathan, Dalton Trans. 49, 6205–6219 (2020). doi:10.1039/D0DT00519C

[9] M. Rajendran, and S. Vaidyanathan, Dalton Trans. (2020). Advance Article, doi:10.1039/D0DT01517B

[10] H. Iwanaga, A. Amano, F. Aiga, K. Harada, and M. Oguchi, J. Alloys Compd., 408–412, 921-925 (2006).

[11] H. Wang, P. He, S. Liu, J. Shi, and M. Gong, Appl. Phys.B 97, 481 (2009). doi:10.1007/s00340-009-3638-1

[12] C. Piguet, and J.C.G. Bunzli, Chem. Soc. Rev. 28, (347), (1999).

[13] H. Xu, Q. Sun, Z. An, Y. Wei, and X. Liu, Coord. Chem. Rev. 293–294, 228–249 (2015).

[14] B. Rajamouli, and V. Sivakumar, Chemistry Select 2, 4138–4149, 2 (2017).

[15] B. Rajamouli, R. Devi, A. Mohanty, V. Krishnan, and S. Vaidyanathan, New J. Chem. 41, 9826–9839 (2017). doi:10.1039/C7NJ02291C

[16] H. Yasuchika, K. Kuichi, and N. Takayuki, NPG Asia Materials 10, 52–70 (2018). doi:10.1038/s41427-018-0012-y

[17] C.L. Robert, M.V. Lidia, C.B. Margie, and S. Yang, Cytometry Part A 69A, 767–778 (2006). doi:10.1002/cyto.a.20321

[18] M. Latva, H. Takalo, V.M. Mukkalia, C. Matakescu, J.C. Rodriguez-Ubis, and J. Kankare, J. Lumin. 75, 149–169 (1997). doi:10.1016/S0022-2313(97)00113-0

[19] S-W Ryu, J. Park, J-K Oh, D. Hoang, LK-W Kwon, Y-H Kim, J.K. Lee, and J.H. Kim, Adv. Funct. Mater. 19, 1650–1655 (2009). doi:10.1002/adfm.200801125

[20] K. Okamoto, et al., Nature Mater 3, 601–605 (2004). doi:10.1038/nmat1198

[21] V. Divya, and M.L.P. Reddy, J. Mater. Chem. C 1, 160–170 (2013). doi:10.1039/C2TC00186A

[22] V. Divya, V. Sankar, K.G. Raghuv, and M.L.P. Reddy, Dalton Trans. 42, 12317–12323 (2013). doi:10.1039/c3dt5117k

[23] T.V. Usha Gangan, and M.L.P. Reddy, Dalton Trans, 44, 15924–15937 (2015). doi:10.1039/C5DT02371H

[24] B. Ziqiang, G. Deqing, G. Min, X. Hao, L. Fuyou, H. Chunhui, W. Kezhi, and J. Linpei, Sci. China, Ser. B: Chem. 47, 326–334 (2004). doi:10.1360/03yb0130
[25] Y. Zheng, J. Lin, Y. Liang, Q. Lin, Y. Yu, Q. Meng, Y. Zhou, S. Wang, H. Wang, and H. Zhang, J. Mater. Chem. 11, 2615–2619 (2001). doi:10.1039/b100558h
[26] B. Rajamouli, P. Sood, S. Giri, V. Krishnan, and V. Sivakumar, Eur. J. Inorg. Chem. 2016, 3900–3911 (2016). doi:10.1002/ejic.201600508
[27] F.S. Liang, Q.G. Zhou, Y.X. Cheng, L.X. Wang, D.G. Ma, X.B. Jing, and F. Wang, Chem. Mater. 15, 1935–1937 (2003). doi:10.1021/cm0257724
[28] Y. Chaolong, X. Jing, M. Jianying, Z. Dongyu, Z. Yunfei, L. Liyan, and L. Mangeng, Photochem. Photobiol. Sci. 12, 330–338 (2013). doi:10.1039/C2PP25284H
[29] W. Zhengliang, Y. Hui, H. Pei, H. Yonghui, Z. Jishou, and T. Huaijun, Dalton Trans. 45, 2839–2844 (2016). doi:10.1039/C5DT04407C
[30] D.B.A. Raj, S. Biju, and M.L.P. Reddy, Dalton Trans. 36, 7519–7528 (2009).
[31] K. Binnemans, Coord. Chem. Rev. 295, 1–45 (2015). doi:10.1016/j.ccr.2015.02.015
[32] K. Binnemans, Chem. Rev. 109, 4283–4374 (2009). doi:10.1021/cr8003983
[33] S.I. Weissman, J. Chem. Phys. 10, 214–217 (1942). doi:10.1063/1.1723709
[34] J.C. Mello, H.F. Wittmann, and R.H. Friend, Adv. Mater. 9, 230–232 (1997). doi:10.1002/adma.19970090308
[35] S. Kasturi, and V. Sivakumar, Chemistry Select 1, 5448–5462 (2016).
[36] M. Sun, H. Xin, K.Z. Wang, Y.A. Zhang, L.P. Jin, and C.H. Huang, Chem. Commun. 6, 702–703 (2003). doi:10.1039/b212467j
[37] M. Guan, Z.Q. Bian, F.Y. Li, H. Xin, and C.H. Huang, New J. Chem. 27, 1731–1734 (2003). doi:10.1039/b305361j
[38] C. Adachi, M.A. Baldo, and S.R. Forrest, J. Appl. Phys. 87, 8049 (2000). doi:10.1063/1.373496
[39] D.B. Ambili, R.B. Francis, M.L.P. Reddy, R.R. Butorac, V.M. Lynch, and A.H. Cowley, Inorg. Chem. 49, 9055–9063 (2010). doi:10.1021/ic1015324
[40] D.M. Leeuw, M.M.J. Simenon, A.R. Brown, and R.E.F. Einerhand, Synth. Met. 87, 53–59 (1997). doi:10.1016/S0379-6779(97)80097-5
[41] J.D. Routledge, M.W. Jones, S. Faulkner, and M. Tropiano, Inorg. Chem. 54, 3337–3345 (2015). doi:10.1021/ic503049m
[42] Y.B. Shu, and W.S. Liu, Inorg. Chem. Front. 2, 927–930 (2015). doi:10.1039/C5QI00134J
[43] R. Pal, and D. Parker, Chem. Commun. 5, 474–476 (2007). doi:10.1039/B616665B
[44] H.B. Cheng, H.Y. Zhang, and Y. Liu, J. Am. Chem. Soc. 135, 10190–10193 (2013). doi:10.1021/ja4018804
[45] M. Jauregui, W.S. Perry, C. Allain, L.R. Vidler, M.C. Willis, A.M. Kenwright, J.S. Snaith, G.J. Stasiuk, M.P. Lowe, and S. Faulkner, Dalton Trans. 32, 6283–6285 (2009). doi:10.1039/b911588a
[46] J. Wang, S. Chan, R.R. Carlson, Y. Luo, G. Ge, R.S. Ries, J.R. Heath, and H.R. Tseng, Nano Lett. 4, 1693–1697 (2004). doi:10.1021/nl049114p
[47] Y.S. Zhao, J. Wu, and J. Huang, J. Am. Chem. Soc. 131, 3158 (2009). doi:10.1021/ja809360y
[48] C. Dou, L. Han, S. Zhao, H. Zhang, and Y. Wang, J. Phys. Chem. Lett. 2, 666 (2011). doi:10.1021/jz200140c
[49] X. Zhou, X. Zhao, Y. Wang, B. Wu, J. Shen, L. Li, and Q. Li, Inorg. Chem. 53, 12275–12282 (2014). doi:10.1021/ic501252x